

Ultrasonic Investigation of the Effect of Mixing Under Reduced Pressure on the Mechanical Properties of Bread Dough

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ABSTRACT

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Mixing is critical to attainment of a desirable gas cell distribution in dough. By varying mixer headspace pressure, changes in the mechanical properties of dough were investigated as a function of the dough's void concentration using low frequency (50 kHz) ultrasonic techniques. For the mixer used, this allowed the volume fraction of voids (ϕ) to be varied from ≈ 0.01 to 0.08. The ultrasonic attenuation of longitudinal waves increased linearly with increases in ϕ . If, as reported, pressure reductions during mixing decrease the number density of the voids but do not affect void size, the change in attenuation is proportional to the number of

voids. By contrast, the velocity of longitudinal ultrasonic waves decreased dramatically with increasing ϕ in the range $0.012 < \phi < 0.03$, dropping from a value near that of water to values well below the velocity of sound in air. At higher ϕ , the velocity decrease was less rapid. The longitudinal elastic modulus determined from these ultrasonic results shows that the mechanical properties of the dough are sensitive to the presence of gas bubbles. At low void fractions, the elastic behavior of dough is also influenced by changes in dough matrix properties.

Gas bubbles are present in wheat flour doughs in considerable numbers (Shimiya and Nakamura 1997), as well as in the final product, such as a loaf of bread, where they represent much more than half of the total volume of the loaf (Shimiya and Nakamura 1997; Scanlon and Zghal 2001). The majority of dough rheology studies have not viewed the presence of these gas bubbles as an area of study in itself (Campbell 1991), despite their importance to the rheological properties of the dough (Charalambides et al 2002). In contrast, the importance of bubbles to breadmaking properties was emphasized by Campbell et al (1998), who viewed breadmaking as a series of aeration stages, with the bubbles being incorporated into the dough during mixing, and then inflated with carbon dioxide during proofing. The focus of their studies (Campbell 1991; Campbell et al 1991, 1998, 2001) was on the size, number, and number-density of the bubbles within the dough, rather than how these bubbles actually contributed to the rheological properties of the dough. It is nonetheless a logical consequence of their work that the breadmaking process will be better understood if the role of the gaseous phase on the properties of dough is investigated directly, so that knowledge of gas bubble structure and its effect on the mechanical properties of dough during mixing and proofing can be related quantitatively to the effect that the gas cells have on the mechanical properties of bread crumb (Scanlon and Zghal 2001).

The gas bubbles are introduced into the dough during the mixing stage when the mixer entrains air into the dough and subdivides it to produce gas cells of small size (Baker and Mize 1941). Baker and Mize (1941) showed that when dough is mixed under vacuum, the air bubbles are essentially eliminated. As a result, the density of the dough mixed at reduced pressures was higher than that of dough mixed under ambient (atmospheric) pressure. More recently, Campbell (1991) and Campbell et al (1998) studied how mixing under reduced pressure affected the aeration of bread dough. They explained how mixing under reduced pressure produces fewer bubbles per unit volume in the dough, but that the size distribution of the bubbles stays the same. Therefore, by mixing the dough under various mixer headspace pressures, doughs with different concentrations of gas bubbles are produced. The

objectives of this study were to use low intensity ultrasound to investigate the extent to which the bubbles influence the mechanical properties of doughs, whose gas content has been manipulated by mixer headspace pressure.

Using Ultrasound to Investigate the Effect of Gas Bubbles on Mechanical Properties of Dough

As a low intensity ultrasonic pulse propagates through a dough sample, the characteristics of the pulse (velocity and attenuation coefficient) are affected by the properties of the dough. By measuring the ultrasonic properties after propagation through the dough, information on the mechanical properties of the dough can be derived, which in turn can predict the quality of the product made from the dough.

The attenuation coefficient of the dough (α) is usually defined in terms of the intensity of the pulse (I) as

$$I(x) = I_0 e^{-\alpha x} \quad (1)$$

where x is the distance that the pulse has traveled and I_0 is the intensity of the ultrasonic signal at the input face of the sample (at $x = 0$). For a system in which bubbles are embedded, the attenuation is expected to depend on the extinction cross-section, σ , of the bubbles as

$$\alpha = \alpha_0 + n\sigma \quad (2)$$

where $n = \phi/V_b$ is the number density of the bubbles, ϕ is the volume fraction of voids, $V_b = (4/3)\pi a^3$ is the volume per bubble, a is the radius of the bubble, and α_0 is the background contribution of the matrix to the total attenuation (Leighton [1994]). The extinction cross-section accounts for both absorption and scattering by the bubbles, and depends on both the ultrasonic frequency and the size of the bubbles. Thus, the attenuation in heterogeneous materials like dough is sensitive to the structure of the material at a resolution that depends on the ultrasonic wavelength.

By contrast, the ultrasonic velocity determines the stiffness or rigidity of the dough, as can be most clearly seen by expressing the velocity in terms of the appropriate (dynamic) elastic modulus. The bulk, shear and Young's moduli can all be determined from measurements of both the longitudinal and shear ultrasonic velocities, although only the longitudinal velocity is considered in this paper. The longitudinal phase velocity of ultrasonic waves is related to the longitudinal modulus (β) of the dough by

$$v = \sqrt{\beta/\rho} \quad (3)$$

where ρ is the density of the dough. For a viscoelastic material, the modulus $\beta = \kappa^{-1} + 4\mu/3$, where κ is compressibility (reciprocal

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of the bulk modulus) and μ is shear modulus. The compressibility and the shear modulus of the dough are determined both by the intermolecular forces within the dough and its structure at microscopic and mesoscopic length scales. Therefore, the types of mechanical information that can be obtained from ultrasonic measurements are quite extensive. The selection of the operating frequency is important and should be optimized to probe the material properties of interest. This is especially true of heterogeneous materials containing bubbles, where strong resonant scattering and absorption may preclude accurate ultrasonic measurements near the resonance frequency (Povey 1997). In this work, measurements were performed at an ultrasonic frequency below the bubble resonance, where both attenuation and velocity were found to be sensitive probes of the bubbles within the dough.

