

Power Law Gels at Finite Strains

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SYNOPSIS

Many complex fluids exhibit power-law responses in their relaxation modulus; examples include foods, soft solids, fractal gels and other polydisperse systems. In the present study we investigate the rheological characteristics of such materials beyond the linear regime using a gluten-water gel as a prototypical system. The material functions of gluten dough under finite strains can be described by combining the linear viscoelastic response of a critical gel (Chambon and Winter 1987) with a Lodge rubber-like network to develop a frame invariant constitutive equation (Winter and Mours 1997). This *generalized gel equation* is a simple but accurate description of the material functions in the linear regime and also at large strains, using only two parameters. We compare the model predictions with experimental measurements in transient shear and elongational flows of gluten gels over a wide range of deformation rates. An essential feature of both the experimental data and the generalized gel model is a strain/rate separability in the system response. Further modifications to the generalized gel equation can be made by incorporating a damping function to include non-linear strain softening effects seen in more complex gels such as wheat flour doughs. From the rheological data, we find compelling evidence that indicates gluten to be a polymeric network consisting of flexible or semi-flexible chains between junction points and has a typical mesh size of approximately 20 nm.

INTRODUCTION

Materials showing power-law relaxation behavior are often encountered in rheology. Examples include many foodstuffs (Rao 1999; Gallegos et al. 2004), biopolymer networks (Gittes and MacKintosh 1998), nanocomposites (Krishnamoorti and Giannelis 1997; Hoffmann et al. 2000) and some liquid crystals (Kundu 2006). Frequently these systems involve interacting microstructural features over multiple length scales. In terms of soft glassy dynamics, power-law material functions are predicted for certain effective temperatures (Sollich et al. 1997; Sollich 1998), while in the field of cellular mechanics, the term power-law rheology is often used to describe the frequency response of protein networks (Fabry et al. 2001; Chaudhuri et al. 2007). As another example, both the Rouse (Rouse 1953) and Zimm (Zimm 1956) models will show power-law behavior under time scales that are longer than the segmental relaxation time but shorter than the longest relaxation time ($\lambda_{\text{seg}} \leq t \leq \lambda_1$). In general, polymeric systems with a large degree of polydispersity or an extremely broad relaxation spectrum will also exhibit power law relaxation over a significant span of time scales. One subset of materials that falls under the broad umbrella of power-law rheology and which has been studied relatively well is the *critical gel* first described by Winter and Chambon (Winter and Chambon 1986; Chambon and Winter 1987). Linear viscoelastic measurements show that in critical gels both the storage and the loss moduli scale as $G', G'' \sim \omega^n$ and the loss tangent is constant over a wide range of frequencies. Theoretical models show that this power law scaling can arise from the fractal nature of a

flocculated gel (Muthukumar 1985; Muthukumar 1989). At the critical gel point, the material forms a percolated, sample-spanning structure that exhibits power-law frequency dependence in the dynamic moduli.

The linear viscoelastic functions of a critical gel have been discussed in detail by Chambon and Winter (Winter and Chambon 1986; Chambon and Winter 1987) and by Larson (Larson 1999). Winter provides an excellent review of these systems that are near the liquid-solid transition (Winter and Mours 1997). However, there have been very few systematic investigation of such materials under finite strain deformations. Venkataraman and Winter (Venkataraman and Winter 1990) adopted the Lodge rubber-like liquid formulation originally suggested by Chambon and Winter (Chambon and Winter 1987) to analyze the non-linear large strain behavior of PDMS gels during start-up of steady shear and creep experiments. They noticed a stress overshoot at shear strains of $\gamma^* \sim 2$ and a subsequent yield at $\gamma^p \sim 4$. Watanabe et al also studied the non-linear rheology of a polyvinyl chloride critical gel. To the best of the present authors' knowledge, no such study exists for critical gels under uniaxial extension.

Finding a suitable material is not easy. Firstly, critical gels are hard to formulate. One needs a reliable and reproducible method to bring the material to the critical gel point and then quench it to prevent additional percolation. Secondly, the percolated structure of gels can collapse under large deformations which will be manifested as strain-softening in rheometric tests. The specific form of the non-linear material response exhibited by a particular critical gel (for example strain-softening or stiffening) provides an additional rheological signature about the microstructure beyond the simple linear response (Phan-Thien et al. 1997; Ng et

al. 2006b; Tanner et al. 2007). We first begin by identifying a suitable candidate material to serve as a model critical gel system that shows relatively simple non-linear behavior.

Curiously, many foodstuffs show power-law/critical gel like behavior (Hossain et al. 2001; Cordobés et al. 2004; Muliawan and Hatzikiriakos 2006). Of particular interest here, are wheat flour-water doughs. Despite these numerous early observations of power-law like frequency response in the linear viscoelastic moduli (Hibberd 1970a; Smith et al. 1970; Berland and Launay 1995; Phan-Thien and Safari-Ardi 1998), Gabriele and co-workers (Gabriele et al. 2001) were the first to use the concept of a critical gel and a power-law relaxation modulus to describe the rheological behavior of dough. This descriptive framework has also been used recently (Gabriele et al. 2006; Ng et al. 2006a) to explore other types of deformation including creep relaxation, uniaxial and biaxial extension. This so-called 'weak gel model' (Gabriele et al. 2001) is extremely attractive because of its relative functional simplicity. Material functions in the linear viscoelastic regime can be well described by only two parameters.

In simple terms, dough may be described in the following way: a viscoelastic matrix of gluten (a branched polymer) filled with hydrated starch particles. In many aspects, the resulting composite is analogous to a carbon-black filled elastomer. The interactions between the polymeric and filler constituents lead to severe non-linearities and complex response (Hibberd 1970b; Edwards et al. 2002). The precise microstructure of the gluten forming the matrix is still poorly understood due to its high molecular weight and the high degree of chain branching, both of which result in poor solubility characteristics. Opinions can be

broadly classified into two schools of thought. One school maintains that gluten, though a high molecular weight compound, takes the shape of a tight globule - neighboring protein molecules aggregate to form a network through hydrogen bonds and hydrophobic interactions (Don et al. 2003b; Don et al. 2003a; Domenek et al. 2004; Hamer et al. 2005). In this article, we refer to this idea as the particulate gel model. The other school believes that the gluten molecule is sufficiently swollen that it forms an entangled matrix or polymeric network with flexible chains spanning between junction points (Belton 1999; Singh and MacRitchie 2001; Belton and Dobraszczyk 2006); we refer to this picture as the polymeric gel model.

Despite the ease of formulating flour-water doughs, obtaining repeatable measurements and understanding the material rheology is difficult due to the strong time-dependent and non-linear softening effects observed in doughs (Bagley et al. 1998). Comprehensive studies on these systems, which can lead to insight into the microstructure, are hampered by the difficulty in collecting reproducible data. In our laboratory, we observe day-to-day variations of up to $\pm 50\%$ in modulus just by simply varying the mixing and testing schedule.

Eliminating the starch fillers to focus exclusively on the rubbery gluten network removes at least one level of complexity. The rheology of gluten doughs had been investigated by various workers (Wang and Kokini 1995; Redl et al. 1999; Uthayakumaran et al. 2002; Don et al. 2003a; Domenek et al. 2004). Uthayakumaran et al reported shear and extension data for gluten gels that has been mixed with different amount of starch (0-100% starch weight content) and contrasted these results with tests performed on wheat flour doughs. They

observed an exponential decrease in the limiting strain of linear viscoelastic behavior with increasing starch content; Lefebvre and co-workers investigated the linear viscoelastic behavior in the long time-scale terminal regime (Lefebvre et al. 2003). Critical-gel-like behavior in gluten doughs has also been observed: Letang et al (Letang et al. 1999) showed that the dynamic moduli both follow a power-law behavior with $n \approx 0.3$ (see equation (12) in section IIIC), they also noted that gluten doughs possess a larger linear range when compared to wheat flour doughs.

To prepare critical gels with a well-defined and reproducible power-law linear viscoelastic response, we follow these earlier studies and isolate the viscoelastic response of the biopolymeric matrix forming the dough. In addition to being a 'model' system with a power-law relaxation spectrum, developing a quantitative understanding of the rheology of gluten is also of great practical interest. Despite the relatively small weight proportion of gluten in a typical flour (5-20%), the viscoelasticity of a wheat flour-water dough is largely determined by this protein phase (Uthayakumaran et al. 2000) and it is widely believed that the bread-making qualities of a wheat flour dough are strongly linked to its mechanical properties (Bloksma 1990b; Bloksma 1990a). In particular, the large strain rheology of the dough has an impact on the texture and distribution of gas cells in the bread (Ewart 1989; van Vliet et al. 1992; van Vliet and Kokelaar 1994). The most commonly-cited relationships are those between final loaf volume, dough extensibility and gluten quantity: beginning from the work of Bailey and others in the first half of the 20th century (Bailey 1913; Shollenberger 1923; Aitken and Geddes 1939) to more recent studies such as those by Sliwinski et al (Sliwinski et

al. 2004a; Sliwinski et al. 2004c), Weegels et al (Weegels et al. 1996) and Dobraszczyk et al (Dobraszczyk and Roberts 1994; Dobraszczyk and Morgenstern 2003; Dobraszczyk 2004). An accurate constitutive and microstructural model will aid in documenting differences between wheat-flour doughs of different gluten content and ‘functionality’ – which are the key mechanical properties relevant to breadmaking. A robust rheological equation of state is also a good starting point for cereal scientists who would like to investigate systematically the effects of other components (e.g. starch, water content etc...), with the aim of increasing the complexity level until ultimately arriving at a real dough system.

There are three primary objectives of this paper. The first is to demonstrate that a gluten dough exhibits the rheological characteristics of a critical gel with relatively-well controlled material properties (i.e. a variability in modulus of less than 10%). We report rheological data for gluten doughs using both shear and extensional deformations that span the linear to non-linear regimes. The second objective is to identify a constitutive model that can provide a description of the stresses arising in non-linear deformations in terms of well-defined material functions which can be measured directly in the linear viscoelastic range. Finally, using the rheological evidence collected, we infer certain aspects regarding the microstructure of the gluten gel.

I GLUTEN DOUGH PREPARATION

Gluten dough was prepared by placing 10g of vital gluten (Arrowhead Mills - ~ 12% moisture content) in a mixograph bowl with 14g of water (total dough moisture content = 63% by weight). The mixture is then stirred, stretched and

folded through the action of the mixograph pins for 12 minutes (Gras et al. 2000). Mixing over this length of time allows the dough to become ‘fully developed’, the appearance of the dough changes from dry and lumpy to a smooth, sticky and elastic paste. No significant changes to the dough properties could be observed when the mixing time was increased. We use a customized mixograph which has been digitally instrumented to record both the rapid temporal fluctuations and longer time variations in the mixograph torque output. Representative data for mixing of a vital gluten gel are shown in Figure 11. The torque signal shows a rise towards a steady plateau after approximately 11 minutes. The magnitude of the short time scale fluctuations (corresponding to stretching of material elements between interacting pairs of pins in the bowl) also remains constant. The dough is removed from the mixing bowl after 12 minutes (720s) of mixing and then allowed to rest for 1 hour at 22° C, before testing.

The window of practical moisture content for preparing a homogeneous gluten gel sample is surprisingly small as compared to a wheat flour dough. At moisture contents of less than 60%, the dough appears to be too dry and some gluten powder around the edge of the mixing bowl remains unincorporated. By contrast if the moisture content exceeds 65%, the dough appears wet, with unincorporated water pooled at the bottom of the bowl.

II RHEOMETRY

Shear rheometry are performed under controlled strain mode on the ARES rheometer and under controlled stress mode on the AR-G2 rheometer (TA instruments). A Peltier plate and a 25mm parallel plate fixture at 1mm separation

were used. Approximately 2 g of gluten dough was placed on the Peltier plate, and the upper plate was then brought down to compress the sample to the specified thickness. Excess dough was trimmed with a razor blade. The Peltier plate was held at a fixed temperature of 22°C, to approximate typical room temperature. Slip was eliminated by applying adhesive-backed sandpaper (600 grit McMaster Carr 47185A51) to the surfaces of both the Peltier plate and the parallel plate tool. Drying of the sample was minimized by painting the exposed surface of the dough with a low-viscosity silicone oil.

Measurements of the transient extensional stress growth were made on a wind-up drum type rheometer (the Sentmanat Extensional Rheometer or SER fixture) which was used in conjunction with the ARES rheometer (Sentmanat et al. 2005). Samples of 2 x 25mm were formed by pressing the gluten dough to a thickness of 2 mm, then cutting to shape using a Guillotine cutter. A thin film of silicone oil was painted onto the sample before mounting on the SER fixture to minimize drying.

III LINEAR VISCOELASTICITY

We first investigate the linear viscoelastic response of the gluten gel. This enables us to compare and contrast our measurements with previously published data on gluten gels (Letang et al. 1999; Uthayakumaran et al. 2002; Lefebvre et al. 2003) and other critical gels (Winter and Chambon 1986; Chambon and Winter 1987; Venkataraman and Winter 1990; Winter and Mours 1997; Watanabe et al. 1998). From these experiments, we extract two key constitutive parameters; the power-law exponent n and the gel strength S of the critical gel.

A. Step Strain Relaxation

Under linear viscoelastic conditions a critical gel will exhibit a power-law behavior in its material functions (Winter and Chambon 1986; Chambon and Winter 1987). For example, following an infinitesimal step strain of amplitude γ_0 at time $t = 0$, the modulus decays like:

$$\frac{\sigma_{xy}}{\gamma_0} \equiv G_{gel}(t) = St^{-n} \quad (1)$$

In Figure 2 we show the extent of power-law relaxation for a typical gluten-water dough. We find that the relaxation can be well described by equation (1) with $S = 1260 \pm 50 \text{ Pa s}^n$, $n = 0.175 \pm 0.005$ for approximately three decades of elapsed time $0.2 < t < 100 \text{ s}$. At short times ($t < 0.05 \text{ s}$), an additional Rouse-like response can also be observed. The overall response of the system can be accurately described by the following expression:

$$G(t) = G_{gel}(t) + G_{Rouse}(t) = St^{-n} + G_R \sum_{k=1}^{\infty} \exp(-tk^2/\lambda_R) \quad (2)$$

Where $G_R \approx 803 \text{ Pa}$ and $\lambda_R = 0.05 \text{ s}$ are the modulus and relaxation time of the Rouse modes. The existence of this short time scale regime is consistent with the generic rheology of polymeric gels described by Winter (Winter and Mours 1997): the Rouse modes characterize the “molecular building blocks” of the critical gel, i.e. they represent the response of the segmental structure size within the gluten network. This segment length scale estimated from network theory $\ell \sim (k_B T / G_R)^{1/3} \approx 20 \text{ nm}$ is close to the typical structural sizes observed with

transmission electron microscope (Amend and Belitz 1991), but is far smaller than the diameter of gluten gel particles ($D \sim 10 \mu\text{m}$) seen through confocal microscope observations of gluten dispersed with SDS (Don et al. 2003a).

