Large-Deformation and Rupture Properties of Wheat Flour Gluten[1]

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ABSTRACT

The rheological properties of a reconstituted wet gluten were studied at 25°C. by determining stress-strain curves in simple tension at seven testing speeds from 0.263 to 26.3 in. per min. In comparison with previously studied doughs from a medium-strength Kansas and a weak Lemhi flour, the wet gluten was found to have a considerably higher modulus, to be more elastic, and to be stronger and less extensible than the doughs. The constant strain rate modulus, F(t), could be represented by: $F(t) = F(t^*)(t/t^*)^n$, where t and t* are the variable and isochronal (fixed) time, respectively. The characteristic exponent n, which is zero for elastic response and −1 for steady-state viscous flow, was found to be −0.17, in contrast to −0.29 and −0.40 for the Kansas and Lemhi flour doughs, respectively. Data that show the marked dependence of the rupture stress and the elongation at break on the extension rate are presented and compared to data on Kansas and Lemhi flour doughs of different water contents.

In their now classic paper of 1937, Schofield and Scott-Blair (1) described experiments which, in their words, "support the view that in a flour dough the gluten forms an elastic network which dominates the mechanical behavior." Despite this early recognition of the important role played by gluten in affecting the rheological properties of dough, very little work on the mechanical behavior of gluten itself has been described in the literature. While Schofield and Scott-Blair stressed the essential similarity of the rheological behavior of gluten and dough, Udy (2) in 1953 emphasized certain differences. From his experiments, he concluded that gluten becomes more resistant to stretching after resting, as contrasted with dough which softens as a result of relaxation of the internal stresses during the rest period. Barney et al. (3) stretched strips of gluten at a constant extension rate with an Instron tester. They represented the data by an empirical equation; the properties of glutens from different flour varieties were compared in terms of the parameters in the equation. Recently, Smith et al. (4) examined the amplitude-dependence of the dynamic shear modulus, $G'(\omega)$, of gluten and various natural and synthetic doughs. They showed that the pronounced amplitude dependence of the shear modulus of doughs is due to the starch; the modulus of gluten was found to be amplitude-independent.

In two recent publications, Tschoegl et al. (5,6) reported on a comprehensive investigation of the large deformation and rupture properties in simple tension of doughs from a medium-strength Kansas flour of good baking quality and from a Lemhi flour of low protein content and poor baking strength; the method and findings are summarized below. The purpose of the present work was to obtain information on the large deformation and rupture properties of gluten, as determined by the same experimental procedure as used in the study of dough, and to contrast the behavior of gluten and dough.

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[1]Contribution from Stanford Research Institute, Menlo Park, Calif. 94025. Reference to a company or product name does not imply approval or recommendation of the product by the U.S. Department of Agriculture to the exclusion of others that may be suitable.

MATERIALS AND METHODS

Experimental Procedure

Stress-strain data were obtained on gluten at 25°C. and at seven cross-head speeds from 0.263 to 26.3 in. per min. The procedure developed by Tschoegl et al. (5,6) for testing wheat flour doughs was followed, except for minor modifications. In testing dough, an oval-shaped ring is stretched at a constant rate while immersed in a liquid of matching density to prevent the ring from deforming under its own weight. The buoying liquid also facilitates temperature control and prevents the dough specimen from drying out. Because gluten rings, unlike dough rings, do not deform under their own weight, it was not necessary to match closely the densities of the ring and the buoying liquid. Therefore, pure mineral oil was used instead of the mineral oil-Freon mixture employed with dough rings. Also, circular, instead of oval-shaped, ring specimens were tested.

The stress (nominal) is obtained from the retractive force, measured by a load cell attached to one of the ring supports, and the initial cross-sectional area of the ring. For dough specimens, the strain is derived from the displacement of the two supports and an experimentally determined effective circumference, which corrects for the nonuniform extension of a ring in the vicinity of the supports. Because the circular gluten rings were observed to stretch uniformly like rubber rings (7), the strain was calculated from the cross-head displacement and the average circumference of a ring.