MATERIALS AND METHODS

Dough Preparation

The samples used in these experiments were milled from Canadian Western Red Spring (CWRS) hard wheat, grade No. 1, with a flour protein content of 12.4%. The wheat was milled in the Canadian International Grains Institute (CIGI) pilot mill (Winnipeg, Manitoba, Canada). Dough samples were prepared by mechanical development of the dough using the Canadian Short Process Method (Preston et al 1982) using flour (100 g), salt (2.4% fwb), and water (63% fwb, to give optimum absorption). The dough was mixed at 165 rpm to 10% past peak consistency at 30°C in a GRL-200 mixer (Hlynka and Anderson 1955). Small subsamples (≈ 4 –12 g) were removed for ultrasonic measurements and for determinations of dough density. The dough was placed in a well-sealed container (Tupperware) to prevent moisture loss during measurements performed on the subsamples. The dough subsamples were allowed to relax between the transducers for 15 min before measurements; the value of the waiting time was chosen as a compromise between full relaxation (Cunningham and Hlynka 1954) and the likelihood of changes in the properties of the dough due to desiccation.

To demonstrate that the waiting time was sufficient to ensure that dough relaxation had negligible effect on the ultrasonic data, the velocity was measured as a function of time for 60 min starting immediately after mixing at atmospheric pressure. Very little change in the velocity is apparent through the experiment (Fig. 1). A least squares fit of a decaying exponential curve to the data showed that the dough relaxation time τ is ≈ 12 min, so that most of the relaxation of the internal stresses that are created by

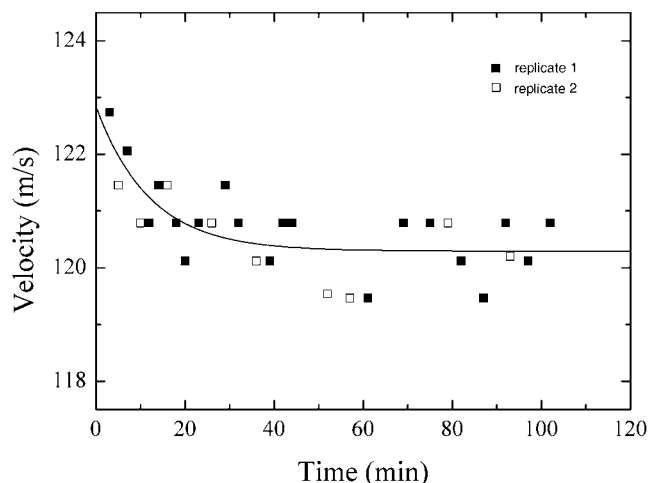


Fig. 1. Ultrasonic velocity in dough mixed at atmospheric pressure as a function of waiting time. Solid curve represents least squares fit of an exponential decay curve to the data, giving a relaxation time τ of 12 min.

stretching the protein molecules during mixing had occurred by the end of the 15-min waiting time. Furthermore, the structural changes resulting from relaxation of the dough have only a small effect (2%) on the ultrasonic velocity. The results of these measurements at 50 kHz are consistent with ultrasonic measurements at much higher frequencies (2–10 MHz) by Létang et al (2001), who reported that only small (a few %) variations in velocity were observed over a 1-hr waiting period.

The headspace pressure was manipulated during mixing by drawing a partial vacuum using a Duo Seal vacuum pump (Welch Scientific C., Skokie, IL), which was connected to an outlet on the mixing bowl. Headspace pressure during mixing was controlled by a needle pressure valve and the actual pressure in the mixing bowl was read from a Marsh B3 pressure meter (Marsh Instrument Co., Skokie IL), which was positioned adjacent to the needle valve, inline between the mixing bowl and the vacuum pump. Pressure was varied between 0.13 atm and atmospheric pressure.

For each headspace pressure, a sufficient number of subsamples was removed from the dough piece to perform the ultrasonic experiments and the dough density determinations. Separate subsamples were used for each sample thickness. At least three replicate dough pieces were prepared for each headspace pressure, obtained using different dough samples prepared under identical conditions on different days.

Ultrasonic Experiments

The ultrasonic velocity and attenuation were measured with a pulsed transmission technique, using the equipment shown in Fig. 2. The dough samples were placed between two transducers, one acting as generator and the other as detector of the ultrasonic pulse that traveled through the sample. The transducers were supported by a custom-made holder to ensure that the transducer faces touching the dough sample were parallel and separated by an accurately controlled distance (d), which determined the sample thickness. The generating transducer was excited by a short positive voltage spike from a Portable Ultrasonic Non-destructive Digital Indicating Tester (PUNDIT 6, CNS Farnell Ltd, Borehamwood, Hertfordshire, UK). The nominal frequency of the transducers was 54 kHz. The transmitted pulse was detected by the second transducer and amplified by a receiver in the PUNDIT, displayed on a digitizing oscilloscope, and downloaded to a computer for analysis.

