Nonlinear viscoelasticity and generalized failure criterion for polymer gels

Bavand Keshavarz,⇤ † Thibaut Divoux,‡ ¶ Sébastien Manneville,§ and Gareth H. McKinley†

Department of Mechanical Engineering, MIT, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA, Centre de Recherche Paul Pascal, CNRS UPR 8641 - 115 avenue Schweitzer, 33600 Pessac, France, MultiScale Material Science for Energy and Environment, UMI 3466, CNRS-MIT, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA, and Univ Lyon, Ens de Lyon, Univ Claude Bernard, CNRS, Laboratoire de Physique, F-69342 Lyon, France

E-mail: bavand@mit.edu

Polymer gels behave as soft viscoelastic solids and exhibit a generic nonlinear mechanical response characterized by pronounced stiffening prior to irreversible failure, most often through macroscopic fractures. Here, we describe this scenario for a model protein gel using an integral constitutive equation built upon the linear and the nonlinear viscoelastic properties of the gel. We show that this formalism predicts quantitatively the gel mechanical response in shear start-up experiments, up to the onset of macroscopic failure. Moreover, we couple the computed stress response with Bailey’s durability criterion for brittle solids in order to predict the critical values of the stress $\sigma_c$ and strain $\gamma_c$ at failure. The excellent agreement between theory and experiments suggests that failure in this soft viscoelastic gel is a Markovian process, and that Bailey’s failure criterion extends beyond hard materials such as metals, glasses, or minerals.

Many biopolymeric gels, foods, and supramolecular networks1–3 share common features with hard materials, including delayed failure,4–7 crack propagation8,9 or work-hardening,10 while their porous microstructure also confers upon them remarkable nonlinear viscoelastic properties.11–15 Polymer gels may endure large strains to failure and dissipate substantial mechanical work enabling the design of tough hydrogels.16–19 However, to date no quantitative link has been made between the nonlinear viscoelasticity of polymer gels and the ensuing failure dynamics.

We apply the concept of a strain damping function, traditionally used for polymeric liquids and rubber-like materials20 and more recently applied to double network gels,21 to quantify the nonlinear viscoelastic response of a prototypical protein gel. The form of the damping function is determined through stress relaxation tests on freshly prepared gels that allow us to probe large deformations while injecting very little energy into the gel. The damping function is used to construct a time-strain separable constitutive equation of K-BKZ (Kaye–Bernstein-Kearsley-Zapas) form22,23 that predicts the gel mechanical response to arbitrary
loading histories. This approach captures the strain-stiffening of the gel during start up of steady shear tests up to the appearance of a stress maximum that is accompanied by the onset of the first macroscopic crack. In order to link the nonlinear viscoelastic response of the gel to its subsequent brittle-like rupture, we adopt the Bailey criterion, which describes the failure as arising from accumulation of irreversible damage.\textsuperscript{24,25} The combination of the stress response predicted by the K-BKZ constitutive formulation with the Bailey criterion allows us to predict the scaling of the critical stress and strain at failure with the applied shear rate.

We consider two acid-induced protein gels with substantially different mechanical properties: the first one shows pronounced strain-hardening, while the second does not. They are prepared by dissolving caseinate powder (Firmenich) at 4\% wt. (resp. 8\% wt.) in deionized water. Homogeneous gelation is induced by dissolving 1\% wt. (resp. 8\% wt.) glucono-\delta-lactone (GDL, Firmenich) in the protein solution.\textsuperscript{26,27}

To characterize the 4\% wt. casein gel, we first perform a series of step strain tests (with strain amplitude $10^{-3} \leq \gamma_0 \leq 5$).\textsuperscript{28} The stress relaxation functions $G(\gamma_0, t) = \sigma(t)/\gamma_0$ associated with each step of strain are reported in Fig. 1 over periods of 4000 s. At low applied strains ($\gamma_0 \lesssim 0.01$), the magnitude of the viscoelastic stress $\sigma(t)$ scales linearly with the imposed strain and the relaxation modulus exhibits a remarkable power-law decrease over four decades of time, which is well modeled by a spring-pot (or fractional viscoelastic element),\textsuperscript{29,30} $G(t) = Vt^{-\alpha}/\Gamma(1-\alpha)$, where $V$ and $\alpha$ are the only two material properties required to characterize the gel, and $\Gamma$ denotes the Gamma function. By fitting the data for $\gamma_0 \leq 0.01$ we find an exponent $\alpha = 0.18 \pm 0.01$ and a prefactor or “quasiproperty” $V = (266 \pm 5)$ Pa.s$^{\alpha}$.\textsuperscript{29,31} At larger applied strains $\gamma_0 \gtrsim 0.01$, the stress relaxation still exhibits a power-law decrease in time, with the same exponent $\alpha$ after $t \gtrsim 0.1$ s but the magnitude of the stress at any given time first stiffens and then softens as $\gamma_0$ is increased.