Preparation of Gluten Specimens

Wet gluten was prepared essentially by the method of Barney et al. (3) from a commercial dry gluten (Pro-Vim from General Mills) containing 12.4% nitrogen and 7.13% moisture. Fifteen grams of dry gluten was weighed into a polyethylene bag and 13 ml. of a 1% sodium chloride solution was added. The bag was closed and the contents were worked by hand into a fairly cohesive mass. After removal from the bag, the mass was further kneaded by hand until homogeneous. The reconstituted wet gluten was replaced in the bag, compressed between plates into a sheet about 1/8 in. thick, and then stored in a refrigerator for about 48 hr. at 0° to 2°C.

After warming for several hours, the gluten sheet was removed from the bag, and specimens were cut. Because of the highly rubbery nature of the wet gluten, it was difficult to cut oval-shaped rings like those used in the previous studies of flour doughs; such rings commonly had nonuniform dimensions and were not suitable for testing. Thus, a cutter was prepared that gave circular rings whose outside and inside diameters were 1.50 and 1.15 in., respectively. Even with this cutter, certain of the rings were nonuniform and these were discarded. The rings selected were rested in mineral oil at room temperature for at least 1 hr. before being tested. The density of the gluten, determined by a flotation method, was about 1.15 g. per ml. The calculated water content of the wet gluten was 50%, corresponding to 100% water absorption.

Analysis of Experimental Data

When a viscoelastic material is stretched at a constant rate, the stress-strain behavior is the result of two competing processes: 1) progressive deformation of elastic components, which produces an increase in the stress; and 2) continuous relaxation, due to viscous dissipation of energy, which tends to reduce the stress. Analysis of the data obtained on doughs (6) showed that, at each temperature and water content, the effects of strain (or extension ratio, λ) and time, t, on the stress, $\sigma(\lambda,t)$, could be separated at all but the highest elongations. Thus, for each dough, the role of the relaxation process and the basic stress-strain relation could be examined independently at each test temperature. The isothermal behavior of a dough was characterized by a time-independent strain function $\Gamma(\lambda)$, and time-dependent, but strain-independent, constant strain rate modulus, F(t). As will be shown below, strain and time effects for gluten were also found to be separable.

To ascertain whether time and strain effects are separable, doubly logarithmic plots are made of true stress[2], $\lambda\sigma$, against the time, t, where the points for each plot represent the time-dependent stress at a single value of the strain[3]; and $t = (\lambda - 1)/\dot{\lambda}$, where $\dot{\lambda}$ is the strain(extension) rate. If the resulting curves, which represent data at various strains, are parallel, then the equation

$$\lambda\sigma(\lambda,t) = F(t)\,\Gamma(\lambda) \qquad (1)$$

must represent the data. Isochronal values of the stress (i.e., values observed at a fixed time which thus refer to a comparable state of relaxation), along with the corresponding strain values, are then read from the plots; from these data, the form of the strain function, $\Gamma(\lambda)$, is established. The constant strain rate modulus, F(t), is then equal to $\sigma(\lambda,t)/\Gamma(\lambda)$. Full particulars of this method of analyzing large-deformation tensile data are given in a previous paper (6).

Rupture data on each dough were also discussed, inter alia, in terms of the failure envelope (7,8), i.e., the curve which connects the end (break) points of stress-strain curves obtained at different extension rates and/or temperatures. These envelopes are useful to characterize the rupture properties not only of elastomers (7,8) but also of doughs (6) and, as discussed subsequently, of gluten.

RESULTS

Figure 1 shows stress-strain curves determined on gluten at three cross-head speeds[4]. The curves have the shape of an elongated S, with an inflection point at about 75% extension. Each "down line" indicates rupture. The area under a curve (a measure of the rupture energy) increases markedly with an increase in the cross-head speed.

In Fig. 2, log $\lambda\sigma$ obtained at different values of $\lambda - 1$ from 0.1 to 2.0 are plotted against log t. The points at each value of strain are connected to give a set of parallel straight lines, as was done previously (6) for data on Kansas and Lemhi

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[2]The true stress is the retractive force per unit of deformed area. For an incompressible material in simple tension, the true stress equals $\lambda\sigma$, where σ is the nominal stress (force per unit of initial undeformed area) and the extension ratio λ is the length of the stretched specimen divided by the initial length.