From each digitized waveform, the arrival time and amplitude of the transmitted pulse were determined. The arrival time was taken as the time at which the minimum (or dip) in the first oscillation

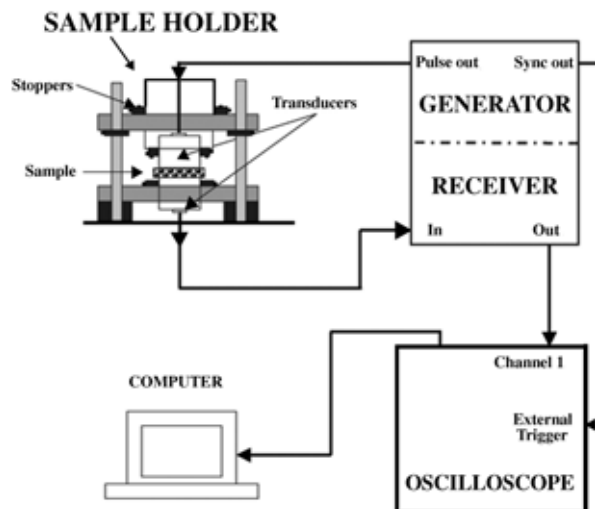


Fig. 2. Experiment for ultrasonic evaluation of dough properties.

occurred (measured relative to the trigger signal which was synchronized with the voltage spike from the pulse generator). The amplitude was determined from the magnitude of the first oscillation of the pulse transmitted through the sample. These measurements were repeated as a function of dough thickness, which was varied from 1–9 mm using the subsamples for a given replicate dough at a given pressure. The analysis of these data obtained as a function of sample thickness allowed the velocity and attenuation to be determined accurately by eliminating baseline offsets in the time and amplitude measurements.

Dough Density Determination

A 25-mL specific gravity bottle with a 2.4-cm diameter neck (VWR Canlab, Mississauga, ON, Canada) was used to determine dough density on subsamples of the dough (≈ 4 g). After weighing, the subsample was placed into the specific gravity bottle; the volume of water displaced allowed the subsample volume to be determined, and hence dough density to be evaluated. At least three subsamples were analyzed for each dough sample. The average coefficient of variation between the subsamples was 0.1.

RESULTS AND DISCUSSION

Dough Densities

The density of the dough as a function of mixer headspace pressure is shown in Fig. 3. As the mixing pressure is reduced from atmospheric pressure (76 cmHg) to 10 cmHg, the density increases according to the linear relationship

$$\rho = 1,285 - 1.43 P \quad (4)$$

Here the density of the dough (ρ) is measured in kg/m^3 and P is the mixing pressure measured in cmHg.

These density results agree with those of Campbell et al (1998), who determined the density of the dough by attaining a neutrally buoyant suspension of the dough mass using a series of calcium chloride solutions. The current data extends the measurements to lower pressures than those reported by Campbell et al (1998), and shows that the same linear trend noted by Campbell et al (1998) is observed over the entire pressure range, confirming their linear extrapolation to determine the gas-free density. Other dough density measurements were reported earlier by Baker and Mize (1941). Their densities for unyeasted dough mixed at atmospheric pressure and under vacuum were 1,150 and 1,250 kg/m^3 . Both these values lie slightly below our experimental values, differences that are

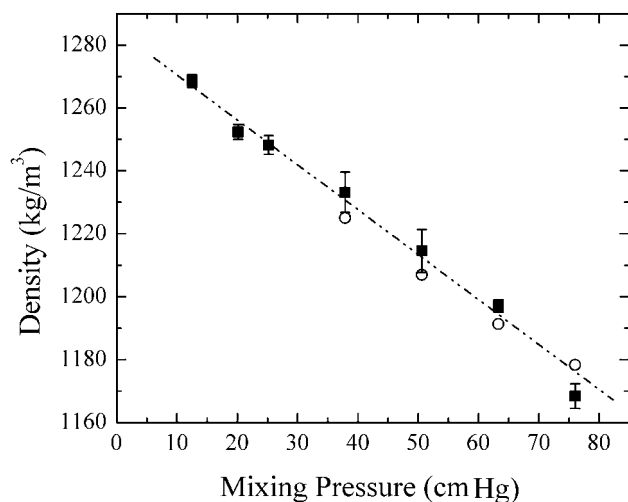


Fig. 3. Density (■) of dough as a function of mixer headspace pressure. Results (○) of Mixer A of Campbell et al (1998) have been added for comparison. Dashed line represents best linear fit to the data. Error bars represent the standard deviation.

perhaps attributable to higher moisture content in their doughs. The results in Fig. 3 enable the relationship between the amount of gas introduced into the sample and the mixer headspace pressure to be established. This relationship can be conveniently expressed in terms of the void fraction (ϕ) because

$$\phi = 1 - \rho/\rho_m \quad (5)$$

Here ρ is the density of the dough at a given mixing pressure and ρ_m is the matrix density (the gas-free dough density). (This expression is exact for “true” voids consisting of a complete vacuum and is valid to an excellent approximation for dough, because the density of the gas is so much less than the dough matrix.) The matrix density ρ_m was determined to be 1,285 kg/m^3 from the y -intercept of Figure 3. Substituting for ρ and ρ_m in Equation 5 gives the relationship between ϕ and P

$$\phi = 1.113 \times 10^{-3} P \quad (6)$$

We will use this relationship throughout to convert the mixing pressure (in cmHg) to void fraction, thereby simplifying the interpretation of the ultrasonic results and their relationship to the aeration properties of the dough.