Departure from the power-law regime at long times ($t > 100\text{s}$) has often been attributed to a long time terminal relaxation and appears to be sensitive to the amount of rest time the sample is allowed before testing (Cunningham and Hlynka 1954; Rao et al. 2000). The fact that dough properties appear to change if left to rest is also well-known to bakers, they refer to this effect as “slackening” (Cunningham and Hlynka 1954). We find that it is in fact related to residual relaxation from the initial mounting and compression of the sample in the test geometry. This particular sample was rested for 1 hour before testing. It was found that by increasing the rest time, the upper temporal limit of the power-law relaxation could be extended; however it is difficult to extract a simple relationship between rest time and onset of this residual relaxation, in part because the specific material history of the loading deformation is unknown.

To help comprehend this behavior, we consider the characteristic or ‘mean’ relaxation time of a viscoelastic material. A power law relaxation modulus with $0 < n < 1$ will imply a characteristic relaxation time that diverges:

$$\lambda_{char} = \frac{\int_0^{\infty} rG(r)dr}{\int_0^{\infty} G(r)dr} = \frac{\int_0^{\infty} Sr^{-n+1}dr}{\int_0^{\infty} Sr^{-n}dr} \rightarrow \infty \quad (3)$$

where $r = t - t'$ is the elapsed time.

Material functions at fully equilibrated initial conditions are therefore difficult to obtain for such systems with power-law relaxation. Unless the material sample was constituted on the rheometer plates, any residual stress from loading will require an infinite amount of time to relax away.

When a sample is first loaded onto the rheometer, the gluten gel is typically compressed from an irregular shape to a flat disc, then cut to shape. Of course, the deformations accumulated in this process are far from simple shear, and will most likely be unevenly distributed throughout the sample. During a typical loading event the compression process in which the sample is squeezed from a thickness of $h_0 = 20$ mm to $h_1 = 1$ mm, we find $\gamma_0 \sim \ln(h_0/h_1) \sim 3$. This strain is significantly larger than the typical step shear strains applied in the stress relaxation tests, therefore residual stress relaxation will be significant. As an illustration, we consider experimentally the situation depicted in the inset of Figure 3. We impose a large uniform torsional shearing strain γ_0 on the sample in the θ -direction at $t = -t_w$ to emulate the effects of sample compression. The material is then allowed to relax for a waiting time t_w before the actual stress relaxation test in which a step strain of γ_a is applied in the same direction at $t = 0$. Assuming that the material response is linear in strain, the stress response measured from $t = 0$, will consist of a superposition of relaxation due to both the initial ‘loading’ strain γ_0 and the subsequent ‘test’ strain γ_a :

$$\sigma_{xy} = S \left[\gamma_a t^{-n} + \gamma_0 (t + t_w)^{-n} \right] \quad \text{for } t \geq 0 \quad (4)$$

For many conventional rheometers, such as the ARES used in these experiments, any residual stress values are automatically “zeroed out” at the beginning of the experiment: as a result, the apparent modulus will be smaller than the true value by an offset $G_{\text{offset}} = S t_w^{-n} \gamma_0 / \gamma_a$. The apparent or measured response is thus:

$$\begin{aligned}
 G_{\text{apparent}}(t) &= \frac{\sigma_{xy}(t)}{\gamma_1} - G_{\text{offset}} \\
 &= S \left[t^{-n} + \frac{\gamma_0}{\gamma_a} \left\{ (t + t_w)^{-n} - t_w^{-n} \right\} \right]
 \end{aligned} \tag{5}$$

The resulting decay in the apparent modulus of a critical gel is plotted in Figure 3 for $\gamma_0 = 3$, $\gamma_a = 0.1$ using a range of values for t_w . We also compare the predictions of the gel equation with measured data obtained in gluten samples with various waiting times ($t_w = 10, 100, 1000$ s). A rapid decay in the apparent modulus occurs at time $t \sim O(t_w)$ due to the subtraction of the residual relaxing stresses and this is captured qualitatively by equation (5).

Very long time scale processes such as the power-law stress relaxation in Figure 2 are therefore difficult to probe because the relative contribution of residual relaxation from initial loading histories will always become significant at long times $t \gtrsim t_w$. From an experimentalist’s point of view, this means that in systems showing power-law relaxation, one can only access time scales that are significantly shorter than the amount of rest time provided to the sample.

B. Continuous and discrete relaxation spectrum

For materials with relaxation processes spanning a wide range of time scales, such as the critical gel, it is sometimes more convenient to express the material properties as a continuous relaxation spectrum over a logarithmic time scale (Ferry 1980; Winter and Mours 1997):

$$G(t) = \int_{-\infty}^{\infty} \tilde{H}(\lambda) \exp\left(-\frac{t}{\lambda}\right) d \ln \lambda \quad (6)$$
$$\tilde{H}(\lambda) = \frac{S}{\Gamma(n)} \lambda^{-n}$$

Where $\tilde{H}(\lambda)$ is the continuous relaxation spectrum of a critical gel and λ is the range of relaxation time scales. Alternatively, it is common for numerical simulations to seek a suitable description of the relaxation modulus in terms of a set of discrete Maxwell relaxation modes with moduli G_k and relaxation times λ_k (Phan-Thien et al. 1997; Charalambides et al. 2006; Dealy 2007). As Dealy (2007) notes, this decomposition is, in general, ad hoc and non-unique; in the case of power-law relaxation, there exists a very elegant relationship between each successive relaxation mode which can be written in the following way (Spriggs 1965):

$$G(t) = \sum_{k=0}^{\infty} G \exp\left(-\frac{t}{\lambda_k}\right) \quad (7)$$
$$\lambda_k = \frac{\lambda_0}{k^\alpha}$$

Where $G_k = G$ sets the scale of the modulus for each mode and α characterizes the rate of relaxation. Relaxation spectra of the form in equation (7) can be converted into an integral form through the Euler Maclaurin series:

$$\sum_{k=0}^K f(k) = \int_0^K f(s) ds + \frac{1}{2} [f(K) + f(0)] + \dots \quad (8)$$

Where K is the desired range of the summation. Substituting equation (7) into equation (8) gives:

$$\sum_0^{\infty} G \exp\left(-\frac{tk^\alpha}{\lambda_0}\right) \approx \int_0^{\infty} G_0 \exp\left(-\frac{ts^\alpha}{\lambda_0}\right) ds + \frac{G_0}{2} \quad (9)$$

After performing the integral and rearranging we obtain:

$$\frac{G_0 \lambda_0^{1/\alpha}}{\alpha} \Gamma(1/\alpha) t^{-1/\alpha} = \frac{G_0}{2} + \sum_{k=1}^{\infty} G_0 \exp\left(-\frac{tk^\alpha}{\lambda_0}\right) \quad (10)$$

Comparing the final result to equation (1), it is clear that the power law relaxation modulus of a critical gel can be approximated by a series of discrete relaxation modes in the form of equation (10) with

$$\begin{aligned} \alpha &= 1/n \\ \lambda_k &= \lambda_0 k^{-1/n} \\ G_0 &= \frac{S}{n\Gamma(n)\lambda_0^n} \end{aligned} \quad (11)$$

A relationship of this form for the single specific case $n = 1/2$ was first noted by Winter et al (Winter and Chambon 1986).

This discrete relaxation spectrum starts from an arbitrary or user-specified maximum time scale λ_0 (which we may expect from Section A to scale

as $\lambda_0 \sim O(t_w)$). Although an infinite summation is indicated in (10), in practice only a finite series of terms $0 \leq k \leq K$ need be considered. Since $n \leq 1$ and $\alpha \geq 1$, the series converges smoothly.

In Figure 4, we compare the predicted relaxation modulus of a critical gel (with properties close to that of gluten) as computed with a range of discrete Maxwell modes to the true power-law response. The discrete spectrum of relaxation modes accurately describes the relaxation modulus over a finite time span from a minimum time $\lambda_{\min} = \lambda_0 / K^{1/n}$ to a maximum time $\lambda_{\max} = \lambda_0$. Beyond this range the relaxation modulus given by (7) rolls off to asymptotic values of $G_{\min} = G_0 / 2$ and $G_{\max} = (K + 1/2)G_0$ respectively. Reconsidering the experimental data in Figure 2, it is clear that we would need at least $K \approx (\lambda_{\max} / \lambda_{\min})^n = (t_w / \lambda_R)^n \approx 7$ discrete relaxation modes (14 model parameters) to approximately describe the relaxation modulus of a gluten gel. The economy of the two parameter description in equation (1) for timescales greater than the Rouse time λ_R and less than the rest time t_w is apparent.

Conceptually, expressing the relaxation spectrum in the forms described in this section reconciles the observed power-law relaxation with the traditional view of exponential stress decay. These spectra represent the range of length-scales present in a fractal network: successive exponential relaxation processes at longer times occur revealing the contributions from progressively longer length scales.

C. Small Amplitude Oscillatory Shear Flow

For a critical gel undergoing small amplitude oscillatory shear flow, the storage and loss moduli will also show power-law behavior. The dynamic moduli can be evaluated by Fourier-transforming equation (1) to obtain (Winter and Chambon 1986):

$$G'_{gel}(\omega) = \frac{G''_{gel}(\omega)}{\tan(n\pi/2)} = \Gamma(1-n) \cos\left(\frac{n\pi}{2}\right) S\omega^n \quad (12)$$

In addition to having dynamic moduli that follow the same power-law exponent n , another distinguishing feature of the critical gel model is the relationship between the loss tangent $\tan \delta$ and n :

$$\tan \delta = \frac{G'_{gel}}{G''_{gel}} = \tan\left(\frac{n\pi}{2}\right) \quad (13)$$

This ratio is unique and independent of ω and S , in contrast to some other power-law models and takes on a different value to that of the SGR model (Fielding et al. 2000).

Of course, the relaxation processes in the Rouse regime can be similarly transformed:

$$G'_R = G_R \sum_{k=1}^{\infty} \frac{(\lambda_k \omega)^2}{1 + (\lambda_k \omega)^2}, \quad G''_R = G_R \sum_{k=1}^{\infty} \frac{(\lambda_k \omega)}{1 + (\lambda_k \omega)^2} \quad (14)$$

where $\lambda_k = \lambda_R/k^2$.

The dynamic moduli obtained from small amplitude controlled stress experiments at a stress amplitude of $\sigma_0 = 50$ Pa are plotted in Figure 5. The

experimental data are in excellent agreement with predictions from the Fourier transformation of the step-strain relaxation response ($G' = G'_{gel} + G'_R, G'' = G''_{gel} + G''_R$ indicated by solid lines). The Rouse-like regime dominates at high frequencies ($\omega \geq 1/\lambda_R$), while at low frequencies some small deviation from a perfect power-law response can be detected, and we attribute this to the residual relaxation described in section A.

We return here briefly to consider the relevance of using doughs formulated from vital gluten powder. The production of vital gluten involves drying and milling which may irreversibly damage or alter the ‘functionality’ of the network that is formed upon hydration. Ideally, the rheology of a gluten network directly washed-out from wheat flour doughs should be investigated. Unfortunately, the mechanical properties of native gluten networks are difficult to control: the washing process involves gently massaging the dough under running water; it is difficult to maintain consistent mechanical work input and ultimate water content. In Figure 5b, we compare the dynamic moduli of the vital gluten dough with those measured in a gluten network that has been washed out from a freshly mixed wheat flour. Both doughs show viscoelastic moduli of similar magnitudes and the segmental relaxation at high frequencies can also be observed in the native gluten dough. This regime transitions smoothly at $\omega \sim \lambda_R^{-1} \approx 20s^{-1}$ to gel-like behavior at low frequencies in the same manner as the vital gluten dough. Similarities in the low frequency power-law regime are partially masked by the greater variability in the native dough. However the close correspondence between the two sets of linear viscoelastic material

functions are sufficient to validate the use of vital gluten doughs as a basis for discussing the role of gluten rheology to realistic breadmaking processes.

D. Creep

Measuring the creep compliance of soft solids and weak gels has certain advantages, and some of the difficulties encountered in directly measuring the relaxation modulus can be bypassed. Most significantly, while the measured forces decays to diminishingly small values at long times in a relaxation test and become obscured by residual relaxation processes (discussed in section A), the applied stress is constant in a creep test and the resulting strain grows in time. Consequently, long time scale processes are often better characterized through creep (Lefebvre et al. 2003).

Creep experiments are performed by incrementing the shear stress from zero to σ_0 such that $\sigma_{xy} = \sigma_0 \hat{H}(t)$, where $\hat{H}(t)$ is the Heaviside step function. From the resulting increase in strain with time $\gamma_{xy}(t)$, we define the creep compliance in the following manner:

$$J(t) = \frac{\gamma_{xy}(t)}{\sigma_0} \quad (15)$$

We can also consider the theoretical predictions of creep compliance for a critical gel. The compliance must satisfy the well known relationship given by Ferry (Ferry 1980):

$$t = \int_0^t G(t-t') J(t') dt' \quad (16)$$

Thus with the relaxation modulus of equation (1) we can calculate the theoretical compliance (Venkataraman and Winter 1990) through the following expression:

$$J(t) = \frac{1}{S\Gamma(1-n)\Gamma(1+n)} t^n \quad (17)$$

Once again, the material function predicted shows a power-law dependence: strain and compliance grow without bound in time as t^n , and no steady state flow viscosity can be measured even as $t \rightarrow \infty$.

In Figure 6, we compare the measured creep compliance of a gluten gel evaluated using equation (15) with the response of an ideal critical gel given by equation (17). The values of the gel strength $S = 1280$ Pa and gel exponent $n = 0.175$ used in equation (17) are obtained independently from step strain relaxation experiments.

One cycle of “damped oscillation” in strain is observed at short times ($t < 0.1$ s). This is a consequence of the coupling between instrument inertia and sample elasticity (Ewoldt and McKinley 2007), therefore only data from $t > 0.1$ s are included in the analysis.

For an applied stress below 3000 Pa, the gluten gel exhibits a linear behavior, i.e. the compliance is independent of applied stress. The qualitative and quantitative agreement with the critical gel model is excellent: the compliance grows as a power-law with exponent $n = 0.175$ over four orders of magnitude in time ($0.1 < t < 2000$ s).

For the case in which a shear stress of $\sigma_0 = 3000$ Pa is applied, the material shows an initial power-law increase. This continues up to a shear strain of $\gamma^* \approx 5$ ($t = 12$ s) when the gluten gel yields abruptly, and this is manifested as a rapid increase in strain and compliance. This is followed by an instability at large strain $\gamma \sim 10$ of the same form depicted in Figure 9. The nature of this “yield” event and progression into non-linearity is explored in greater detail in section IV using controlled strain experiments.