[3]In this paper, the Cauchy strain is designated by $\lambda - 1$, which represents the increase in length of a specimen divided by its initial length. The more common symbol ϵ is not used because it is often reserved to symbolize an infinitesimal strain.

[4]Stress values are given throughout this paper in millibars. One mbar equals 1,000 dynes/sq.cm., or 0.0145 p.s.i.

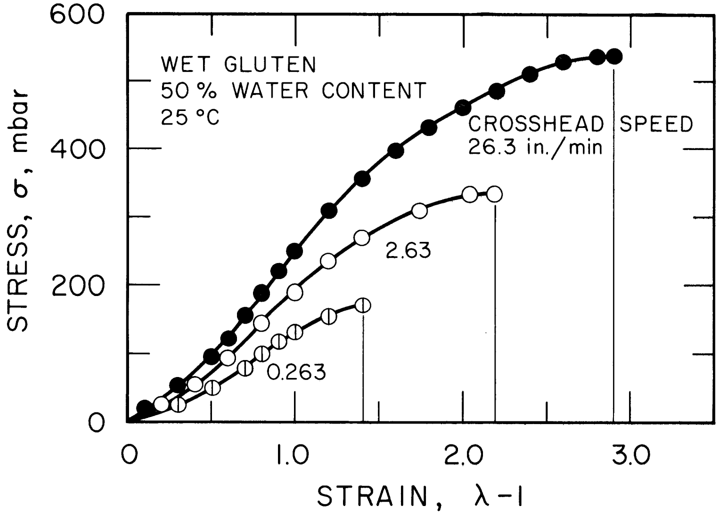

Fig. 1. Stress-strain curves for gluten at three cross-head speeds that correspond to extension rates of 0.126, 1.26, and 12.6 min.$^{-1}$

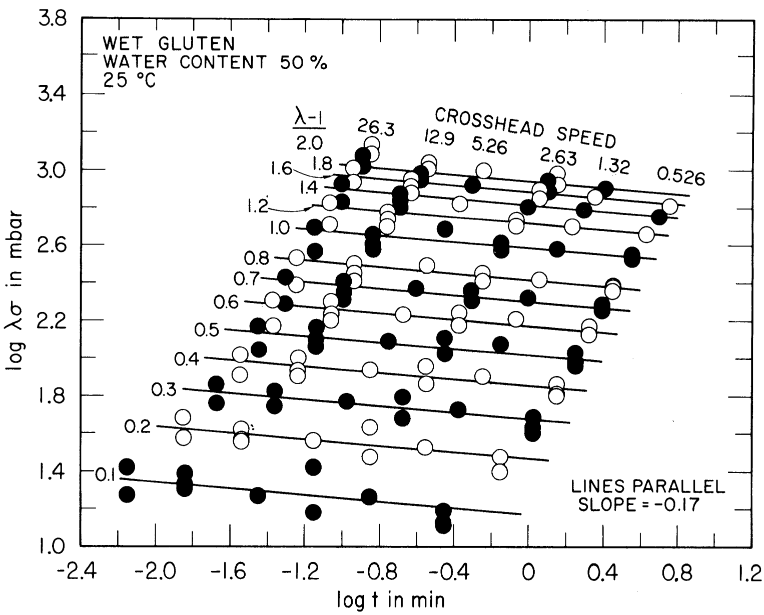

Fig. 2. Data obtained at constant extension rates shown on doubly logarithmic plot of true stress against time. Values of stress at indicated strains are represented by the parallel lines.

flour doughs. Each diagonal band of points represents data at the cross-head speed given at the top of the band. At most cross-head speeds, replicate tests were made and the results are included in Fig. 2. As the data yield parallel lines, whose slope is -0.17, the data conform to equation 1, within the experimental uncertainty.