Attenuation Coefficient Measurements at Various Headspace Pressures

The attenuation coefficient α was measured as the amplitude of the transmitted ultrasonic signal for samples mixed at the same headspace pressure but with different sample thicknesses. The signal amplitudes were then plotted as a function of sample thickness and fitted by a single exponential decay curve plus a (small) constant background. Typical results are shown in Fig. 4, which indicates that an exponential decay of the ultrasonic amplitude with thickness does indeed characterize the experimental data very well, as predicted by Equation 1. This procedure allows spurious effects, such as bond losses and interfacial reflections, that reduce the amplitude but are independent of sample thickness, to be eliminated from the attenuation measurements, allowing the true attenuation of the dough to be accurately measured. The exponentially decaying curves shown in Fig. 4 indicate that as the mixing headspace pressure decreases, the amplitude increases and the decay rate decreases. Therefore, as the mixing pressure is lowered, the

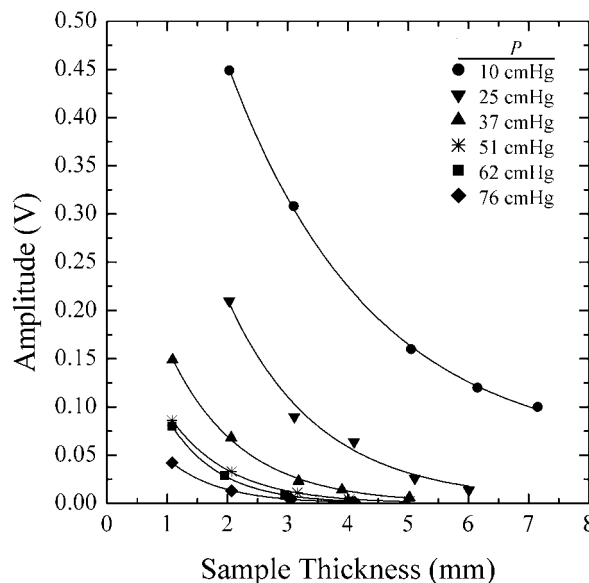


Fig. 4. Typical results for ultrasonic signal amplitude as a function of sample thickness for dough mixed under different headspace pressures. Symbols represent experimental data; solid curves are fits to the data of the decaying exponential function $A(L) = A_0 \exp(-\alpha L/2) + B$ where L represents sample thickness and B represents the background contribution.

samples become less absorbent or there is less scattering of the ultrasonic signal. To examine this behavior further, the attenuation coefficient α determined from the fits to the exponential decay curves, was plotted as a function of the void fraction ϕ (Fig. 5). It can be observed that the attenuation coefficient increases in a linear fashion as the void fraction increases. A linear fit to the data gives

$$\alpha = 0.267 + 8.3 \phi \quad (7)$$

It is clear that the attenuation increases in proportion to the amount of gas trapped in the dough, and that the bubbles (or voids) make a significant contribution to α for $\phi > 0$. The y -intercept of the above linear fit gives the background effect to the total attenuation coefficient, the contribution of the dough matrix to the attenuation coefficient. This result may be simply interpreted using Eq. 2 for the attenuation in a system containing bubbles. According to Campbell et al (1998), the decrease in dough density as a function of mixing pressure is due to a reduction in the number of gas bubbles per unit volume. They supported this hypothesis with microscopic measurements of bubble size distributions in slices of frozen dough samples 30 μm thick. Using this method, Campbell et al (1991) were able to measure the size distribution of bubbles covering the range 25–1,000 μm , and concluded that this distribution did not change significantly as mixing pressure was varied. If the radius of the gas cells does remain constant, the number density (n) is directly proportional to ϕ ($n = 3\phi/4\pi a^3$), and the extinction cross-section should be independent of mixing pressure. This could not be the case if bubble sizes rather than bubble numbers were varying. Thus, these noninvasive ultrasonic measurements support the hypothesis of Campbell et al (1998) that variation in mixer headspace pressure affects gas cell numbers but not sizes because Fig. 5 shows such a linear relationship between α and ϕ .

By taking the average radius (a) of the gas cells to be 75 μm (Campbell et al 1998) and substituting this value in the expression given above for n in terms of ϕ , Equation 2 becomes

$$\alpha = \alpha_0 + (566\sigma)\phi \quad (8)$$

Here the attenuation coefficients are expressed in mm^{-1} and the cross section is in mm^2 . Comparing Equations 7 and 8 enables the extinction cross-section (σ) to be estimated, giving 0.015 mm^2 at this frequency, which is close to the geometrical cross section πa^2 . Thus, Equation 8 shows explicitly how the attenuation coefficient α is predicted to depend on the amount of gas (ϕ) introduced into the sample during mixing, and that for constant σ , the predicted behavior of the attenuation coefficient as a function of void fraction is the same as that observed experimentally.