Since $\alpha$ is insensitive to the strain amplitude, we use the concept of strain-time separability\textsuperscript{32} to quantify the strain dependence of the stress relaxation response by computing the damping function,\textsuperscript{20} defined as $h(\gamma_0) = \langle G(\gamma_0, t)/G(t) \rangle_t$, where $\langle \ldots \rangle_t$ denotes the time average for $1 \leq t \leq 1000$ s for each of the step-strain experiments. The resulting damping function in Fig. 2 thus

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Relaxation modulus $G(\gamma_0, t)$ vs time $t$ determined by step strain tests for the 4\% wt. casein gel. Colors from yellow to black represent strain values ranging from $\gamma_0 = 0.002$ to $\gamma_0 = 5$. The black line is the best power-law fit for $\gamma_0 \leq 0.01$. Inset: exponent $\alpha$ extracted from power-law fits to the data.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Strain damping function $h(\gamma_0)$ of a 4\% wt. casein gel (same color code as in Fig. 1). The solid black line is the best fit function proposed in\textsuperscript{35} which captures the stiffening behavior, but does not account for the softening part of the gel response at strains larger than $\gamma_0 \approx 0.5$. The red continuous line is the best fit function $\tilde{h}(\gamma)$ describing the data (see text). Inset: same data plotted on semilogarithmic scale.}
\end{figure}
Figure 3: (a) Stress response $\sigma$ vs time $t$ (lower axis) and vs strain $\gamma = \dot{\gamma}_0 t$ (upper axis) of a 4\% wt. casein gel to a constant shear rate $\dot{\gamma}_0 = 10^{-3} \text{s}^{-1}$ initiated at $t = 0$. The gray dashed line corresponds to the linear viscoelastic response [Eq. (2)]. The black line corresponds to the K-BKZ equation constructed using only the strain-hardening part of the damping function, $h^*(\gamma_0)$ (solid black line in Fig. 2). The continuous red line corresponds to the K-BKZ equation, which includes both the hardening and the softening components of the damping function. Lower inset: same data on semilogarithmic scales. Upper inset: sketch and images of the side view of Couette cell at different strains recorded simultaneously to the experiment reported in the main graph. (b) Same as (a) for $\dot{\gamma}_0$ ranging from $10^{-3}$ s$^{-1}$ to 0.6 s$^{-1}$. Dashed lines indicate the linear response [Eq. (2)], and the continuous lines correspond to the K-BKZ predictions using $\bar{h}$ [Eq. (3)]. (c) Normalized stress responses vs strain $\gamma$ for all constant shear rate experiments.

fully characterizes the strain dependence. The gel displays a linear response (i.e. $h = 1$) up to $\gamma_0 = 0.1$, whereas for intermediate strain amplitudes, the gel exhibits a pronounced strain-stiffening, that is characterized by a maximum value $h \simeq 2.2$ reached at $\gamma = 0.5$. Finally, for even larger strains, the material softens and $h$ decreases abruptly. Its behavior is reasonably well fitted by a power-law function of the imposed strain with an exponent $-3$. We emphasize here that for all step strain tests, the gel remains visually intact even at strain amplitudes as large as $\gamma_0 \simeq 5$.\(^{33}\)