Values of stress at 1 min. were read from the lines in Fig. 2. The resulting 1-min. (isochronal) stress-strain data were then plotted in several ways to determine which measures of stress and strain give a direct proportionality between stress and strain over the widest range. In the upper portion of Fig. 3, the true stress is plotted against the Cauchy strain, $\lambda-1$, and also against the Hencky strain, $\epsilon_H = \ln \lambda$. The lower portion of the figure shows the nominal stress plotted against both $\lambda-1$ and ϵ_H as well as against the neohookean strain, $\lambda-\lambda^{-2}$. This latter strain measure was considered because the statistical theory of rubberlike elasticity (9) gives the stress-strain relation:

$$\sigma = E_e (\lambda-\lambda^{-2})/3 \tag{2}$$

where E_e is the equilibrium tensile modulus. The same stress and strain measures (except for the neohookean strain) are plotted on doubly logarithmic coordinates in Fig. 4. (When stress is directly proportional to strain, a doubly logarithmic plot gives a straight line of unit slope.)

In contrast to dough, the stress-strain relation for gluten is nonlinear above about 25% extension, regardless of the stress and strain measures employed. The plots of $\lambda\sigma$ against either $\lambda-1$ or ϵ_H deviate from linearity at quite small extensions, but those of σ against either $\lambda-1$, ϵ_H, or $\lambda-\lambda^{-2}$ are linear up to about 25% extension. As each of these strain measures gives essentially an equivalent representation of the data when the nominal stress σ is used, the strain function for gluten is:

$$\Gamma(\lambda) = \lambda-1 \cong \epsilon_H \cong (\lambda-\lambda^{-2})/3 \quad \text{for } 0 < (\lambda-1) < 0.25 \tag{3}$$

The factor three is required in the strain measure $(\lambda-\lambda^{-2})/3$ so that $\sigma/\Gamma(\lambda)$ will equal the modulus in tension, as can be seen from equations 1 and 2. It is not surprising that these strain measures are essentially equivalent, because ϵ_H and $(\lambda-\lambda^{-2})/3$ reduce to $\lambda-1$ at small strains; even at $\lambda-1 = 0.25$, the measures ϵ_H and $(\lambda-\lambda^{-2})/3$ equal 0.23 and 0.21, respectively.

In contrast to the behavior of gluten, it was found previously (6) that

$$\Gamma(\lambda) = \epsilon_H/\lambda \tag{4}$$

up to about 170% extension for Kansas flour doughs and up to 90% or more for Lemhi flour doughs.

Although the plots of log σ against either log $(\lambda-1)$ or log ϵ_H in Fig. 4 give, approximately, lines of unit slope at small extensions, the lines are not coincident; hence, the two strain measures give slightly different values of the modulus. The plots of σ vs. ϵ_H and of log σ vs. log ϵ_H (Figs. 3 and 4) give F(1) = 140 millibars (mbar), which is considered to be the best estimate of the constant strain rate modulus evaluated at 1 min.