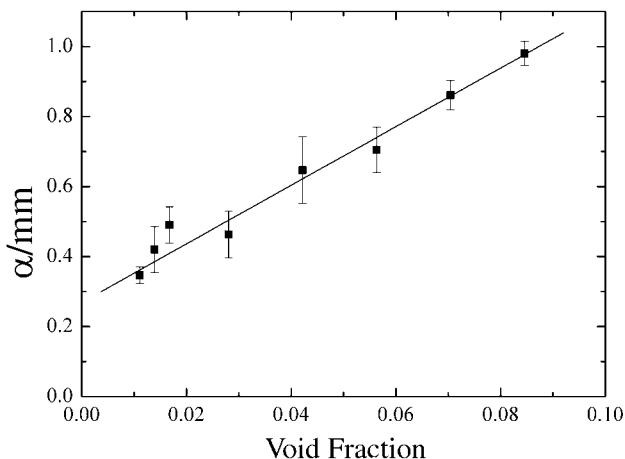


Fig. 5. Attenuation coefficient of dough (α) as a function of void fraction. Experimental data with error bars (standard deviation) and best linear fit to the data.

Ultrasonic Velocity of Dough Mixed at Various Headspace Pressures

A typical example of the measured arrival time (t) plotted versus sample thickness is shown in Fig. 6, illustrating the expected linear dependence of transit time on thickness. The velocity is then simply given by the inverse of the slope of the straight line fitted to the data: $v = (\text{slope})^{-1} = \Delta d/\Delta t$, where d is the sample thickness. In addition to improving the statistical accuracy of the velocity measurement by averaging over several readings, this method eliminates timing offset errors in determining the arrival time of the phase oscillations in the pulse at the detector relative to the time they entered the sample. This procedure was repeated for all pressures to measure the velocity dependence on void fraction varied by manipulating mixer headspace pressure (Fig. 7). These data show that the velocity decreases dramatically in the range of $0.012 < \phi < 0.03$, dropping from a velocity near to that of water (1,500 m/sec at 20°C) to values well below the velocity of sound in air (320 m/sec at 20°C). At higher ϕ values, the velocity decrease is less rapid. In the low void fraction region, a change in the void fraction of only 0.018 from its value at $\phi = 0.03$ is associated with

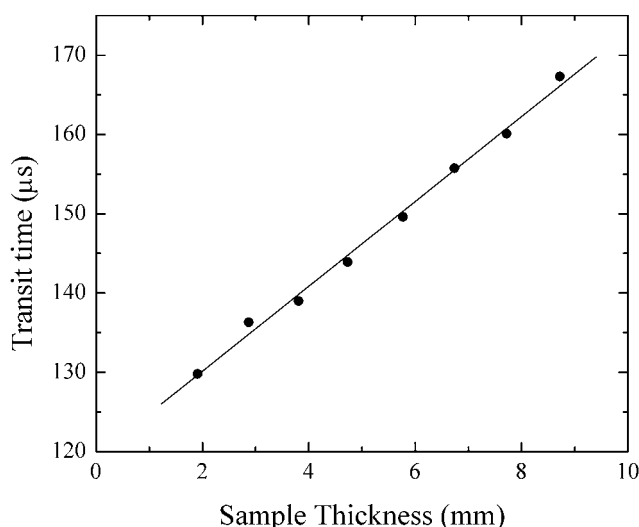


Fig. 6. Typical values of transit time through dough as a function of sample thickness for samples taken from the same dough piece (mixed at a pressure of 51 cmHg).

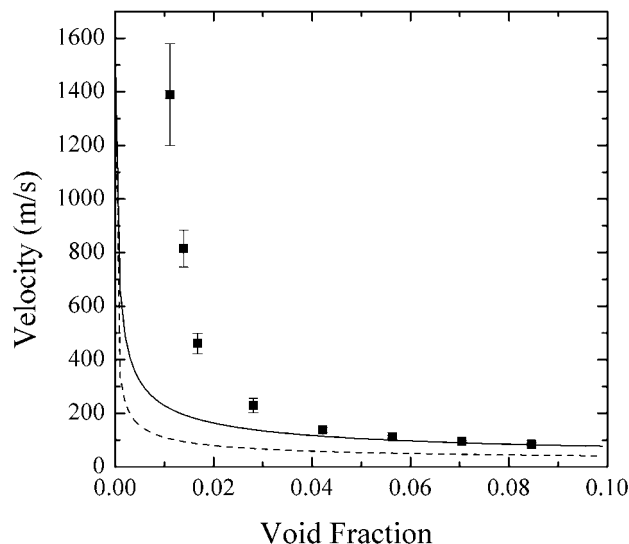


Fig. 7. Velocity and associated error bars of sound through dough mixed at various pressures. Solid and dashed curves represent the Hashin and Shtrikman upper and lower bounds, respectively.

a 10-fold change in the velocity. Thus, the velocity at this frequency is extremely sensitive to the presence of voids in the dough, especially at low ϕ .

To relate these changes in the ultrasonic velocity more directly to the mechanical properties of dough, the longitudinal elastic modulus of the doughs was calculated from the data using Equation 3. Because the attenuation in dough is appreciable at these frequencies, the modulus is complex, and both the velocity and attenuation contribute to the real and imaginary moduli, β' and β'' . This dependence can be accounted for by considering the velocity in Equation 3 to be complex, where the complex velocity, v_c , is related to the complex wavevector, k_c , by $k_c = \omega/v_c$. Here $\omega = 2\pi f$ is the angular frequency and $k_c = \omega/v - i\alpha/2$. The resulting expressions for the longitudinal moduli are (Povey 1997)

$$\beta' = \frac{\rho v^2 (1 - \alpha^2 v^2 / 4\omega^2)}{(1 + \alpha^2 v^2 / 4\omega^2)^2} \quad (9)$$

$$\beta'' = \frac{2\rho v^3 \alpha / 2\omega}{(1 + \alpha^2 v^2 / 4\omega^2)^2} \quad (10)$$