Over the duration of the experiments, no steady state was observed for any of the shear stresses tested, this feature of gluten and dough rheology has also been discussed in detail by Lefebvre and co-workers (Lefebvre et al. 2003; Lefebvre 2006).

E. General Linear Viscoelastic Response

We have demonstrated through small amplitude oscillations, stress relaxation and creep measurements that gluten doughs exhibit a linear viscoelastic response that is strongly reminiscent of a polymeric critical gel. We now conclude this section by considering the linear viscoelastic stress response to an arbitrary deformation together with a brief summary of the historical development of the gel equations.

Using the Boltzmann superposition principle, we can write an integral constitutive equation for an arbitrary deformation history:

$$\boldsymbol{\sigma}(t) = \int_0^t S(t-t')^{-n} \dot{\boldsymbol{\gamma}}(t') dt' \quad (18)$$

where $\dot{\boldsymbol{\gamma}}(t) = \nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^T$ is the infinitesimal strain rate tensor (Bird et al. 1987). However, it must be stressed that this equation is only valid for infinitesimally small deformations. The response under finite strains is the subject of the following section.

The relaxation function of a critical gel (equation (1)) is also known as the Nutting's equation (Nutting 1921) and has long been used as an empirical approximation of material functions. Well before the concept of a critical gel was proposed, Scott Blair (Scott Blair et al. 1947) generalized Nutting's equation by adopting the framework of fractional calculus (Oldham and Spanier 1974) and arrived at the differential form of equation (18) given in the following expression:

$$\boldsymbol{\sigma}(t) = \frac{S}{\Gamma(1-n)} \frac{\partial^n}{\partial t^n} \boldsymbol{\gamma}(t) \quad (19)$$

Equation (19) can be considered to be a generalization of the mechanical analogs of springs ($n = 0$) dashpots ($n = 1$) and is often referred to as a Scott Blair element (Mainardi 1997). Scott Blair himself described the material parameters S and n as *quasi-properties* (Scott Blair et al. 1947), he suggested that the non-integer exponents are a consequence of a "non-Newtonian equilibrium" and are closely correlated with perceptions of texture and firmness. Friedrich and Heymann (Friedrich and Heymann 1988) recognized this link between fractional calculus models and the critical gel, they generalized the stress relaxation function to include the post- and pre-gel states that exists near the solid-liquid transition.

Despite the sharp conceptual difference with traditional models that show exponentially decaying stress, these fractional calculus models have proven to be

of great practical utility because they allow engineers to accurately model damping properties for many viscoelastic polymers with a minimum number of parameters. Winter and Mours noted that the damping properties (characterized by the loss tangent) is independent of temperature and frequency (Winter and Mours 1997); however, a critical gel can still undergo dynamic oscillations at a characteristic frequency when coupled with a free mass. A convenient example is the viscoelastic ringing already encountered during the initial transient response of creep experiments depicted in Figure 6. We can write the equation of angular motion for the instrument coupled with the viscoelasticity of the sample as:

$$I\ddot{\phi} + b \frac{S}{\Gamma(1-n)} \frac{\partial^n \phi}{\partial t^n} = P(t) \quad (20)$$

Where I is the instrument moment of inertia, b is the geometry factor, ϕ [rad] is the angle of plate rotation and P (Ewoldt and McKinley 2007) is the instrument-applied torque. For our experiments shown in Figure 6 we have:

$$\begin{aligned} I &= 21.04 \times 10^{-6} \text{ Nms}^2 \\ b &= \pi R^4 / (2h) = 3.9 \times 10^{-5} \text{ m}^3 \\ R &= \text{plate radius} = 12.5 \times 10^{-3} \text{ m} \\ h &= \text{sample thickness} = 1 \times 10^{-3} \text{ m} \end{aligned} \quad (21)$$

The ringing frequency is given by the minima of the (complex) characteristic equation:

$$-\omega^2 I + b \frac{S}{\Gamma(1-n)} (i\omega)^n = 0 \quad (22)$$

This frequency can be evaluated numerically and is found to be 68.5 rad s^{-1} ($t^* = 0.09 \text{ s}$) which is in good agreement with the heavily damped ringing

frequency observed in creep experiments. Such excellent agreement is perhaps surprising, since the fixture response during the initial transients should also be influenced by the Rouse modes of the system ($t \sim \lambda_R = 0.05$ s).

IV CRITICAL GEL RESPONSE UNDER FINITE STRAIN

We have examined the linear viscoelasticity of a critical gel and showed that for time-scales greater than the segmental relaxation time λ_R , the rheology can be economically described by two parameters, the gel strength S , and the gel exponent n . As mentioned in the introduction, characterizing the non-linear deformation of a critical gel is essential in many applications. For example, in adhesives applications (Winter and Mours 1997), information on the strain to failure can be useful. In bread and gluten dough, researchers have found little or no correlation between linear viscoelastic material functions and baking qualities. This of course should not be surprising, because non-linear deformation (kneading, proofing, baking etc...) feature prominently in the process of breadmaking (Bloksma 1990b; Dobraszczyk and Roberts 1994; Dobraszczyk and Morgenstern 2003; Sliwinski et al. 2004c; Sliwinski et al. 2004b).

A. Large Step Strain Relaxation

We begin probing the non-linear deformation of the gluten gels by simply increasing the amplitude γ_0 of the step strain relaxation tests discussed in section IIIA. The results are plotted in Figure 7a.

Qualitatively, the relaxation modulus at large strain amplitude is observed to be a function of both time and strain $G = G(t, \gamma_0)$. Both the Rouse segmental

relaxation and power-law gel regimes are still clearly visible. Since it is the power-law/critical gel region that we are most interested, we can gain insight into this non-linear behavior by seeking a function that will collapse the data in this regime onto a single curve. The power-law exponent of the relaxation remains approximately constant despite the increase in strain, therefore a simple vertical shift factor – or damping function – suffices to collapse the data. In other words, the data can be taken to be time-strain separable in the power-law regime:

$$G(t, \gamma_0) = G(t)h(\gamma_0) = St^{-n}h(\gamma_0) \quad (23)$$

The resulting damping function is plotted in Figure 7b. The strain softening effect in the gluten gel is relatively weak, especially when compared to the highly-filled wheat flour systems, in which non-linearity begins at extremely small strains (Sofou et al. 2007). To quantitatively compare the two sets of data, they are fitted to a simple algebraic function that is motivated by the form commonly used to describe strain-softening in entangled melts $h(\gamma) = 1 / (1 + (q\gamma)^{2k})$ (Ng et al. 2006b). The rate of softening $k = 0.4$ is the same for both systems; the onset of non-linear behavior corresponding to a critical strain $\gamma_0^* \sim q^{-1}$ occurs at $\gamma_0^* \sim 0.04$ for wheat flour dough but not until $\gamma_0^* \sim 5$ for gluten systems.

The weak damping characteristic of gluten dough is consistent with critical gels that are formed from randomly cross-linked networks of flexible polymeric strands. Even though particulate gels can also form self-similar fractal structures that exhibit power-law rheology in their linear viscoelastic material functions, they are typically “brittle”. Non-linear behavior of particulate gels are commonly

characterized by rapid softening or yielding at strains that are seldom greater than unity i.e. $\gamma_{Particulate}^* < 1$ (Buscall et al. 1988; Larson 1999).

In fact, the behavior seen here is very similar to the damping function for critical gels polyvinylchloride in dioctyl phthalate (PVC-DOP) reported by Watanabe et al (Watanabe et al. 1998). They argue that in contrast to highly entangled systems which show reptation dynamics, the recovery of polymer chains to their equilibrium length occurs at the same rate as orientation rearrangements in fractal networks; thus resulting in a damping function that is close to unity. The similar lack of reptation dynamics or a distinct yielding process observed in the present work strongly suggests that gluten gels should also be viewed as a polymeric network rather than a particulate gel or highly entangled melt.

The large range of linear response also suggests that gluten doughs can be treated up to moderately large strains approximately as a quasi-linear elastic material (Bird et al. 1987). If we are to express the constitutive equation for the gluten gel as an integral model of the factorized Rivlin-Sawyer form, a simplification to the strain-dependent function can be made, such that $h(\gamma) \approx 1$; the non-linearity in the constitutive equation associated with large strains is then contained exclusively in the deformation tensors. This leads to greatly simplified constitutive equations and analytical solutions are possible for a wide variety of flow conditions. The construction of such a constitutive model will be the subject of the following section.

B. Transient Experiments

For quasi-linear models under finite deformation, the infinitesimal strain rate tensor $\dot{\gamma}$ in equation (18) must be replaced by a finite strain rate tensor $\frac{\partial}{\partial t'} C^{-1}(t, t')$ to preserve frame invariance (Bird et al. 1987). $C^{-1}(t, t')$ is the Finger strain tensor. We can write a frame invariant constitutive equation (Winter and Mours 1997) by considering a linear superposition of stress relaxation modes associated with this finite rate of strain $\frac{\partial}{\partial t'} C^{-1}(t, t')$:

$$\begin{aligned}\sigma(t) &= -\int_0^t G(t-t') \frac{\partial}{\partial t'} C^{-1}(t, t') dt' \\ &= -\int_0^t S(t-t')^{-n} \frac{\partial}{\partial t'} C^{-1}(t, t') dt' \quad \text{for the gel equation}\end{aligned}\tag{24}$$

This form of constitutive equation (with an unspecified form of $G(t-t')$) is generically referred to as a Lodge rubber-like network model (Lodge 1964). We refer to the particular constitutive model in equation (24) with a power-law relaxation modulus as the *generalized gel model*.

By analogy to the discussion in section III E, equation (24) can also be expressed in a differential form:

$$\sigma(t) = -\frac{S}{\Gamma(1-n)} D^n [C^{-1}(t, t')]\tag{25}$$

where the fractional differential operator denoted D^n is the convected fractional derivative which satisfies material objectivity (Drozdov 1997).

In the limits of infinitesimal strains, equations (24) and (25) reduce to (18) and (19) respectively. To explore the constitutive response of gluten gels at large strains, we now consider the form of $C^{-1}(t, t')$ and $\frac{\partial}{\partial t'}C^{-1}(t, t')$ for specific modes of deformation commonly used in rheometric testing and the resulting form of the stress tensor.

C. Start-up of Steady Shear

In a step shear rate experiment, in which the rate of shearing strain is incremented from zero to $\dot{\gamma}_0$, such that $\dot{\gamma}_{xy}(t) = \dot{\gamma}_0 \hat{H}(t)$, the finite strain and rate tensor takes the form:

$$\begin{aligned} \mathbf{C}^{-1} &= \begin{bmatrix} 1 + \dot{\gamma}_0^2 (t - t')^2 & \dot{\gamma}_0 (t - t') & 0 \\ \dot{\gamma}_0 (t - t') & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \text{ for } 0 \leq t' \leq t \\ &= \begin{bmatrix} \dot{\gamma}_0^2 t^2 & \dot{\gamma}_0 t & 0 \\ \dot{\gamma}_0 t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{ for } t' < 0 \end{aligned} \quad (26)$$

$$\begin{aligned} \frac{\partial}{\partial t'} \mathbf{C}^{-1} &= \begin{bmatrix} -2\dot{\gamma}_0^2 (t - t') & -\dot{\gamma}_0 & 0 \\ -\dot{\gamma}_0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \text{ for } 0 \leq t' \leq t \\ &= 0 \quad \text{for } t' < 0 \end{aligned} \quad (27)$$

Inserting the respective components into equations (24) or (25) gives an expression for the transient growth in the shear stress:

$$\begin{aligned}
\sigma_{xy} &= -\int_0^t S(t-t')^{-n} [-\dot{\gamma}_0] dt' \\
&= S\dot{\gamma}_0 \int_0^t (t-t')^{-n} dt'
\end{aligned} \tag{28}$$

Substituting $r = t - t'$ and integrating, we find:

$$\sigma_{xy}^+ = S\dot{\gamma}_0 \int_0^t r^{-n} dr = S\dot{\gamma}_0 \left[\frac{r^{1-n}}{1-n} \right]_0^t = \frac{S\dot{\gamma}_0}{1-n} t^{1-n} \tag{29}$$

So that the shear stress in a critical gel grows in time without bound as a power-law with t^{1-n} . The total strain imposed is $\gamma = \int_0^t \dot{\gamma}_0 dt' = \dot{\gamma}_0 t$. We also note that the response (28) is factorizable into shear-strain and shear-rate contributions:

$$\begin{aligned}
\sigma_{xy}^+(\dot{\gamma}_0, \gamma) &= \frac{S}{1-n} \dot{\gamma}_0^n \gamma^{1-n} \quad \text{for } \gamma \geq 0 \\
&= S f(\dot{\gamma}_0) \Phi_{xy}(\gamma)
\end{aligned} \tag{30}$$

Where $f(\dot{\gamma}_0) = \dot{\gamma}_0^n$ and $\Phi_{xy}(\dot{\gamma}_0) = \gamma^{1-n}/(1-n)$.

In Figure 8 we demonstrate the ability of this generalized gel equation to predict the growth in the shear stress of gluten gels during the start-up of steady shear flow. After an initial short time response ($t \leq 0.1s$) which is governed by the Rouse modes convoluted with the finite response function of the rheometer, the material functions increase as power laws (i.e. straight lines on a log-log scale). The shear stress increases with shear strain as γ^{1-n} (equation (30)) and the data can be collapsed onto a single power law strain function $\Phi_{xy}(\gamma)$ by factoring out

the rate-dependent component, $f(\dot{\gamma}_0) = \dot{\gamma}_0^n$. All of the samples show slip and/or fracture at large strains $\gamma \sim 10$ despite our efforts to prevent slip (Section I).

At the highest strains and shear rates tested ($\gamma > 5, \dot{\gamma}_0 > 0.1s^{-1}$), the gluten gels exhibit a stress overshoot, in contrast to the softening observed in the previous section for step strain relaxation. The rheological significance of this overshoot remains unclear. Phan-Thien and coworkers (Phan-Thien et al. 1997) attempted to model the overshoot behavior through the use of a highly non-linear strain function that incorporates both strain stiffening and softening of the form:

$$\begin{aligned}\sigma_{PT}(\gamma) &= G\Psi_{PT}(\gamma)(C^{-1} - aC) \\ \Psi_{PT}(\gamma) &= \frac{1}{(1 + \Gamma_1^2\gamma^2)^{(1-m)/2}} \exp(-\Gamma_2^4\gamma^4)\end{aligned}\quad (31)$$

Where Γ_1 , Γ_2 , a and m are material constants, C is also known as the left-Cauchy-Green tensor. However in our experiments, we observed this phenomenon to be closely associated with a torsional elastic instability as depicted in Figure 9. This instability occurred shortly after the transient shear stress deviated from the predicted power-law form and becomes extremely severe at the point of stress softening: the sample rolls up and is ejected from the geometry gap. The flow is no longer viscometric at the onset of this instability and therefore we have made no attempts to model it constitutively.