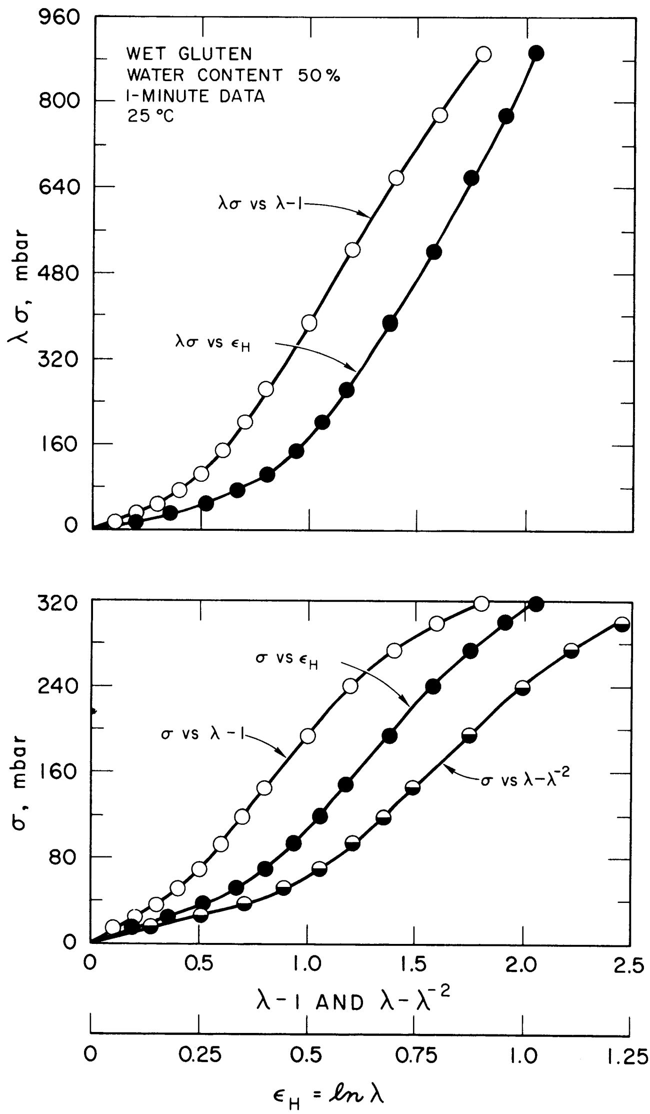

Fig. 3. One-minute (isochronal) stress data plotted against different strain measures. Upper panel shows true stress; lower panel shows nominal stress.

The time-dependence of the modulus, F(t), can be represented over the time range examined by:

$$F(t) = F(t^*)\ [t/t^*]\, n \qquad (5)$$

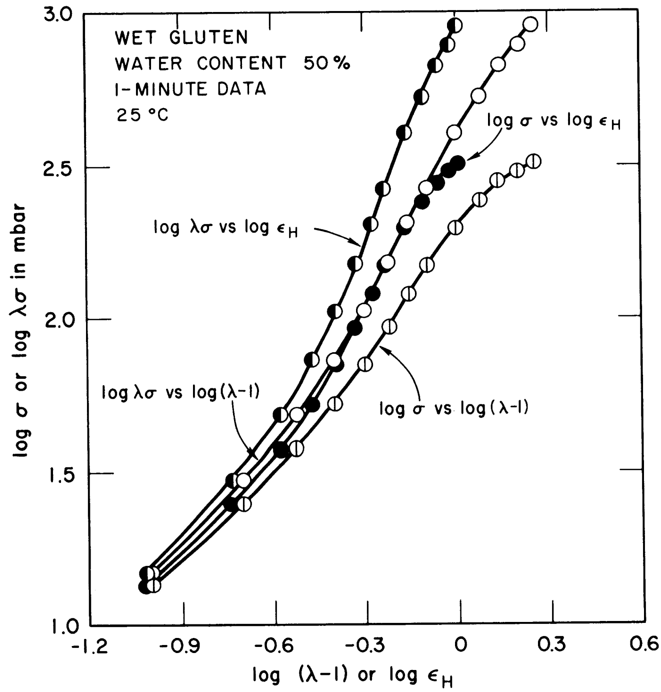

Fig. 4. Doubly logarithmic plots of 1-min. (isochronal) stress-strain data. Separate curves result from using different measures of stress and strain.

where t^* is the isochronal (fixed) time, which for convenience can be taken to equal 1 min., and $n = -0.17$ the characteristic exponent (6). The same equation, but with different values for the exponent, was found applicable to Kansas and Lemhi doughs (6).

Figure 5 shows the failure envelope given by a plot of log $\lambda_b\sigma_b$ vs. log $(\lambda_b - 1)$, where the subscript b refers to break (rupture) values. Thus, $\lambda_b\sigma_b$ is the true stress at break, and $\lambda_b - 1$ is the strain at break. With an increase in strain rate, the rupture point tends to move upward along the line; similar behavior is shown by rupture data obtained on elastomers and doughs (6). Within the experimental precision, the data conform to the straight line represented by: $\log \lambda_b\sigma_b = 1.84 \log (\lambda_b - 1) + 2.38$.

DISCUSSION

A comparison of the present results with those obtained (6) earlier on medium-strength Kansas and weak Lemhi flour doughs reveals a number of differences in the properties of gluten and dough. A somewhat more reliable comparison could perhaps be made if the gluten studied had been washed from either the Kansas or Lemhi flour instead of having been reconstituted from a commercial dry gluten. It is believed, however, that the present results show clearly