Substituting the ultrasonic data for the velocity and attenuation coefficient, along with the measured density, into Equations 9 and 10 enabled the longitudinal moduli β' and β'' to be calculated over the entire range of void fractions studied (Fig. 8A). Not only is there a very considerable increase in both moduli as ϕ is decreased but, quite remarkably, the ratio β''/β' changed from a value of ≈ 0.25 at ambient pressure to a value >1 at the lowest ϕ (Fig. 8B). Therefore, on a percentage basis, losses of mechanical energy (β''/β') are large even at the lowest ϕ where the attenuation is the smallest (Fig. 5). The fact that the losses are so substantial at the lowest ϕ is surprising and suggests that, in addition to the changes in the longitudinal modulus caused directly by reducing the number of gas bubbles, there are changes to the elasticity of the dough matrix as the void fraction is varied.

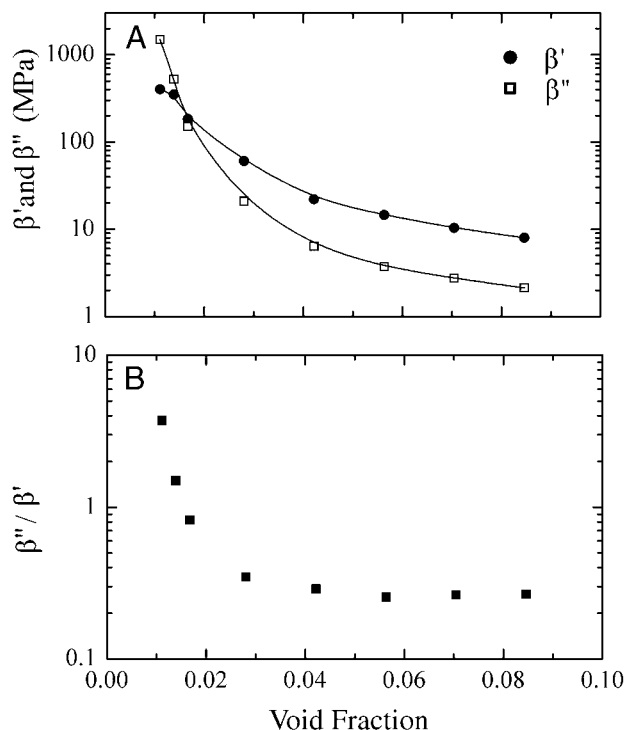


Fig. 8. Behavior of longitudinal moduli (A) and ratio of imaginary and real parts (B) as a function of void fraction in the dough. Moduli and ratios were derived from data in Figs. 3, 5, and 7.

To examine this suggestion, bounds for the phase velocity in dough were calculated from the bounds on the bulk and shear modulus of two-phase materials determined by Hashin and Shtrikman (1963). These bounds represent the upper and lower values of the ultrasonic velocity in dough that can be predicted from the elastic moduli and volume fractions of the two constituent phases: the dough matrix and the gas bubbles. The Hashin-Shtrikman bounds give the narrowest possible range of allowed values for the velocity when one only has knowledge of the volume fractions and not the microstructure. The bounds were calculated using the best estimates of the constituent moduli for dough mixed under ambient conditions to take advantage of existing rheological data for the shear modulus.

For the gas bubbles, the bulk and shear moduli are those of air, 150 kPa and 0, respectively (Anderson 1989). For the dough matrix, the bulk modulus was taken to be 3 GPa, which is close to the bulk modulus of water, and is consistent with the ultrasonic velocity measured in dough at high frequencies (Létang et al 2001), where the velocity is expected to approach the dough matrix value. The shear modulus of the dough matrix was taken to be 400 kPa, which is consistent with an extrapolation to 50 kHz (the frequency of the ultrasonic experiments) of lower frequency, small-strain rheology measurements (Campos et al 1997; Létang et al 1999; Phan-Thien et al 2000). This estimate of the real part of the shear modulus of the matrix is the average extrapolated value of the frequency-dependent storage modulus measured by Phan-Thien et al (2000) and Létang et al (1999), whose data extrapolate to 200 and 600 kPa, respectively, at 50 kHz. This estimate is also consistent with the magnitude of the complex shear modulus based on extrapolation of the work of Campos et al (1997), which gives ≈ 500 kPa. These values for the bubble and dough matrix moduli give the upper and lower bounds for the ultrasonic velocity shown by the solid and dashed curves in Fig. 7, which shows that only for the largest void fractions do the ultrasonic velocities fall between these bounds. In particular, for $\phi < 0.03$, it is clear that the experimental values of the velocity deviate significantly beyond the upper bounds, and this deviation increases as the void fraction decreases. To understand the implications of these deviations, it is worth noting that for a medium such as dough, which contains regions of very high compressibility (the bubbles), the lower bound over the range of void fractions investigated is determined almost entirely by the compressibility of the bubbles, as in the Wood's approximation (Wood 1941); the upper bound lies above the lower bound by an amount that is predominantly determined by the shear modulus of the matrix. Thus, the fact that the measured velocities at low ϕ lie so far above the rigorous Hashin-Shtrikman bounds, calculated using the best estimates of the constituent moduli for dough mixed under ambient conditions, is a strong indication that the shear modulus of the dough matrix must itself become significantly larger as the volume fraction is reduced. In short, the striking behavior of the ultrasonic velocity shown in Fig. 7 can be taken as evidence that the dough matrix properties must change as a function of void fraction.