It has been shown\(^{34,35}\) that the strain-hardening portion of the damping function can be captured in a power series expansion $h^*(\gamma_0)$,\(^\text{36}\) with the fractal dimension $d_b$ of the stress-bearing network backbone as the only fitting parameter. Here we find $d_b = 1.3 \pm 0.1$ in good agreement with other measurements for polymer gels (see black line in Fig. 2).\(^{37}\) To capture both the hardening and the subsequent softening behavior, we use the following functional form

$$\bar{h}(\gamma_0) = [1 + (\gamma_0/\gamma_m)^2]/[1 + |\gamma_0/\gamma_M|^5],$$

where $\gamma_m = 0.34$ and $\gamma_M = 0.57$ are fitting parameters that respectively mark the departure from linearity and the location of the strain maximum shown in Fig. 2. This functional form serves as a useful fitting function which we now show can be used to predict the viscoelastic stress growth in start up of steady shear and the magnitude of the stress at failure without any adjustable parameter.

In Fig. 3(a), we show the evolution of stress and onset of cracking when a 4\% wt. casein gel is submitted to a constant shear rate $\dot{\gamma}_0 = 10^{-3} \text{s}^{-1}$. The stress growth $\sigma(t)$ can be separated into three consecutive regimes: a linear viscoelastic regime, characterized by power-law growth of $\sigma(t)$ up to $\gamma = \dot{\gamma}_0 t = 0.2$, followed by a strain-stiffening regime in which $\sigma$ shows a steeper increase up to a critical strain $\gamma_c \simeq 0.8$ at which point the stress goes through a maximum stress denoted $\sigma_c$. Finally, the stress exhibits an abrupt decrease. The gel remains vi-
usually intact and homogeneous initially, and the first macroscopic fracture appears at the stress maximum when \( \gamma \approx \gamma_c \) and \( \sigma \approx \sigma_c \) (see Movie 1 in the SI). We predict the viscoelastic stress response using a K-BKZ formulation:\textsuperscript{22,38–40} 

\[
\sigma(t) = \int_{-\infty}^{t} G(t - t') h(\gamma) \dot{\gamma}(t') dt' 
\]

The initial regime in Fig. 3 is fully accounted for by the linear viscoelastic response \( G(t) \). Since \( h(\gamma) = 1 \) in this regime the stress can be found analytically:\textsuperscript{41,42} 

\[
\sigma(t) = \int_{0}^{t} G(t - t') \dot{\gamma}_0 dt' = \frac{V \dot{\gamma}_0 t^{1-\alpha}}{(1-\alpha) \Gamma(1-\alpha)}.
\]

Equation (2) nicely describes the experimental data for \( \gamma \lesssim 0.2 \) without any additional fitting parameter [see dashed gray line in Fig. 3(a) and (c)]. To predict the nonlinear behavior, we substitute the power-law form of the relaxation modulus \( G(t) \) into Eq. (1)\textsuperscript{20,40,43} and rearrange to give:

\[
\sigma(t) = \frac{V \dot{\gamma}_0}{\Gamma(1-\alpha)} \int_{0}^{\dot{\gamma}_0 t} h(\gamma) \gamma^{-\alpha} d\gamma 
\]

where \( \gamma = \dot{\gamma}_0 t \) is the total accumulated strain at time \( t \). To capture the strain-stiffening we substitute the strain hardening form of the damping function \( h^{\ast}(\gamma) \), into Eq. (3) to obtain the prediction shown by the solid black line in Fig. 3(a) and (c). This captures the nonlinear response at moderate strains, but leads to an ever-increasing rate of stress growth. The softening part of the damping function is crucial to account for the stress evolution observed experimentally during shear start-up. Substituting \( \tilde{h} \) in Eq. (3) and integrating numerically we obtain the red line in Fig. 3(a) and (c) which accurately predicts the mechanical response of the protein gel, including the numerical magnitude of the stress maximum, without any adjustable parameter. The initial stiffening behavior is described by the numerator of \( \tilde{h} \), while the denominator is responsible for the subsequent plateauing of the predicted stress response. The ultimate decrease of the stress observed experimentally in Fig. 3(a)

![Figure 4: Critical stress \( \sigma_c \) (a) and critical strain \( \gamma_c \) (b) vs. applied shear rate for both a 4\% (○) and a 8\% (□) casein gel. The dashed and continuous lines show the prediction resulting from the combination of the Bailey criterion and the stress response computed either from just the linear response (dashed lines) or the full K-BKZ equation using \( h^{\ast} \) (solid lines).](image)

must be associated with the growth of macroscopic fractures that cannot be accounted for by the K-BKZ formulation in Eq. (1), which assumes a homogeneous strain field. Repeating shear start-up experiments for various \( \dot{\gamma}_0 \) confirms that Eq. (3) quantitatively predicts the gel response over almost three decades of shear rate [Fig. 3(b)]. The universal nature of the response is evident by the rescaling of the experimental data onto a single master curve [Fig. 3(c) and see corresponding Fig. S2(a) in the SI for the 8\% wt. gel].