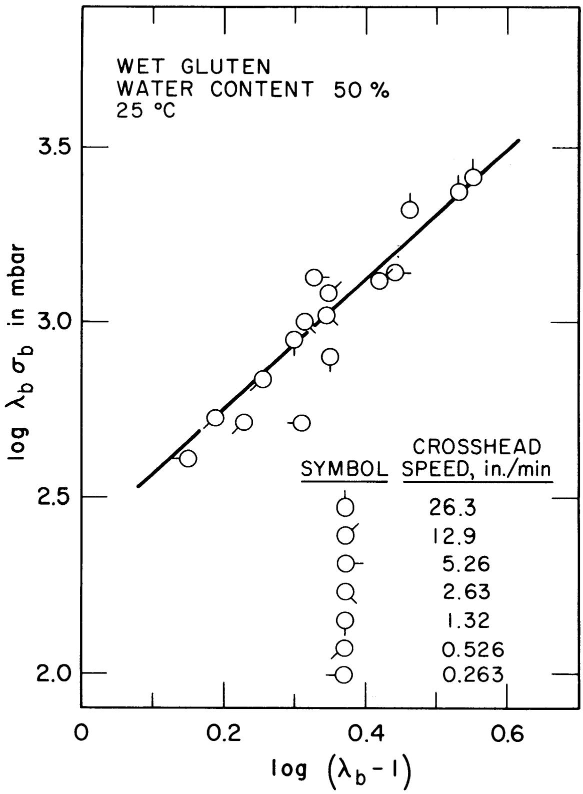

Fig. 5. Failure envelope for gluten given by doubly logarithmic plot of true rupture stress, $\lambda_b\sigma_b$, against strain at break, λ_b-1.

certain distinct differences between wet gluten and flour doughs. Some comparison between dough and the gluten washed from it has been made by Heaps et al. (10).

The stress-strain curves of gluten (Fig. 1) are quite unlike those of typical doughs, shown in Figs. 4 to 8 in ref. 5 and Fig. 1 in ref. 6. For the doughs, the curve given by a plot of σ vs. $\lambda-1$ passes through a maximum at about 75% extension; thereafter, the stress remains relatively constant or increases somewhat. For gluten, the slope of the stress-strain curve increases progressively until the extension reaches about 75%; afterwards, it decreases gradually. Also, gluten is stronger and "shorter" (less extensible) than are doughs.

In terms of isochronal stress-strain data, the nominal stress for gluten at extensions up to about 25% is proportional to any one of the three strain measures given by equation 3. Above 25% extension, the stress increases rapidly with strain, indicating an increased resistance to deformation. For example, the plot of $\lambda\sigma$ vs. $\lambda-1$ in Fig. 3 gives essentially a straight line at extensions above 75%; its slope equals 650 mbar, a fourfold greater value than F(1) obtained from the initial slope.

For elastomers (9), a plot of σ vs. $\lambda-1$ gives a curve that is concave toward the

$\lambda-1$ axis, ordinarily at extensions up to several hundred percent; thereafter provided rupture does not intervene, the curve becomes sharply convex upward. The shape of this latter portion of the curve results because the network chains are highly extended and the retractive force in individual chains increases rapidly with further extension; this effect is often accentuated by stress-induced crystallization. Although certain underlying concepts in the theory of rubberlike elasticity are no doubt applicable to gluten, it is not clear to what extent and in what manner these concepts can be applied. In contrast to elastomers, the stress-strain curve for gluten is initially convex upward and finally concave downward.

The 1-min. constant strain rate modulus, F(1), for gluten is 140 mbar at 25°C. In contrast, the 1-min. modulus for the Kansas flour dough of 45.8% water absorption is 39 mbar and that for a Lemhi dough of 44.3% water absorption about 20 mbar. Hence, the modulus of gluten under these comparable test conditions is considerably larger than that for most doughs.