Nevertheless, the fact that linear deformation persists without yield up to large strains is once again a strong indication that gluten doughs are polymeric gel networks consisting of flexible or semi-flexible filaments. This class of systems include many biopolymer gels that often exhibit extremely large linear range and

has non-linear regimes that are typified by a stiffening behavior before yield (Storm et al. 2005; Chaudhuri et al. 2007), in a manner very similar to the behavior of the gluten gel.

In fact the behavior of these gluten gels also bears a strong resemblance to the data reported by Venkataraman and Winter (Venkataraman and Winter 1990) on a synthetic critical gel. The PDMS they studied also forms a cross-linked polymeric network with flexible chains between junction points; they observed a relatively large linear range during start-up of steady shear flow ($\gamma^* \sim 2$) and a mild stress overshoot at large strains. However, the separability of the measured material response into rate-dependent and strain dependent functions cannot be checked in this previous study because data at only a single shear rate ($\dot{\gamma}_0 = 0.5 \text{ s}^{-1}$) was presented.

In these start-up experiments, we can also follow the evolution in the first normal stress difference of the gluten gels. From equation (24) we find:

$$\begin{aligned}
N_1^+(\dot{\gamma}_0, t) &\equiv \sigma_{xx}(t) - \sigma_{yy}(t) = -\int_0^t S(t-t')^{-n} [-2\dot{\gamma}_0^2(t-t')] dt' \\
&= 2S\dot{\gamma}_0^2 \int_0^t (t-t')^{1-n} dt' \\
&= 2S\dot{\gamma}_0^2 \left[-\frac{1}{2-n} (t-t')^{2-n} \right]_0^t \\
&= \frac{2S}{(2-n)} \dot{\gamma}_0^2 t^{2-n} \\
&= \frac{2S}{(2-n)} \dot{\gamma}_0^n \gamma^{2-n}
\end{aligned} \tag{32}$$

Notably, this result is again strain/strain-rate separable and can be written in the form:

$$\sigma_{xx}(t) - \sigma_{yy}(t) = Sf(\dot{\gamma})\Phi_N(\gamma) \quad (33)$$

Where, as in equation (30), the function $f(\dot{\gamma}_0) = \dot{\gamma}_0^n$ and the strain function for the normal stress difference is $\Phi_N = 2\gamma^{2-n}/(2-n)$.

In Figure 10 we show that the first normal stress difference measured in a gluten water dough system can also be described quite well by equation (32). The data shows a positive power-law increase in the normal stress difference with strain (typical of polymer networks) corresponding to an exponent of γ^{2-n} . The values of $S = 1280 \text{ Pa s}^n$ and $n = 0.175$ are consistent with those obtained from linear viscoelastic measurements. These curves can also be approximately collapsed onto a single curve by factoring out the rate-dependent component $f(\dot{\gamma}) = \dot{\gamma}_0^n$. The normal force data show less perfect superposition when compared with the measured shear stress response. When the plates are brought together during loading and the sample is squeezed into a disc shape, the axial compressive strain can result in substantial normal forces even when slow compression rates and long waiting times are employed, and this contributes to the observed variability at low deformation rates. The effect of this residual stress relaxation is analogous to that described in section IIIA. Nonetheless, the power-law growth in N_1 at large shear rates is very clear across several decades in stress. It is interesting to note that in the generalized gel equation, the ratio between transient shear stress and normal stress difference is given by $N_1/\sigma_{xy} = 2\gamma(1-n)/(2-n)$. For an ideal critical gel, this relationship is valid even in the limit of infinitely rapid deformations. This modified elastic response can be contrasted with that expected of typical viscoelastic materials which show purely elastic behavior at time shorter than the most rapid relaxation time: the Lodge-Meissner relationship (Larson 1988) shows that the stress ratio approaches $N_1/\sigma_{xy} = \gamma$. The modified elastic behavior noted above is a

distinguishing feature of a critical gel but might not be of practical utility in determining the gel point, especially for materials with small values of n . Furthermore, for gluten gels, the presence of a cut-off at the segmental relaxation time scale λ_R reported in section IIIA will obscure the observation of this relationship at very high shear rates when $Wi_R = \lambda_R \dot{\gamma}_0 > 1$.

D. Start-up of Uniaxial Extensional Flow

Elongational deformations provide a litmus test for the robustness of the generalized gel equation. The applicability of a rheological constitutive equation such as the critical gel model is greatly increased if material parameters obtained from small amplitude shear experiments can be used to predict the rheological behavior under vastly different flow conditions such as those observed under large extensional strains.

In strong flows such as uniaxial elongation, the integral expression to be evaluated for the stress becomes slightly more involved because the components of the finite strain-rate tensor increase exponentially with strain rather than polynomially. For extensional stress growth following inception of a uniaxial extensional flow at a finite constant strain rate, the Finger strain tensor $\mathbf{C}^{-1}(t, t')$

and finite rate of strain tensor $\frac{\partial}{\partial t'} \mathbf{C}^{-1}(t, t')$ are:

$$\begin{aligned}
\mathbf{C}^{-1} &= \begin{bmatrix} \exp[-\dot{\epsilon}_0(t-t')] & 0 \\ 0 & \exp[2\dot{\epsilon}_0(t-t')] \end{bmatrix} \text{ for } 0 \leq t' \leq t \\
&= \begin{bmatrix} \exp[-\dot{\epsilon}_0(t')] & 0 \\ 0 & \exp[2\dot{\epsilon}_0(t)] \end{bmatrix} \text{ for } t' < 0
\end{aligned} \tag{34}$$

$$\begin{aligned}
\frac{\partial}{\partial t'} \mathbf{C}^{-1} &= \begin{bmatrix} \dot{\epsilon}_0 \exp[-\dot{\epsilon}_0(t-t')] & 0 \\ 0 & -2\dot{\epsilon}_0 \exp[2\dot{\epsilon}_0(t-t')] \end{bmatrix} \text{ for } 0 \leq t' \leq t \\
&= 0 \text{ for } t' < 0
\end{aligned}$$

The normal stress difference predicted by the generalized gel equation in steady uniaxial extension is then:

$$\sigma_{zz}(t) - \sigma_{rr}(t) = \int_0^t S(t-t')^{-n} \dot{\epsilon}_0 \left\{ 2 \exp(2\dot{\epsilon}_0[t-t']) + \exp(-\dot{\epsilon}_0[t-t']) \right\} dt' \tag{35}$$

We first perform a change of variable to recast the solution into a separable form composed of a rate-dependent term and a strain-dependent integral. Substituting for the Hencky strain $\epsilon(t) = \dot{\epsilon}_0 t$ and the strain difference $r = \dot{\epsilon}_0(t-t')$, we obtain:

$$\Delta\sigma(\epsilon) = S \dot{\epsilon}_0^n \int_0^\epsilon r^{-n} \left\{ 2 \exp(2r) + \exp(-r) \right\} dr \tag{36}$$

The extensional stress growth in a critical gel can once again be written in terms of rate- and strain-dependent components by factorizing equation (36) to give:

$$\Delta\sigma(\dot{\epsilon}_0, \epsilon) = S f(\dot{\epsilon}_0) \Phi_{Ext}(\epsilon) \tag{37}$$

where

$$\begin{aligned}
f(\dot{\epsilon}_0) &= \dot{\epsilon}_0^n \\
\Phi_{Ext} &= \int_0^\epsilon r^{-n} \left\{ 2 \exp(2r) + \exp(-r) \right\} dr
\end{aligned} \tag{38}$$

The integral for the strain dependent function can be integrated repeatedly by parts to yield a solution in the form of a summation. However, this approach is rather cumbersome and the result converges slowly. It is more convenient to consider approximations to the expression at large and small strain limits.

For small strains (i.e. $\varepsilon \ll 1$), equation (37) approaches the linear viscoelastic limit:

$$\begin{aligned}\Delta\sigma(\dot{\varepsilon}_0, \varepsilon) &\rightarrow \frac{3S}{1-n} \dot{\varepsilon}_0^n \varepsilon^{1-n}, \text{ as } \varepsilon \rightarrow 0 \\ \Phi_{Ext} &\simeq \frac{3\varepsilon^{1-n}}{1-n}\end{aligned}\quad (39)$$

The corresponding Trouton ratio approaches:

$$Tr^+ = \frac{\sigma_{Ext}(\dot{\varepsilon}_0, \varepsilon)}{\sigma_{xy}(\dot{\gamma}_0, \gamma)} \rightarrow 3, \text{ for } \varepsilon \ll 1 \quad (40)$$

where $\dot{\gamma}_0 = \sqrt{3}\dot{\varepsilon}_0$ and $\gamma = \sqrt{3}\varepsilon$ is used in evaluating the ratio.

At large strains (i.e. $\varepsilon \gg 1$), an asymptotic approximation can be made such that:

$$\begin{aligned}\Delta\sigma &\simeq S\dot{\varepsilon}_0^n \varepsilon^{-n} \exp(2\varepsilon) \\ \Phi_{Ext} &\simeq \varepsilon^{-n} \exp(2\varepsilon) \\ Tr^+ &\simeq (1-n)\varepsilon^{-1} \exp(2\varepsilon)\end{aligned}\quad (41)$$

An approximation is made to equation (38) by considering a function that smoothly connects the two limits (equation (39) and (41):

$$\begin{aligned}\Delta\sigma_{Ext}^+ &\simeq S\dot{\varepsilon}_0^n \varepsilon^{-n} \left[\exp(2\varepsilon) + \frac{(1+2n)}{1-n} \varepsilon - 1 \right] \\ \Phi_{Ext}^+ &\simeq \varepsilon^{-n} \left[\exp(2\varepsilon) + \frac{(1+2n)}{1-n} \varepsilon - 1 \right] \\ Tr^+ &\simeq \frac{(1-n)}{\varepsilon} [\exp(2\varepsilon) - 1] + (1+2n)\end{aligned}\quad (42)$$

Equations in (42) are a surprisingly accurate approximation and is barely distinguishable from the true solution over the range of strains discussed in this article.

We examine the response of gluten gels experimentally under uniaxial extension using a wind-up drum type rheometer. The geometry is shown in Figure 11. A Sentmanat Extensional Rheometer (SER) fixture (Sentmanat 2004) is mounted onto the ARES rheometer. Samples of gluten gel ($L_0 = 12.5\text{mm}, H_0 = W_0 \approx 2\text{mm}$) are held in place between two cylinders by clamps and then stretched uniaxially as the cylinders are rotated by the drive system of the rheometer. The resulting torque and sample deformation are measured independently through the ARES torque transducer and digital video imaging respectively. Figure 12 illustrates the measurements obtained during a typical experiment.

The counter rotating cylinders apply a nominal strain rate of:

$$\dot{E} = \frac{2\Omega R}{L_0} \quad (43)$$

However, the true strain rate in the sample is also independently measured from video images. A thin film of oil is painted onto the surface of the sample to eliminate evaporation and sample drying, this film can also inadvertently lead to slip in the contact area with the rotating cylinders (Ng et al. 2006b). Measurements with polyisoprene have shown that if the sample aspect ratio is small, i.e. $\Lambda = H/W \ll 1$, the deformation will deviate from uniform uniaxial stretching (Nielsen et al. 2006) and approaches the planar limit instead as $\Lambda \rightarrow 0$. In the present experiments, the aspect ratio is close to unity ($\Lambda \sim 1$), therefore the

actual deformation can be well approximated by homogeneous uniaxial stretching. Video imaging at 100 frames/sec. confirms the assumptions of uniform uniaxial deformation and no-slip at the cylinder-sample interface. The strain rate calculated from lateral contraction of the sample $\dot{\epsilon}(t)$ is identical to the imposed longitudinal strain $\dot{\epsilon}(t)$, and the width $W(t)$ of the sample thus decays as a simple exponential:

$$\begin{aligned}\dot{\epsilon} &= -\frac{2}{W(t)} \frac{dW(t)}{dt} \simeq \dot{\epsilon} \\ W(t) &\simeq W_0 \exp(-\dot{\epsilon}t/2)\end{aligned}\tag{44}$$

From the torque $P(t)$ and sample width $W(t)$ measurements collected, it is straight forward to calculate the true evolution in the normal stress difference during uniaxial elongation:

$$\sigma_{zz}(t) - \sigma_{xx}(t) = \frac{P(t)}{2RH_0W_0} \exp(+\epsilon(t))\tag{45}$$

The results from three different strain rates $\dot{\epsilon}_0 = 0.03, 0.3, 3.0 \text{ s}^{-1}$ are plotted in Figure 13a. The experiments for each strain rate were repeated to confirm their reproducibility; because of sample-to-sample variability such reproducibility is not often achieved in typical dough systems (Bagley et al. 1998; Ng et al. 2006b). Deviations between individual experiments at the same strain rate are only discernible at small strains. These differences can be attributed to slightly different preloads associated with the backlash inherent to the SER gearing system, and the torque signal for data collected at strains $\epsilon < 0.1$ have been omitted for analysis purposes. The samples were stretched at constant strain

rates till they ruptured, usually around total Hencky strains of $\varepsilon \sim 2-3$, corresponding to the point when the torque measurement drops rapidly. Some fluctuations are apparent at low stresses, however these only occur below the stated resolution of the torque transducer; $\Delta\sigma_{\min} = (P_{\min}) / (2RH_0W_0)$. For typical values of sample dimensions $H_0 = 2\text{mm}$, $W_0 = 2\text{mm}$ and cylinder radius $R = 5.25\text{ mm}$, we find the minimum resolvable stress to be approximately $\Delta\sigma_{\min} = 5 \times 10^3\text{ Pa}$.

Once again we can separate the rate- and strain-dependent contributions by using equation (37). The tensile stress growth data can be collapsed onto a single master curve of the strain function by dividing the tensile stress difference by $f(\dot{\varepsilon}_0) = \dot{\varepsilon}_0^n$ as shown in Figure 13b. The strain function $\Phi_{Ext}(\varepsilon)$ is well described by equation (38), and the gel parameters used to collapse the data at different rates are obtained through the linear viscoelastic step-strain relaxation experiments discussed in section IIIA ($S = 1260\text{ Pa s}^n$ and $n = 0.175$) i.e. we do not refit the material properties and there are no adjustable parameters.

As we also noted in equation (3), the effective characteristic time constant for a critical gel diverges ($\lambda_{char} \rightarrow \infty$), therefore the effective Deborah number in a critical gel also approaches infinity and nonlinear elastic effects always become important. As a result, the tensile stress growth measured at all strain rates will deviate from the linear viscoelastic power-law response $\Phi_{Ext} = 3\varepsilon^{1-n} / (1-n)$ at moderate strains $\varepsilon > 1$. At large Hencky strains, the stress response approaches the asymptotic approximation of the form $\Delta\sigma_{Ext}^+ \approx St^{-n} \exp(2\varepsilon)$. This large strain

behavior highlights the fact that a critical gel does indeed lie on the point of solid-liquid transition: the material exhibits both neo-Hookean-like affine network deformation $\Delta\sigma_{Ext}^+ \sim f(x_1) = \exp(2\varepsilon) = x_1^2$ (where $x_1 = (W/W_0)^{-2}$ is the principal stretch in the SER device) as well as fading memory dependence in time, $\Delta\sigma_{Ext}^+ \propto t^{-n}$.