There are two potential mechanisms that might be responsible for changes in the properties of the dough matrix, and hence the measured velocity in the dough over the experimental void fraction region. First, the effect of the decrease in moisture content of the dough as the mixing pressure is reduced was examined. Moisture changes will affect the velocity by stiffening the dough matrix. To investigate this effect, moisture loss was measured by comparing the weight of the dough after mixing to the sum of the initial weights of the individual ingredients (flour, water, and salt). Moisture losses were small; they ranged from 3.2% when the dough was mixed at atmospheric pressure to 6.7% when mixing at 10 cmHg. These results are in agreement with the measurements of Baker and Mize (1937), who reported dough moisture loss of 6% when dough was mixed under vacuum. According to Létang et al (2001),

CONCLUSIONS

who used higher frequency measurements (at 2–10 MHz) to investigate the effect of water content on the velocity of dough-water mixtures, the ultrasonic velocity change associated with a moisture loss of $\approx 3\%$ is ≈ 120 m/sec. The observed change in the current velocity measurements between the dough mixed at ambient and vacuum is $\approx 1,400$ m/sec. Therefore, the moisture loss arising from reduction of the mixing pressure is not likely to be the main cause of the dramatic increase in the velocity or longitudinal modulus at low ϕ .

Another mechanism that could give rise to significant changes in the moduli of the dough matrix is the decrease in the amount of oxygen as ϕ is reduced, thereby affecting the intermolecular bonding within the matrix (Baker and Mize 1937). Oxygen's effect on the properties of dough during mixing has been attributed to bonding changes in a number of molecules, including lipids (Smith and Andrews 1957) and proteins (Dempster et al 1954; Bloksma and Bushuk 1988). Of particular significance to its role in affecting the mechanical properties of dough as measured by ultrasound is any effect that oxygen would have on the degree of polymerization of the gluten network, regardless of whether the polymerization arises from disulfide (Dempster et al 1954; Bloksma and Bushuk 1988) or tyrosine (Tilley et al 2001) cross-links within the dough matrix. To account for observed changes in the mechanical properties of the dough (Fig. 8) as a result of this oxidative cross-linking, one must assume, as proposed by Baker and Mize (1937), that "mixing has arranged the molecules... of the dough in reactive relationship to each other". By the end of mixing, this arrangement is likely to be a parallel alignment of the glutenin polymers. In the low oxygen environment, these aligned polymers would give rise to a large number of noncovalent interactions, particularly when, according to the model of glutenin structure proposed by Belton (1999), a large number of "trains" are formed. Therefore, this large number of noncovalent interactions is deemed responsible for the large values of the longitudinal moduli at low ϕ (Fig. 8A). With the introduction of cross-links due to the presence of oxygen, both moduli decrease, and the ratio β''/β' also decreases (Fig. 8B). The effect of cross-linking on reducing the ratio β''/β' through network formation is well established in polymer systems (Ferry 1970), but in such systems cross-linking is also usually accompanied by an increase in the real part of the complex modulus. To account for the reduction in the longitudinal modulus with increasing oxygen content of the dough, the number (or strength) of noncovalent interactions must decrease. One conceivable mechanism is the formation of loops in the glutenin network (Belton 1999), which break up a significant number of noncovalent bonds as the glutenin polymers rearrange to accommodate the cross-linking (oxidation induces crumpling of the trains of glutenin polymers and disrupts the noncovalent bonding). The easier movement of the loop configurations compared with the trains when subjected to ultrasonic oscillation would account for the lower values of the longitudinal modulus at higher values of ϕ .

Some support for the absence of network formation when dough is mixed under vacuum comes from the work of Baker and Mize (1937). They observed that prolonged mixing under vacuum or with nitrogen or hydrogen produced no deterioration in dough handling properties even for mixing times as long as 40 min. In the absence of a network, the stresses applied to the polymers do not lead to their scission during prolonged mixing, and no deterioration occurs. By contrast, for air-mixed doughs in which a network exists, the stresses will lead to the mechanical degradation of the glutenin polymers that has been associated with overmixing (MacRitchie 1975).

Therefore, there is some independent evidence to support the picture of dough matrix properties that emerges from the ultrasonic experiments, namely that effects of oxygen on the dough matrix appear to be the results of an increase in covalent cross-links in the glutenin network and a concomitant decrease in noncovalent interactions.

Low frequency (50 kHz) ultrasonic velocity and attenuation measurements have been successfully used to investigate the role of gas bubbles and the surrounding matrix in determining the mechanical properties of mechanically developed dough. These experimental results show that both ultrasonic velocity and attenuation are sensitive to the presence of gas bubbles in dough. The attenuation coefficient increased in proportion to the amount of gas occluded within the dough. This observation suggests that the attenuation can be modeled by a background matrix value plus a contribution due to scattering and absorption from the bubbles, given by the product of the number density of bubbles and the ultrasonic extinction cross-section. This simple physical interpretation of these attenuation measurements does suggest an important potential application to use ultrasonic measurements to determine both the concentration and the size distribution of gas bubbles in dough once definitive measurements of the cross-section and its frequency dependence have been performed.

The velocity of longitudinal ultrasonic waves changed considerably as the amount of gas within the sample varied, with the velocity varying by more than an order of magnitude as the void fraction ϕ varied from 0.01–0.07. The density, attenuation coefficient, and velocity data were used to calculate the longitudinal elastic modulus of the dough, and this increased significantly as the void fraction was lowered. The sharp increase in the velocity (and the elastic moduli) is not likely due to the decrease in the number of gas bubbles alone. This suggests that ultrasound not only provides information about the contribution of the gas bubbles to the mechanical properties of the dough, but it also points to another potential application of the ultrasonic velocity measurements, providing a means of probing changes in the intermolecular bonding in the dough matrix as the mixing environment is manipulated.