In Fig. 4 we show the locus of the stress maximum (\( \sigma_c, \gamma_c \)) for different imposed shear rates, for both the 4\% wt. and 8\% wt. casein gels. The critical stress \( \sigma_c \) increases as a weak power law of \( \dot{\gamma}_0 \) with an exponent \( \xi = 0.18 \pm 0.01 \) for the 4\% wt. casein gel and \( \xi = 0.13 \pm 0.01 \) for the 8\% wt. gel respectively [Fig. 4(a)]. By contrast, the critical strain \( \gamma_c \) displays a power-law increase with \( \dot{\gamma}_0 \) for the 8\% casein gel, whereas the 4\% casein gel shows a yield strain that is rate independent [Fig. 4(b)].

To account quantitatively for the different scalings with \( \dot{\gamma}_0 \) of the critical crack parameters \( \sigma_c \) and \( \gamma_c \), we apply the failure criterion introduced by J. Bailey, which successfully describes the rupture of much stiffer samples such as glasses\textsuperscript{44} and elastomeric-like materials.\textsuperscript{45} This criterion assumes that the failure process is Markovian, i.e. the failure of the material results from the accumulation of local...
failure events that are independent.\textsuperscript{25} This appears to be the case for the brittle-like failure scenario of casein gels that are well modeled by Fiber Bundle Models,\textsuperscript{6,46,47} which themselves verify such assumptions. The Bailey criterion reads \(\int_0^{\tau} dF / [\sigma(t)] = 1\), where \(\tau\) denotes the sample lifespan under an arbitrarily given active loading process \(\sigma(t)\), and \(F(\sigma_0)\) is the dependence of the time to rupture for creep experiments under constant imposed stress \(\sigma_0\).\textsuperscript{24} Independent creep tests have been performed on the same casein gels\textsuperscript{6} and indicate that \(F(\sigma_0) = A \sigma_0^{-\beta}\) where \(A = (7.6 \pm 0.1) \times 10^{13}\) s.Pa\(^{\beta}\) and \(\beta = 5.5 \pm 0.1\) for the 4\% wt. gel\textsuperscript{6} and \(A = (5.0 \pm 0.1) \times 10^{18}\) s.Pa\(^{\beta}\) and \(\beta = 6.4 \pm 0.1\) for the 8\% wt. gel [see Fig. 3 in the SI]. We have also independently determined the functional form of the rheological response to an arbitrary loading history [Eq. (2) and (3)]. When combined with Eq. (3) computed with \(h = 1\), the Bailey criterion leads to the following expressions for the critical strain and stress:

\[
\gamma_c(\gamma_0) = S_\gamma \gamma_0^{(1-\alpha\beta)/[1+(1-\alpha)\beta]} \tag{4}
\]

\[
\sigma_c(\gamma_0) = S_\sigma \gamma_0^{1/[1+(1-\alpha)\beta]} \tag{5}
\]