We observe no need to incorporate additional strain-dependent damping in the gluten gel which would lead to non-affine deformation in Figure 13b. This is in contrast to analogous measurements with wheat flour doughs which show exponential, but sub-affine, stress growth at large strains (Ng et al. 2006b). These differences are consistent with our step shear strain measurements in Figure 7. The gluten gels rupture at Hencky strains of $\varepsilon \sim 3$ before such non-linearities would become important.

As a final confirmation that gluten gels should be considered as flexible elastic networks, we note that few (if any) particulate gels can withstand such large stretch ratios ($x_1 = (W/W_0)^{-2} \approx 20$) without yield or rupture. by contrast such behavior is rather common for crosslinked polymeric networks such as rubber elastomers, collagen etc...

V CONCLUSIONS

In this paper we have demonstrated that a vital gluten dough exhibits a power-law relaxation modulus characteristic of that observed in polymeric networks at the liquid-solid transition i.e. the response of a critical gel. We applied the *generalized gel equation* by incorporating the well-known relaxation modulus for a

critical gel into the Lodge rubber-like-liquid formulation. We performed a comprehensive set of experiments on a gluten dough and showed that the generalized gel equation provides an accurate description of the rheological response in flow situations ranging from linear to non-linear deformations in both shear and extension. We also demonstrated the implications for these slowly-relaxing systems of residual stress relaxation from deformation incurred during sample loading. The power-law decay in relaxation modulus $G(t) = St^{-n}$ at long times was found to be substantially affected by the waiting time t_w .

The linear viscoelasticity of gluten doughs can be well-characterized by the two-parameter critical gel model over a wide range of timescales and this is an indication of the self similarity in the polymeric network comprising the gluten gel. At very short length scales $l \sim 20$ nm, this self similarity breaks down as the structure of individual strands in the network become important and is reflected by the Rouse regime observed at short time scales $t \sim \lambda_R = 0.05$ s.

At large strains, the gluten gel only shows a very weak damping behavior which is consistent with the idea of strong physical crosslinks in a fractal polymeric network. We contrast this observation with examples of entangled and particulate gel systems that have strong damping functions due, respectively, to either the mismatch in the rotation/stretch relaxation times or to plastic yielding events between neighboring particles.

In start-up of steady shear flow, power-law growth in both the shear stress and the normal stress difference are observed, and these are in good agreement with the generalized gel equation up to $\gamma^* \sim 5$. Beyond this critical strain, the shear

stress exhibits an overshoot and attains a peak value at $\gamma^P \sim 12$. Just before the point of peak stress, the gluten gel undergoes an edge instability that eventually leads to the sample being ejected from the geometry at $\gamma^E \sim 30$. In uniaxial extension, the transient response of the tensile stress difference progressively changes from power-law growth in the linear viscoelastic regime to an exponential increase in agreement with the constitutive prediction of the generalized gel equation. This exponential growth can be observed for a wide range of deformation rates ($0.03 \leq \dot{\epsilon}_0 \leq 3 \text{ s}^{-1}$) up to the point of rupture at Hencky strains of $\epsilon_{\text{rupture}} \sim 3$.

We can compare these observations with earlier experiments performed on critical gels of cross-linked polydimethylsiloxane. In start-up of steady shear flow, Venkataraman and Winter (Venkataraman and Winter 1990) observed a similar departure from linearity at $\gamma^* \sim 2$ followed shortly by an overshoot and a peak in shear stress at $\gamma^P \sim 4$. The rheological signatures of the PDMS and gluten gels are qualitatively similar; but evidently, the gluten system has a significantly larger range of quasi-linearity. The percolated gel structure of the gluten remains intact even under large deformations pointing to significant tensile strength of the gluten backbone and strong interchain binding at network junctions.

The strain/rate factorization observed in the present experiments (in both shearing and extensional flow) strongly supports the extension of the simple linear viscoelastic gel model to large strains by application of the Lodge rubber-like network formulation. Finally, we note that because of the power-law

dependence of the relaxation modulus, critical gels exhibit a special form of viscoelastic behavior: They will show characteristics akin to those of ideal elastic networks, with increasingly affine deformation of the form $\Delta\sigma_{Ext}^+ \sim \exp(2\varepsilon)$ observed up to large Hencky strains $\varepsilon \sim 3$ in uniaxial elongation; however, at the same time, they also exhibit nonlinear viscous characteristics with a fading power-law dependence in time $\Delta\sigma_{Ext}^+ \propto t^{-n}$. In addition to the measurements presented here, we have also performed large amplitude oscillatory shear (LAOS) tests to further assess the predictions of the proposed rheological equation of state, these results will be discussed in a later publication.

To summarize, the rheological evidence provides a compelling indication that the gluten gel is a polymeric network consisting of flexible or semi-flexible filaments between network junctions. This is not necessarily incompatible with the particulate microgel structure sometimes observed under confocal microscopy (Peighambardoust 2006). These observable length scales might lie beyond those that can be practically probed by rheological measurements within a reasonable time window. Exactly what individual roles di-sulphide bonds, hydrogen bonds and physical entanglements play in the resulting gel structure is still hotly debated (Ewart 1989; Belton 1999; Letang et al. 1999; Singh and MacRitchie 2001; Don et al. 2003a; Domenek et al. 2004). Future rheological tests to progressively large strains may be able to shed light on the individual contributions of each type of crosslink; preliminary experiments on disrupting the network structure by dissolving the gluten gels in sodium dodecyl sulphate (SDS) or in concentrated urea solution indicate that hydrogen bonding plays a central role in the formation of networks structure.

The ability of such a simple two parameter constitutive model to predict quantitatively the material functions for vital gluten doughs over several orders of magnitude in stress and time scales is both surprising and encouraging. Food stuffs are notorious for being “hopelessly non-model” (Fischer et al. 2006); and soft solids or wheat flour doughs are considered one of the worst offenders (Bagley et al. 1998). The model behavior of gluten gels may prove to be invaluable in providing a framework or foundation from which more complex models that fully capture the functionality of a realistic flour-water dough formulation can be constructed. For example, it provides a natural framework for incorporating a damping function to capture more complex non-linear behavior (Ng et al. 2006b; Tanner et al. 2007).

Moving forward, the logical step to take next is to reintroduce these additional non-linear effects through the addition of a well-characterized filler. Obviously in real bread doughs the filler of interest consists of the starch particles. Unfortunately, simply mixing wheat starch, vital gluten powder and water already reintroduces excessive complexity. The rheology of the resulting dough changes significantly with time and it is challenging to obtain reproducible data (Ng and McKinley 2006); this is due to the gradual swelling and strong interactions between starch particles. An alternative route may be to separate the effects of the filler; for example, by first asking what is the effect of filling the gluten gel with non-reactive hard spheres such as glass beads (Edwards et al. 2002)? Preliminary rheological data collected on such a system in our laboratory (Ng and McKinley 2006) suggests that many of the characteristic differences between a critical gluten gel and real dough systems, e.g. non-linear strain

softening, can indeed be explained by the interactions of the elastic network with these hard particles and this will form the subject of future work.

Acknowledgments

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Figure Captions

Figure 1 Mixograph output for 24g of gluten dough at 63% moisture content by weight. After the gluten dough has been fully developed, it is removed from the mixograph at 720s.

Figure 2 Stress relaxation behavior of a gluten gel. The relaxation modulus approaches a power-law as expected for a critical gel with $S = 1260 \pm 50 \text{ Pa s}^n$, $n = 0.175 \pm 0.005$ over a wide range of time $0.2 \leq t \leq 100\text{s}$. At short times, an additional Rouse relaxation regime can be observed, with $G_R \approx 803 \text{ Pa}$ and $\lambda_R = 0.05 \text{ s}$.

Figure 3 Deviations from power-law relaxation due to the effects of loading history for various values of sample rest time. Dashed lines represent predictions from the critical gel equation for the apparent modulus (equation (5)) with $t_w = 0.1, 1, 10, 100, 1000, 10000 \text{ s}$ and $t_w \rightarrow \infty$ (dotted line). Open symbols are measured data for gluten gels with $t_w = 10, 100, 1000 \text{ s}$. Inset illustrates the strain protocol imposed on the sample during the experiment. Note that the rheometer resets or 'zeroes' the stress at $t = 0$.

Figure 4. Expressing the power-law relaxation of a critical gel as a series of Maxwell modes. Deviations can be seen at either end of the spectrum corresponding to the longest λ_0 and shortest $\lambda_K = \lambda_0 K^{-1/n}$ time scales of the summation.

Figure 5 a) Storage and loss moduli measured in small amplitude oscillation. Solid lines represent predictions from equation (12) and incorporating Rouse modes: $S = 1260 \text{ Pa s}^n$, $n = 0.17$, $G_R = 803 \text{ Pa}$, $\lambda_R = 0.05 \text{ s}$. These parameters were obtained from independent measurements of the relaxation modulus $G(t)$. b) Comparison between dynamic moduli of vital gluten and native (i.e. 'washed') gluten doughs, showing strong qualitative similarities in the frequency response.

Figure 6 Creep compliance of a gluten gel. Dashed line represents predictions of the critical gel model from equation (17) with gel strength $S = 1280 \text{ Pa s}^n$ and gel exponent $n = 0.175$: these parameters are obtained independently from step strain relaxation experiments. Data at $t < 0.1 \text{ s}$ for $\sigma_0 = 30 \text{ Pa}$ are included to illustrate the observed "creep ringing".

Figure 7 a) Stress relaxation function $G(t)$ of gluten dough for a range of finite step shear strains with magnitude γ_0 . b) Damping function for finite strain amplitude stress relaxation experiments. Lines correspond to algebraic fit to the data set, $h(\gamma) = 1 / \left(1 + (q\gamma_0)^{2k} \right)$. Unfilled gluten dough ($q = 0.2, k = 0.4$) shows substantially reduced damping compared to highly-filled wheat flour-water dough systems ($q = 25, k = 0.4$).

Figure 8 a) Transient shear stress during start-up of shear flow as a function of time measured for shear rates $0.003 \leq \dot{\gamma}_0 \leq 3.0 \text{ s}^{-1}$. The calculated response from the critical gel component and Rouse modes for $\dot{\gamma}_0 = 0.03 \text{ s}^{-1}$ are plotted as dashed lines. Deviation from equation (28) at $t \leq 0.05 \text{ s}$ is a result of the finite rise time ($\sim 50 \text{ ms}$) of the motor. b) All curves can be collapsed onto a master strain function $\Phi_{xy}(\gamma) = \gamma^{1-n} / (1-n)$ (solid line) by factoring out the rate dependence $f(\dot{\gamma}_0) = \dot{\gamma}_0^n$.

Figure 9 Torsional elastic instability at $\dot{\gamma}_0 = 1 \text{ s}^{-1}$. a. Initial conditions, b. Onset of instability; Initially vertical lines drawn on the sample with ink indicate uniform deformation up to this point; c. Sample becomes asymmetric and is retracted away from point of view while being ejected from the other side of the geometry, d. Sample rolls up and is ejected from rheometer.

Figure 10. a) Power-law growth in the first normal stress difference as a function of time measured for shear rates $0.003 \leq \dot{\gamma} \leq 3.0 \text{ s}^{-1}$. b) All curves can be collapsed onto a master strain function $\Phi_N(\gamma)$ by factoring out the rate dependence $f(\dot{\gamma}_0) = \dot{\gamma}_0^n$. The solid line is the strain function $\Phi_N = 2\gamma^{2-n} / (2-n)$ given in equation (33) with $n = 0.175$ determined from linear viscoelastic measurements.

Figure 11 Schematic of the Sentmanat Extensional Rheometer (SER). The sample of initial cross-section area $W_0 \times H_0$ and gage length L_0 is stretched between two counter-rotating cylindrical drums.

Figure 12 Wind-up drum rheometry of a gluten gel using the SER fixture. Deformation and torque measurements were provided by the host ARES rheometer while true strain measurements were made by studying images collected with high-speed digital videography (at 100 frames/sec). Initial width of sample is $W_0 = 2 \text{ mm}$. Solid line is the calculated variation in width under ideal uniaxial elongation given by equation (44)

Figure 13 a) Tensile stress difference in gluten gels during transient uniaxial elongation at rates of $\dot{\epsilon}_0 = 0.03, 0.3, 3.0 \text{ s}^{-1}$. At least two runs were performed at each strain rate to ensure reproducibility. b) Scaled stress function plotted against Hencky strain showing power-law growth at small strains and exponential growth at large strains.

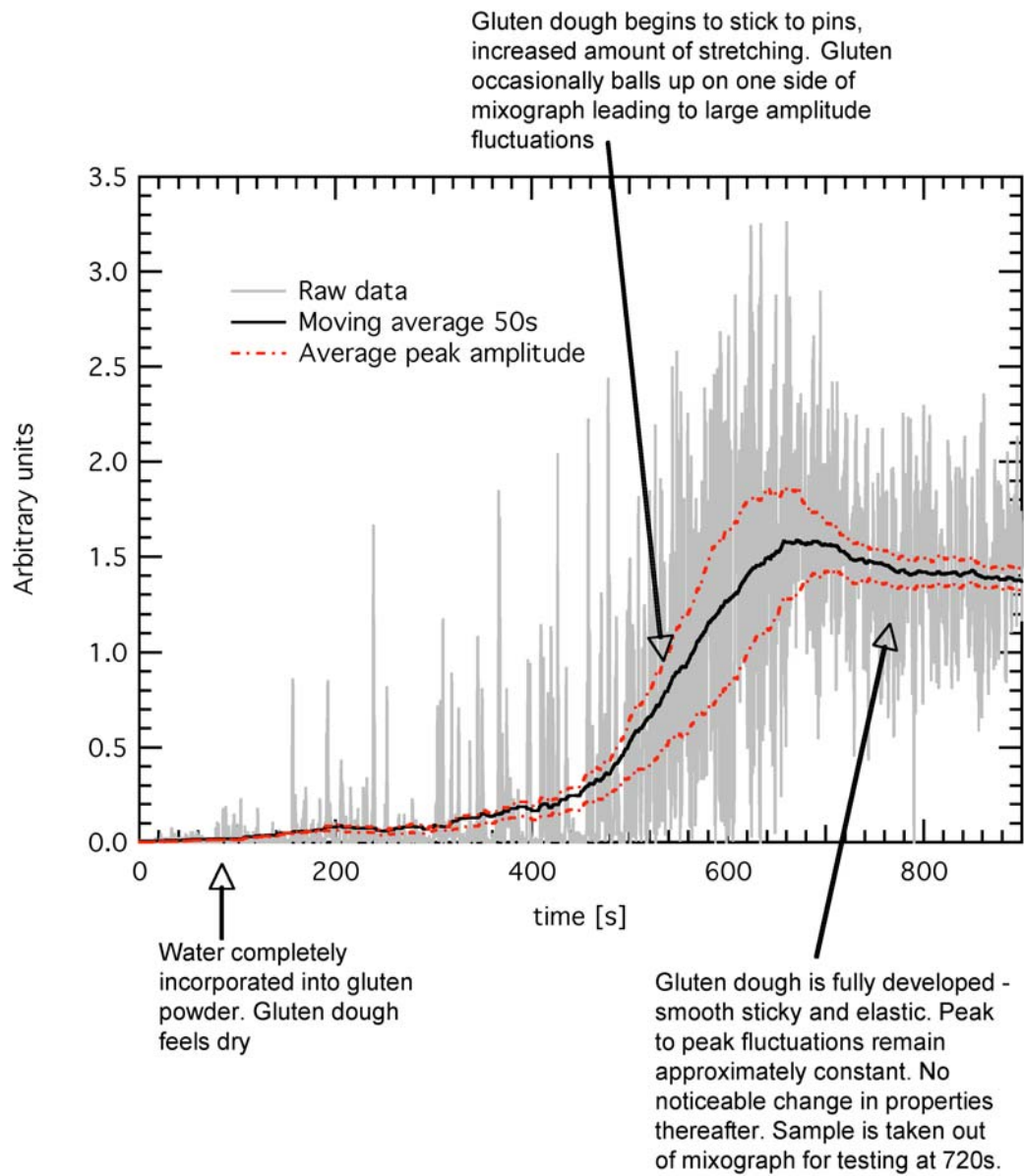


Figure 1 Mixograph output for 24g of gluten dough at 63% moisture content by weight. After the gluten dough has been fully developed, it is removed from the mixograph at 720s.