On the other hand, the dynamic shear modulus of gluten, determined at frequencies from 0.1 to 100 Hz and at a peak-strain amplitude of 6.4×10^{-4}, has been found (4) to be considerably smaller than that for a number of flour doughs under the same test conditions. For gluten containing 55.2% water, the storage shear modulus G' is 900 mbar at 10 Hz; for Kansas and Lemhi doughs having water absorptions of 45.8 and 49.2%, respectively, the corresponding moduli are 3,600 and 2,250 mbar. For doughs, however, the dynamic modulus is strongly amplitude-dependent, whereas for gluten it is amplitude-independent; the dependence on amplitude has been shown to arise from a breakdown of aggregates or structures of starch particles in dough. At a strain amplitude of about 2×10^{-2}, the moduli of the above-mentioned doughs are smaller by a factor of about three; hence, at this strain amplitude, the moduli of the doughs and gluten are comparable. Under large deformations, such as obtained in the tensile tests at constant strain rates, the starch aggregates should be largely broken down, giving a sizable reduction in the modulus of a dough. (Although the modulus F(1) for doughs was evaluated from a strain function that appeared to increase in direct proportion to the stress, stress-strain data at extensions below 10% were not used in the evaluation of the modulus; the major portion of the disruption of aggregates no doubt occurred at strains considerably below 10%.)

Another factor to consider is the time-dependence of the modulus. For gluten, the characteristic exponent in equation 4 is −0.17; for the Kansas and Lemhi flour doughs, the exponents are −0.29 and −0.40, respectively. As explained previously (6), the exponent is zero when a material responds elastically, whereas it is −1 when the response is steady-state viscous flow. Thus, the characteristic exponent for gluten indicates that its response is decidedly more elastic than that of either of the two flour doughs. As a consequence, the modulus of gluten will increase less rapidly with a decrease in time than that for a dough; thus, the moduli for the doughs will tend toward that of gluten as the observational time scale is reduced.

Because the data on gluten were obtained at one temperature only, the effect of temperature on the rheological properties is not known.

Figure 5 shows that the testing rate has a marked effect on the breaking stress, $\lambda_b\sigma_b$, and strain at break, λ_b-1. With a 100-fold increase in rate, $\lambda_b\sigma_b$ increases sixfold and λ_b-1 increases 2.5-fold. For the Kansas and Lemhi flour doughs, $\lambda_b\sigma_b$

TABLE I. RUPTURE PROPERTIES OF WHEAT FLOUR DOUGHS AND GLUTEN[a]

Material	Water Absorption %	Water Content %	$\lambda_b\sigma_b$ mbar	λ_b-1
Gluten	...	50.0	1,350	2.43[b]
Kansas dough	39.2	38.2	331	6.5
	45.8	41.0	186	7.8
	52.5	43.6	132	8.9
Lemhi dough	44.3	40.4	37	4.5
	49.2	42.4	25	5.8

[a]Data are at an extension rate of 2.53 $min.^{-1}$; for gluten, this corresponds to a cross-head speed of 5.26 in. per min. The data for the flour doughs were read from the curves in Fig. 19 of ref. 6.

[b]Average of two determinations.

increases somewhat more (about ninefold) with a similar increase in rate (Fig. 19 of ref. 6); the percentage increase in λ_b-1 for the doughs is either greater or less than that for the gluten, depending on the flour type and water content.

The rupture properties for the flour doughs and gluten are compared in Table I which presents data at 25°C. at an extension rate of 2.53 $min.^{-1}$ Table I shows that, with an increase in dough water content, $\lambda_b\sigma_b$ decreases substantially and λ_b-1 increases considerably. Also, the values of $\lambda_b\sigma_b$ and λ_b-1 for the Lemhi doughs are markedly lower than those for the Kansas doughs. In contrast, $\lambda_b\sigma_b$ for the gluten is fourfold greater than that for the strongest dough, and λ_b-1 is markedly less than that for the weakest dough. (Interestingly, the breaking stress of swollen elastomers[5] is roughly the same as that of gluten.)

The present data do not allow an estimate to be made of the equilibrium modulus of gluten, if indeed one exists. However, the data obtained on gluten and flour doughs show that starch affects the rheological behavior of dough in quite a different manner from that of a reinforcing filler in an elastomer. Although it has been clearly shown (4) that aggregates, or a continuous structure, of starch particles are responsible for the amplitude-dependence of the modulus, the relative contributions of the starch and gluten phases to the modulus were not clearly established. It is difficult to compare in a scientifically meaningful manner the properties of gluten and dough, because in dough the distribution of water between the starch and gluten phases and the amount of free water are not known. A change in water content modifies not only the intensity (magnitude) of the modulus but also the relaxation times; both factors must be accounted for before a full understanding can be obtained of the manner in which starch affects the rheological properties of dough.

Acknowledgments

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