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LITERATURE CITED

- Anderson, H. L. 1989. *A Physicist's Desk Reference*. American Institute of Physics: New York.
- Baker, J. C., and Mize, M. D. 1937. Mixing doughs in vacuum and in the presence of various gases. *Cereal Chem.* 14:721-734.
- Baker, J. C., and Mize, M. D. 1941. The origin of the gas cell in bread dough. *Cereal Chem.* 18:19-34.
- Belton, P. S. 1999. On the elasticity of wheat gluten. *J. Cereal Sci.* 29:103-107.
- Bloksma, A. H., and Bushuk, W. 1988. Rheology and chemistry of dough. Pages 131-217 in: *Wheat: Chemistry and Technology*, II. 3rd Ed. Y. Pomeranz, ed. Am. Assoc. Cereal Chem.: St. Paul, MN.
- Campbell, G. M. 1991. The aeration of bread dough during mixing. PhD thesis. University of Cambridge: Cambridge, England.
- Campbell, G. M., Rielly, C. D., Fryer, P. J., and Sadd, P. A. 1991. The measurement of bubble size distributions in an opaque food fluid. *Trans. Inst. Chem. Eng. Part C* 69:67-76.
- Campbell, G. M., Rielly, C. D., Fryer, P. J., and Sadd, P. A. 1998. Aeration of bread dough during mixing: Effect of mixing dough at reduced pressure. *Cereal Foods World* 43:163-167.
- Campbell, G. M., Herrero-Sanchez, R., Payo-Rodriguez, R., and Merchan, M. L. 2001. Measurement of dynamic dough density and effect of surfactants and flour type on aeration during mixing and gas retention during proofing. *Cereal Chem.* 78:272-277.
- Campos, D. T., Steffe, J. F., and Ng, P. K. W. 1997. Rheological behavior of undeveloped and developed wheat dough. *Cereal Chem.* 74:489-494.
- Charalambides, M. N., Wanigasooriya L., Williams, J. G., and Chakrabarti, S. 2002. Biaxial deformation of dough using the bubble inflation technique. I. *Experimental. Rheol. Acta* 41:532-540.
- Cunningham, J. R., and Hlynka, I. 1954. Relaxation time spectrum of

- dough and the influence of temperature, rest, and water content. *J. Appl. Phys.* 25:1075-1081.
- Dempster, C. J., Hlynka, I., and Anderson, J. A. 1954. Extensograph studies of the improving action of oxygen in dough. *Cereal Chem.* 31:240-249.
- Ferry, J. D. 1970. *Viscoelastic Properties of Polymers*, 2nd Ed. Pages 34-58, 247-291, 397-465. John Wiley and Sons: New York.
- Hashin, Z., and Shtrikman, S. 1963. A variational approach to the theory of the elastic behaviour of multiphase materials. *J. Mech. Phys. Solids* 11:127-140, 376.
- Hlynka, I., and Anderson, J. A. 1955. Laboratory dough mixer with an air-tight bowl. *Cereal Chem.* 32:83-87.
- Leighton T. G., 1994. *The Acoustic Bubble*. Academic Press: San Diego, CA.
- Létang, C., Piau, M., and Verdier, C. 1999. Characterization of wheat flour-water doughs. I. Rheometry and microstructure. *J. Food Eng.* 41:121-132.
- Létang, C., Piau, M., Verdier, C., and Lefebvre, L. 2001. Characterization of wheat-flour-water doughs: A new method using ultrasound. *Ultrasonics* 39:133-141.
- MacRitchie, F. 1975. Mechanical degradation of gluten proteins during high-speed mixing of doughs. *J. Polym. Sci. Symp.* 49:85-90.
- Phan-Thien, N., Newberry, M., and Tanner, R. I. 2000. Non-linear oscillatory flow of a soft solid-like viscoelastic material. *J. Non-Newtonian Fluid Mech.* 92:67-80.
- Preston, K. R., Kilborn, R. H., and Black, H. C. 1982. The GRL Pilot mill. II. Physical dough and baking properties of flour streams milled from Canadian red spring wheats. *Can. Inst. Food Sci. Technol. J.* 15:29-36.
- Povey, M. J. W. 1997. *Ultrasonic Techniques for Fluids Characterization*. Academic Press: San Diego, CA.
- Scanlon, M. G., and Zghal, M. C. 2001. Bread properties and crumb structure. *Food Res. Int.* 34:841-864.
- Shimiya, Y., and Nakamura, K. 1997. Changes in size of gas cells in dough and bread during breadmaking and calculation of critical size of gas cells that expand. *J. Texture Stud.* 28:273-288.
- Smith, D. E., and Andrews, J. S. 1957. The uptake of oxygen by flour dough. *Cereal Chem.* 34:323-336.
- Tilley, K. A., Benjamin, R. E., Bagorogoza, K. E., Okot-Kotber, B. M., Prakash, O., and Kwen, H. 2001. Tyrosine cross-links: Molecular basis of gluten structure and function. *J. Agric. Food Chem.* 49:2627-2632.
- Wood, A. B. 1941. *A Textbook of Sound*. G. Bell and Sons: London.

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