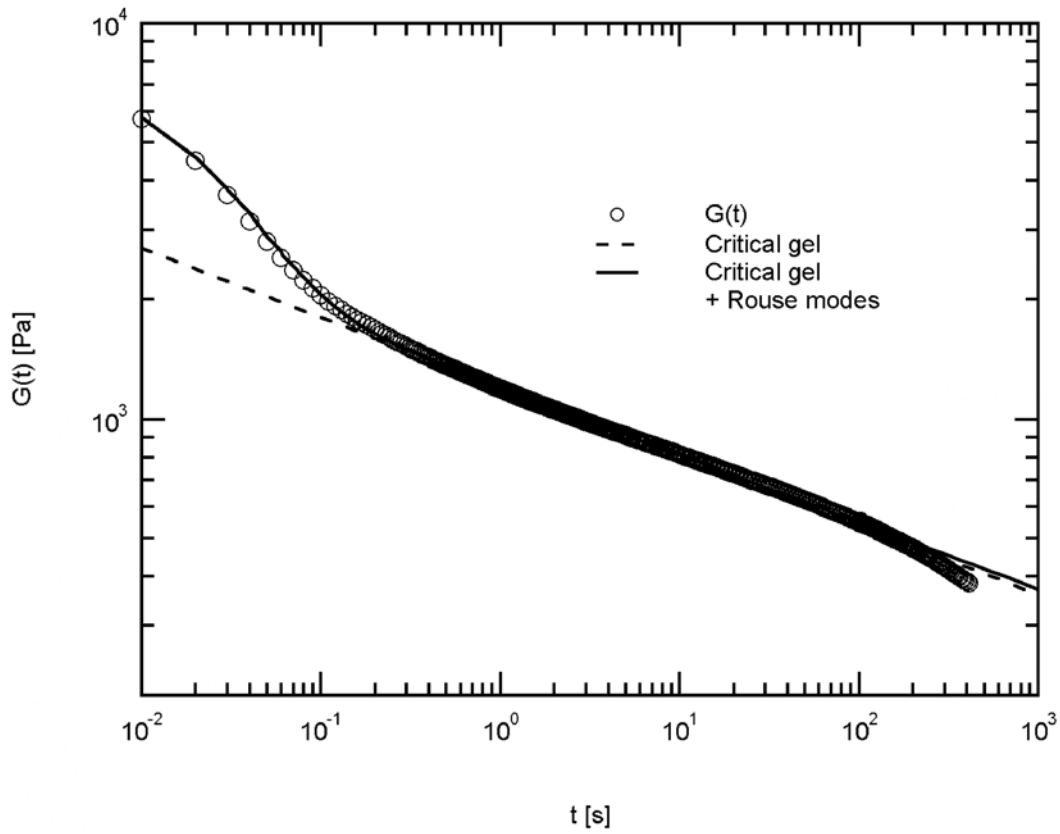


Figure 2 Stress relaxation behavior of a gluten gel. The relaxation modulus approaches a power-law as expected for a critical gel with $S = 1260 \pm 50 \text{ Pa s}^n$, $n = 0.175 \pm 0.005$ over a wide range of time $0.2 \leq t \leq 100\text{s}$. At short times, an additional Rouse relaxation regime can be observed, with $G_R \approx 803 \text{ Pa}$ and $\lambda_R = 0.05 \text{ s}$.

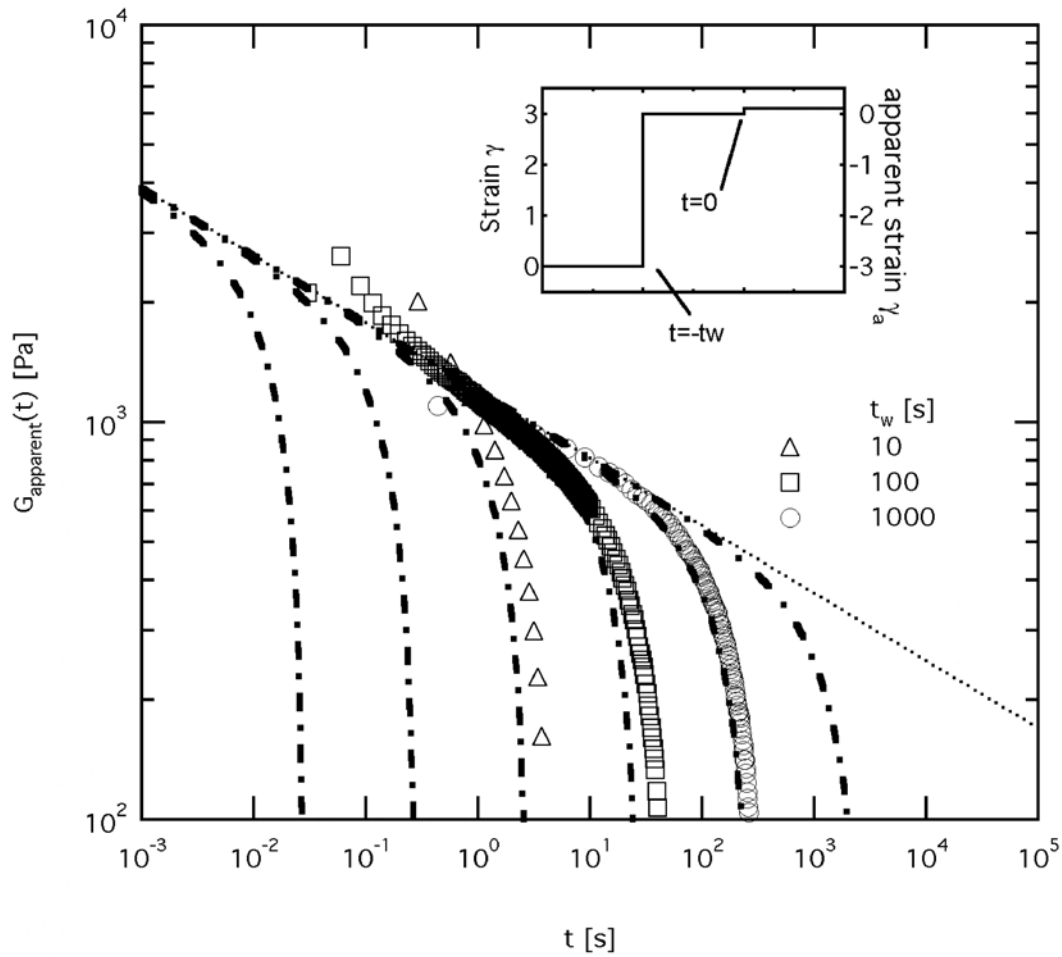


Figure 3 Deviations from power-law relaxation due to the effects of loading history for various values of sample rest time. Dashed lines represent predictions from the critical gel equation for the apparent modulus (equation (5)) with $t_w = 0.1, 1, 10, 100, 1000, 10000$ s and $t_w \rightarrow \infty$ (dotted line). Open symbols are measured data for gluten gels with $t_w = 10, 100, 1000$ s. Inset illustrates the strain protocol imposed on the sample during the experiment. Note that the rheometer resets or 'zeroes' the stress at $t = 0$.

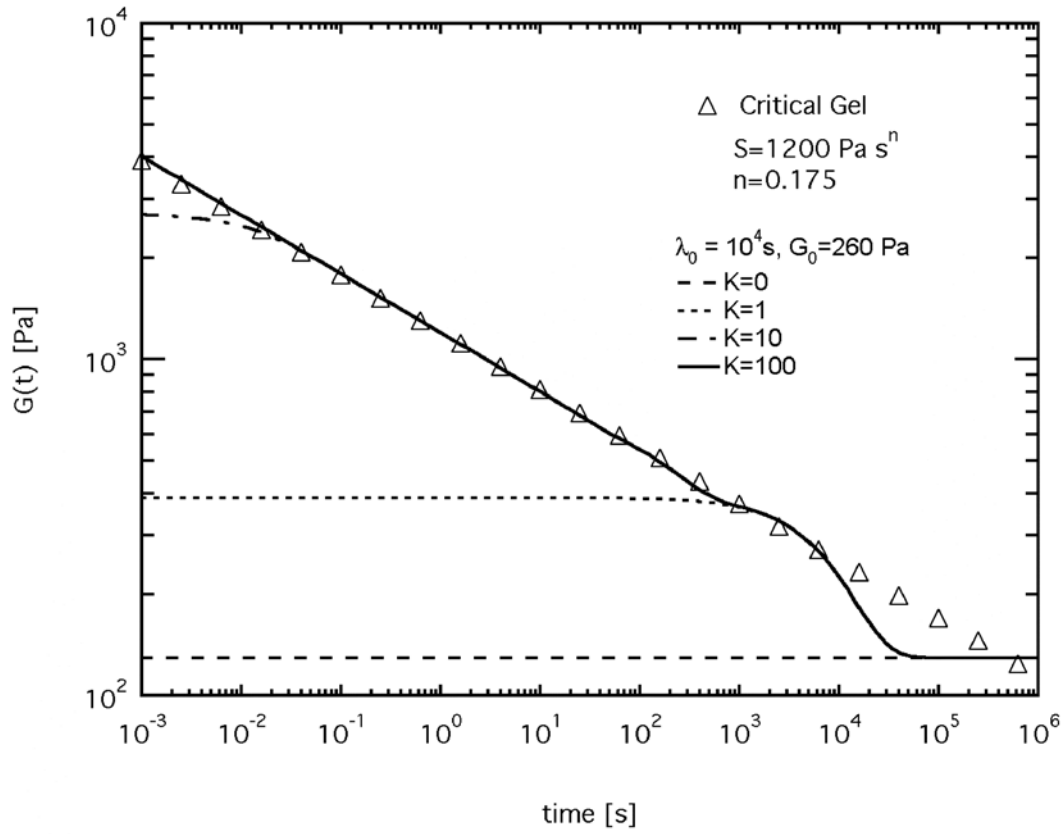


Figure 4. Expressing the power-law relaxation of a critical gel as a series of Maxwell modes. Deviations can be seen at either end of the spectrum corresponding to the longest λ_0 and shortest $\lambda_K = \lambda_0 K^{-1/n}$ time scales of the summation.

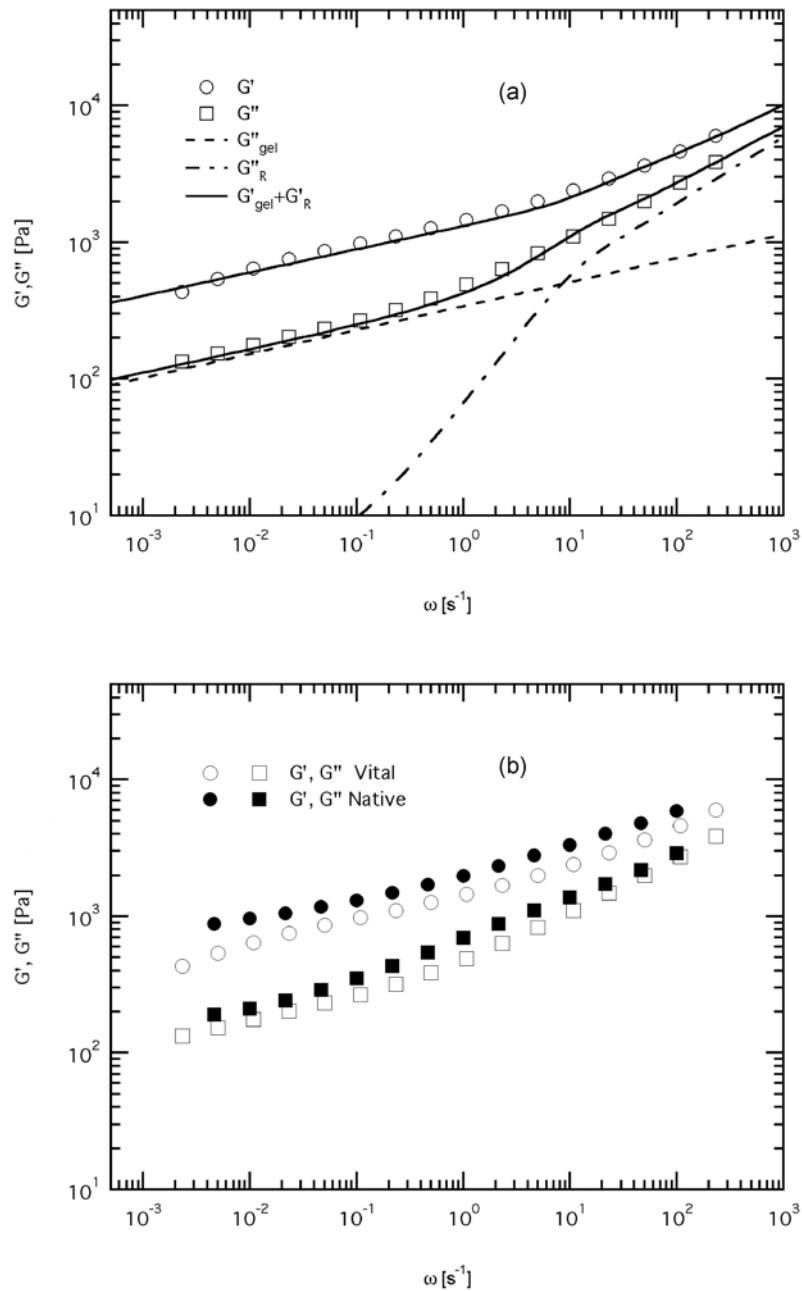


Figure 5 a) Storage and loss moduli measured in small amplitude oscillation. Solid lines represent predictions from equation (12) and incorporating Rouse modes: $S = 1260 \text{ Pa s}^n$, $n = 0.17$, $G_R = 803 \text{ Pa}$, $\lambda_R = 0.05 \text{ s}$. These parameters were obtained from independent measurements of the relaxation modulus $G(t)$. b) Comparison between dynamic moduli of vital gluten and native (i.e. 'washed') gluten doughs, showing strong qualitative similarities in the frequency response.

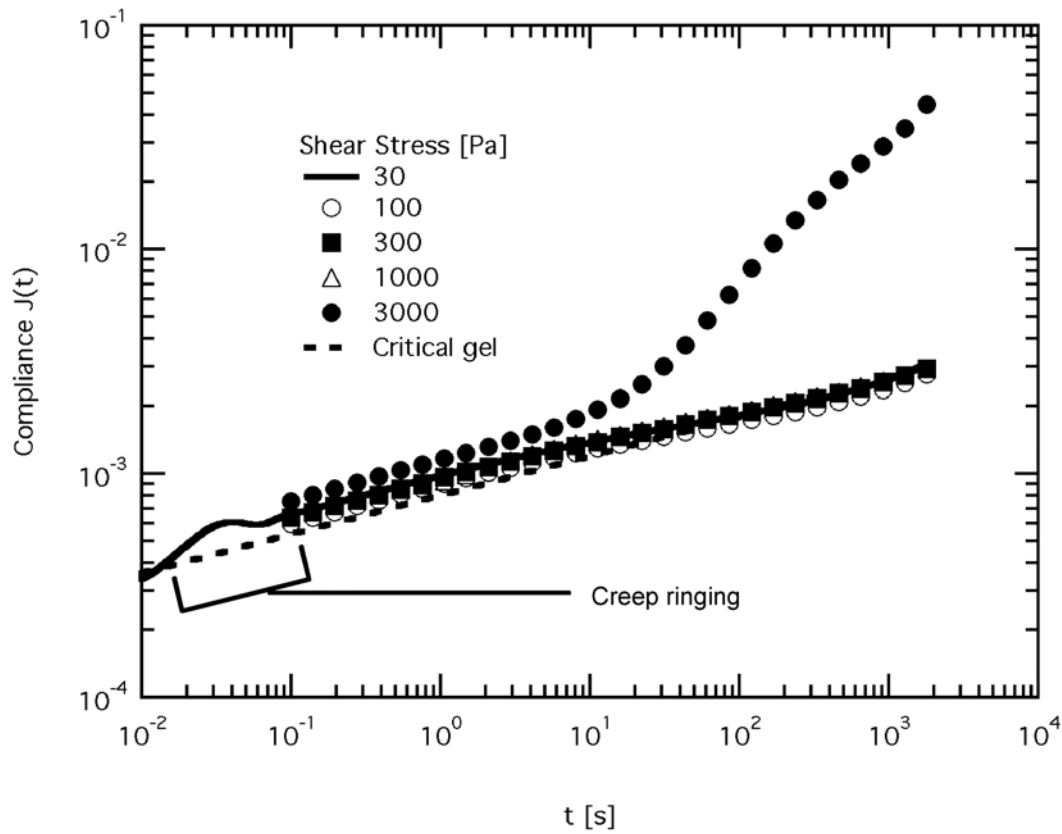


Figure 6 Creep compliance of a gluten gel. Dashed line represents predictions of the critical gel model from equation (17) with gel strength $S = 1280 \text{ Pa s}^n$ and gel exponent $n = 0.175$: these parameters are obtained independently from step strain relaxation experiments. Data at $t < 0.1 \text{ s}$ for $\sigma_0 = 30 \text{ Pa}$ are included to illustrate the observed “creep ringing”.

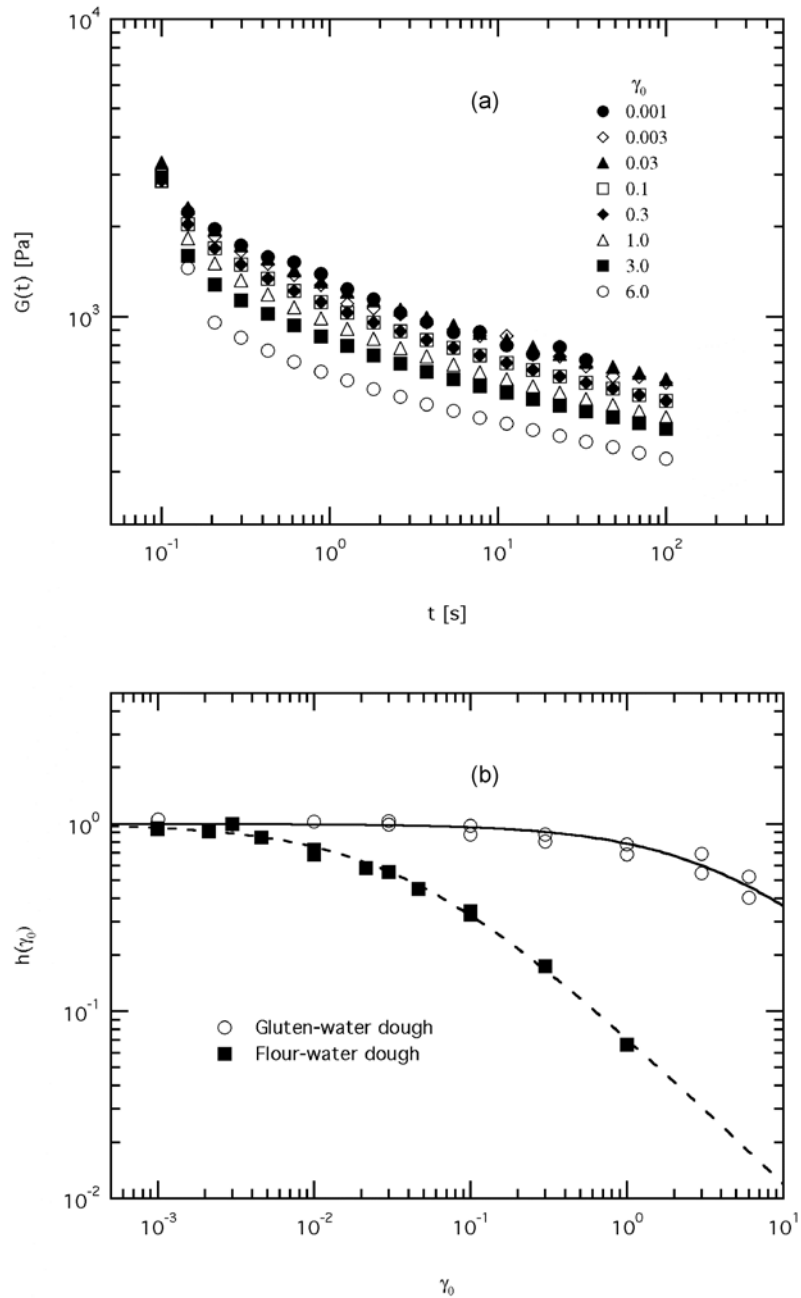


Figure 7 a) Stress relaxation function $G(t)$ of gluten dough for a range of finite step shear strains with magnitude γ_0 . b) Damping function for finite strain amplitude stress relaxation experiments. Lines correspond to algebraic fit to the data set, $h(\gamma) = 1 / (1 + (q\gamma_0)^{2k})$. Unfilled gluten dough ($q = 0.2, k = 0.4$) shows substantially reduced damping compared to highly-filled wheat flour-water dough systems ($q = 25, k = 0.4$).

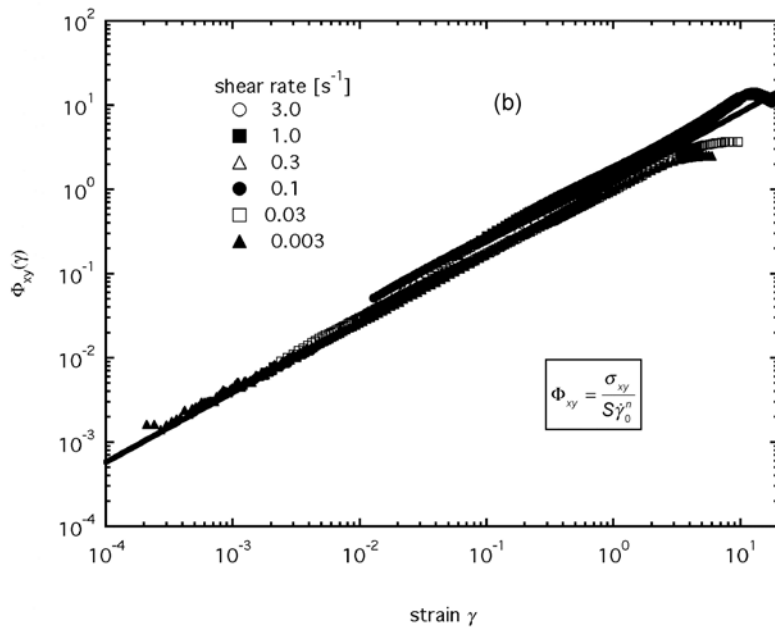
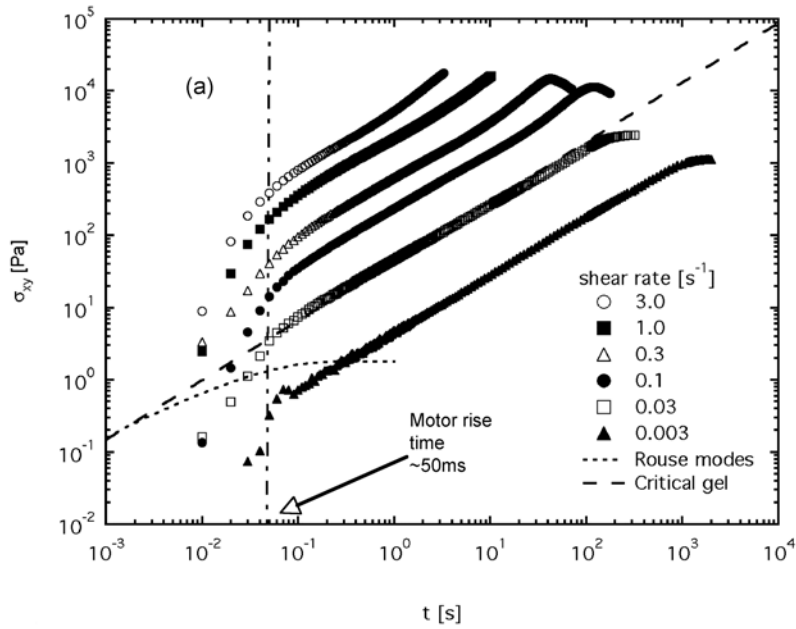


Figure 8 a) Transient shear stress during start-up of shear flow as a function of time measured for shear rates $0.003 \leq \dot{\gamma}_0 \leq 3.0 \text{ s}^{-1}$. The calculated response from the critical gel component and Rouse modes for $\dot{\gamma}_0 = 0.03 \text{ s}^{-1}$ are plotted as dashed lines. Deviation from equation (28) at $t \leq 0.05 \text{ s}$ is a result of the finite rise time ($\sim 50 \text{ ms}$) of the motor. b) All curves can be collapsed onto a master strain function $\Phi_{xy}(\gamma) = \gamma^{1-n}/(1-n)$ (solid line) by factoring out the rate dependence $f(\dot{\gamma}_0) = \dot{\gamma}_0^n$.

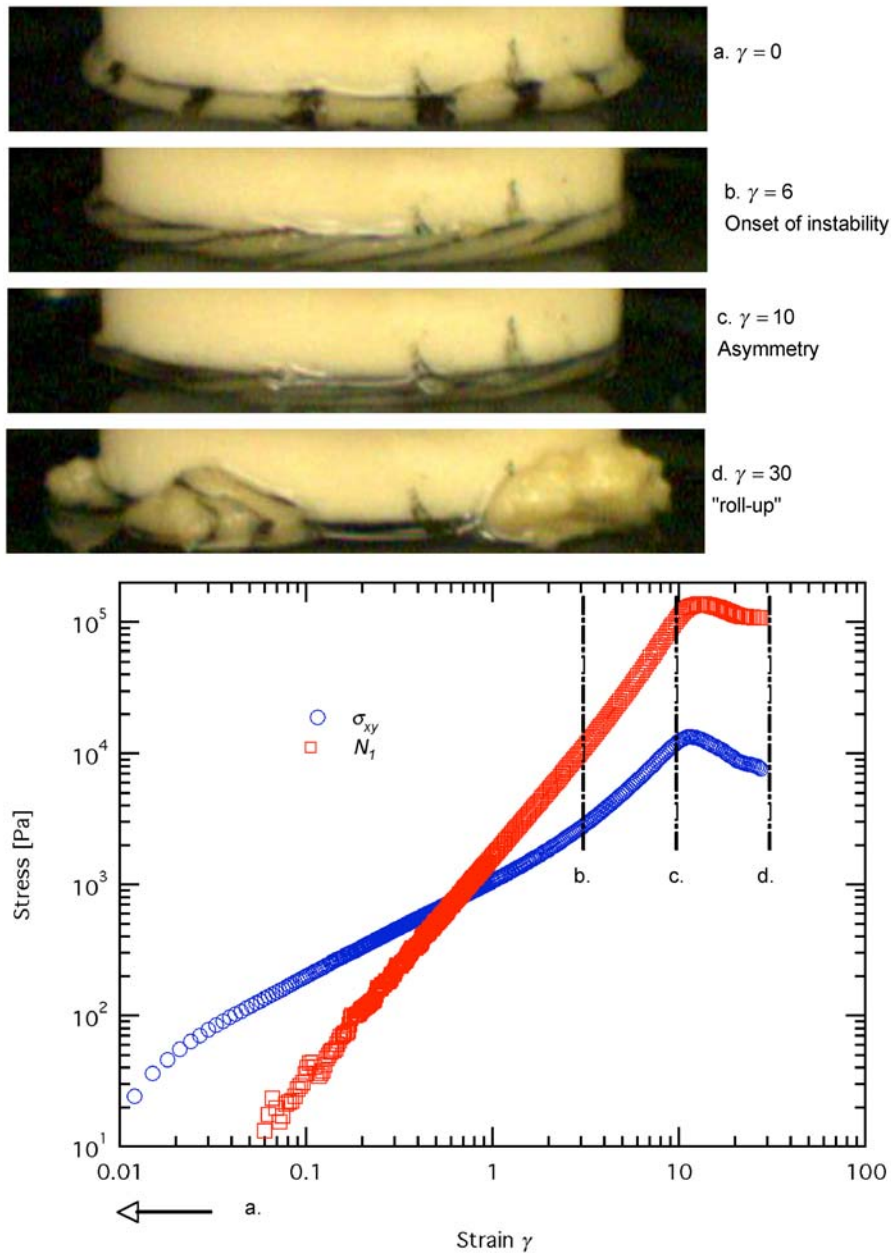


Figure 9 Torsional elastic instability at $\dot{\gamma}_0 = 1 \text{ s}^{-1}$. a. Initial conditions, b. Onset of instability; Initially vertical lines drawn on the sample with ink indicate uniform deformation up to this point; c. Sample becomes asymmetric and is retracted away from point of view while being ejected from the other side of the geometry, d. Sample rolls up and is ejected from rheometer.

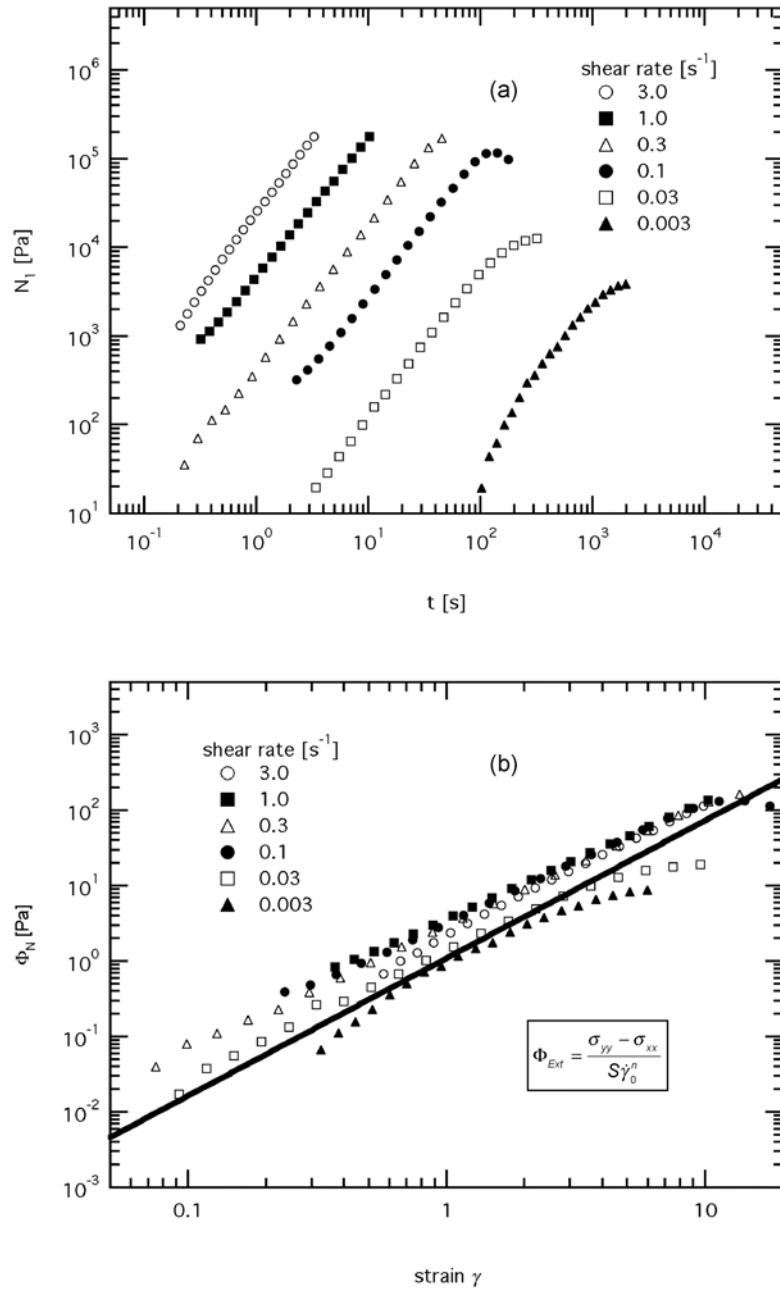


Figure 10. a) Power-law growth in the first normal stress difference as a function of time measured for shear rates $0.003 \leq \dot{\gamma} \leq 3.0 \text{ s}^{-1}$. b) All curves can be collapsed onto a master strain function $\Phi_N(\gamma)$ by factoring out the rate dependence $f(\dot{\gamma}_0) = \dot{\gamma}_0^n$. The solid line is the strain function $\Phi_N = 2\gamma^{2-n}/(2-n)$ given in equation (33) with $n=0.175$ determined from linear viscoelastic measurements.

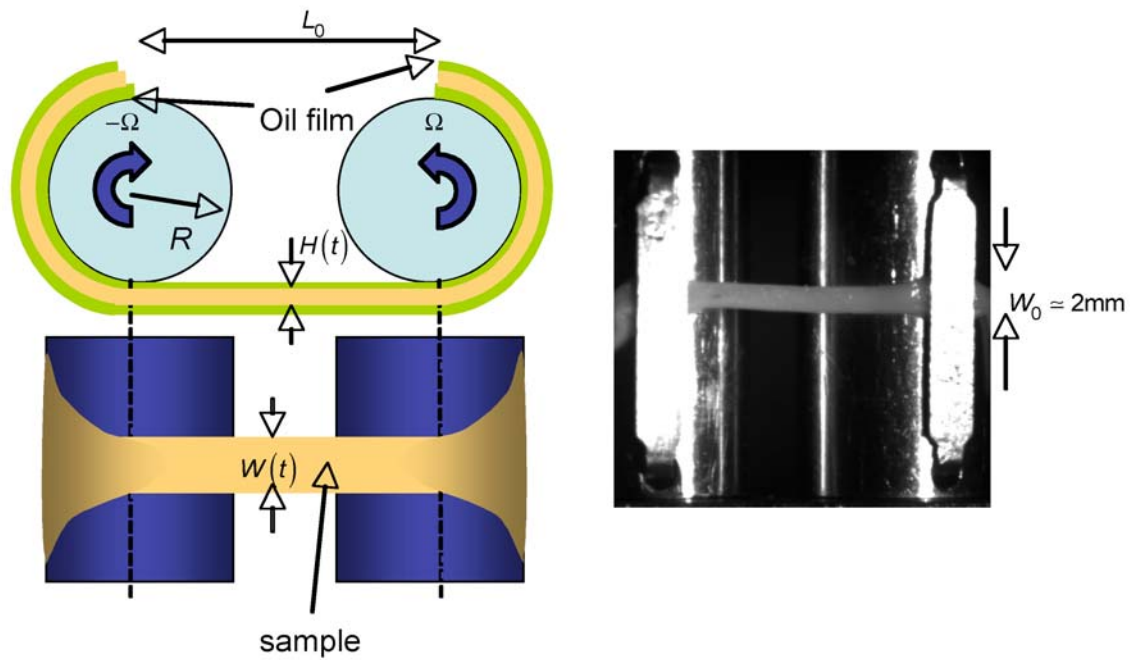


Figure 11 Schematic of the Sentmanat Extensional Rheometer (SER). The sample of initial cross-section area $W_0 \times H_0$ and gage length L_0 is stretched between two counter-rotating cylindrical drums.

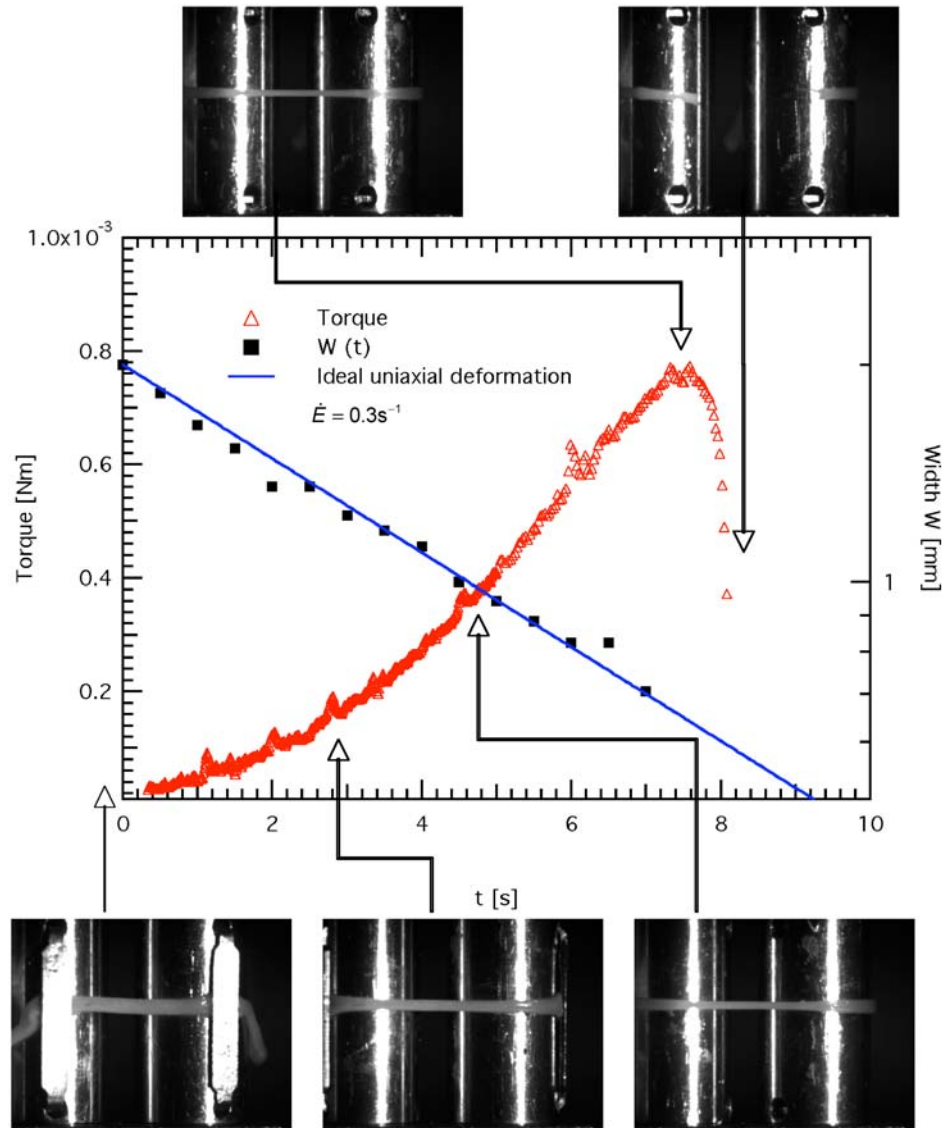


Figure 12 Wind-up drum rheometry of a gluten gel using the SER fixture. Deformation and torque measurements were provided by the host ARES rheometer while true strain measurements were made by studying images collected with high-speed digital videography (at 100 frames/sec). Initial width of sample is $W_0 = 2 \text{ mm}$. Solid line is the calculated variation in width under ideal uniaxial elongation given by equation (44)

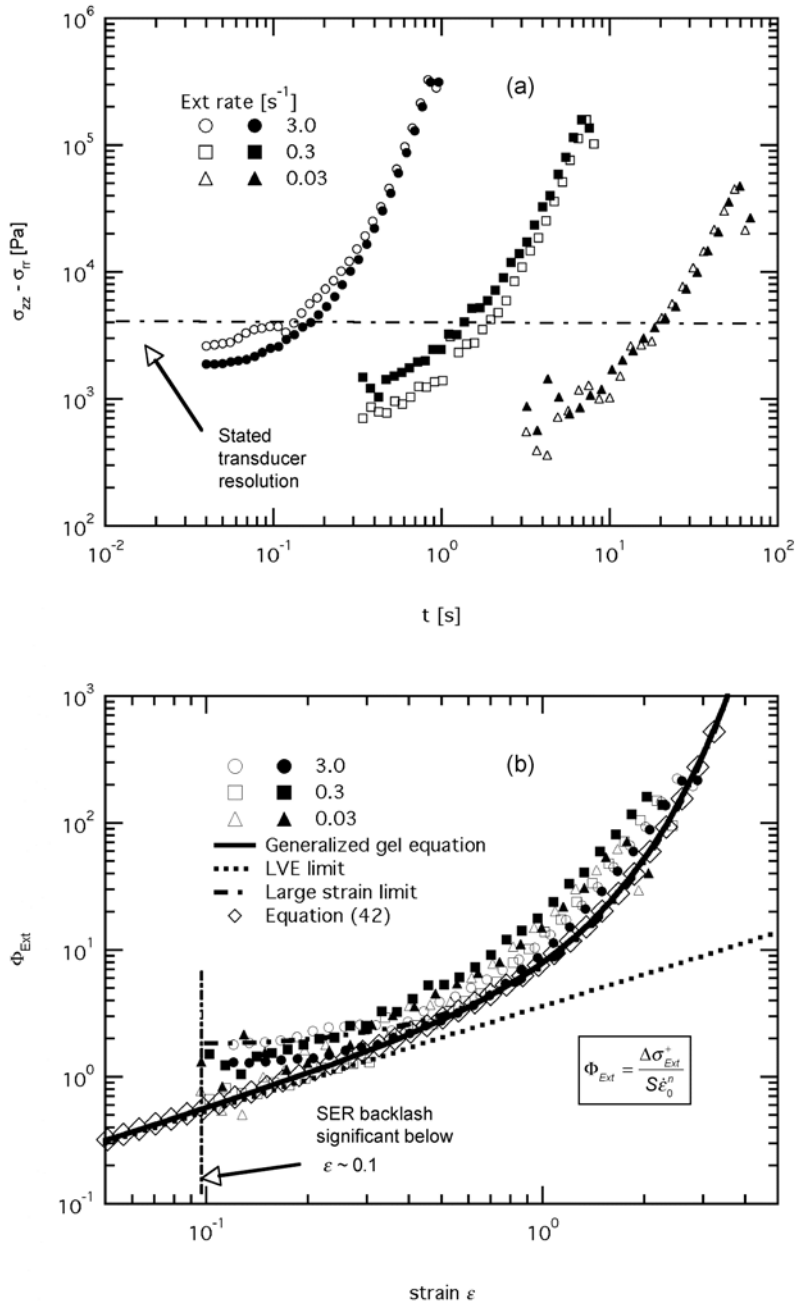


Figure 13 a) Tensile stress difference in gluten gels during transient uniaxial elongation at rates of $\dot{\epsilon}_0 = 0.03, 0.3, 3.0 \text{ s}^{-1}$. At least two runs were performed at each strain rate to ensure reproducibility. b) Scaled stress function plotted against Hencky strain showing power-law growth at small strains and exponential growth at large strains.