where the prefactors \(S_\sigma\) and \(S_\gamma\) are analytic functions of \(\alpha, \beta\) and \(\gamma_0\).\textsuperscript{48} Whether the critical stress and strain are constant or increase/decrease with \(\gamma_0\) thus depends on both the parameters in the linear viscoelastic kernel \(G(t)\) and on the form of the failure law \(F(\sigma_0)\). For example, in the 8\% wt. casein gel (for which \(\alpha = 0.04 \pm 0.01\) and \(\beta = 6.4 \pm 0.1\)) we find that the critical strain increases with \(\gamma_0\) since the exponent in Eq. (4) is \((1 - \alpha\beta)/[1 + (1 - \alpha)\beta] \approx 0.10 \pm 0.01\). For both the 4\% wt. and 8\% wt. gels, the agreement between the theoretical scaling (dashed lines in Fig. 4) and experiments for \(\sigma_c\) and \(\gamma_c\) is excellent, again without any adjustable parameter. However, the prefactor \(S_\gamma\) is clearly overestimated for the 4\% wt. casein gels (dashed line in Fig. 4). Indeed, 4\% wt. casein gels display a pronounced stiffening responsible for the early rupture of the gel, which is not captured by the linear viscoelastic formulation Eq. (2). However, when combined with the Bailey criterion, direct numerical integration of Eq. (3) computed with \(h^*\), accounting for strain-stiffening, yields the correct value of the prefactor for both 4\% and 8\% casein gels (solid lines in Fig. 4).

We have shown using soft viscoelastic casein gels that combining (i) the K-BKZ formalism and (ii) Bailey’s failure criterion establishes a self-consistent framework to capture the linear and non-linear response of viscoelastic protein gels under shear, up to the materials’ yield point. This approach also predicts the scaling of both the critical stress and critical strain at failure in shearing flows. Other geometries (e.g. three-point bending) and other kinematics (e.g. extensional flows) remain to be tested. Nonetheless, the present results thus extend the validity of Bailey’s criterion to soft viscoelastic gels, further reinforcing the emerging analogies between soft and hard materials.\textsuperscript{49}

Acknowledgement

The authors thank M. Bouzid and E. Del Gado for enlightening discussions, and A. Parker for providing the casein and GDL. This work was funded by the MIT-France seed fund and by the CNRS PICS-USA scheme (#36939).

References

(1) R. Mezzenga, P. Schurenberger, A. Burbidge, and M. Michel, Understanding foods as soft materials, Nature Mater. 4, 729 (2005).

(2) J. Thiele, Y. Ma, S. Bruers, S. Ma, and W. Huck, 25th Anniversary Article: Designer Hydrogels for Cell Cultures: A Materials Selection Guide, Advanced Materials 26, 125 (2014).

(3) M. Webber, E. Appel, E. Meijer, and R. Langer, Supramolecular biomaterials, Nature Mater. 15, 13 (2016).

(4) D. Bonn, H. Kelley, M. Prochnow, K. Ben-Djemiaa, and J. Meunier, Delayed fracture of an inhomogeneous soft solid, Science 280, 265 (1998).

(5) P.J. Skrzeszewska, J. Sprakel, F.A. de Wolf, R. Fokkink, M.A. Cohen Stuart, and J. van der Gucht, Fracture and self-healing in a well-defined self-assembled polymer network, Macromolecules 43, 3542 (2010).
(6) M. Leocmach, C. Perge, T. Divoux, and S. Maneville, Creep and fracture of a protein gel under stress, Phys. Rev. Lett. 113, 038303 (2014).

(7) S. N. Karobi, T.L. Sun, T. Kurokawa, F. Luo, T. Nakajima, T. Nonoyama, and J.P. Gong, Creep Behavior and Delayed Fracture of Tough Polyelectrolyte Hydrogels by Tensile Test, Macromolecules 49, 5630 (2016).

(8) T. Baumberger, C. Caroli, and D. Martina, Solvent control of crack dynamics in a reversible hydrogel, Nature Mater. 5, 552 (2006).

(9) K.A. Erk, J.D. Martin, Y.T. Hu, and K.R. Shull, Extreme Strain Localization and Sliding Friction in Physically Associating Polymer Gels, Langmuir 28, 4472 (2012).

(10) K. Schmoller, P. Fernández, R. Arevalo, D. Blair, and A. Bausch, Cyclic hardening in bundled actin networks, Nature Com. 134, 1 (2010).

(11) C. Storm, J. Pastore, F. MacKintosh, T.C. Lubensky, and P. Janmey, Nonlinear elasticity in biological gels, Nature 435, 191 (2005).

(12) I.K. Piechocka, R.G. Bacabac, M. Potters, F.C. MacKintosh and G.H. Koenderink, Structural Hierarchy Governs Fibrin Gel Mechanics, Biophys. J. 98, 2281 (2010).

(13) K.A. Erk, K.J. Henderson and K.R. Shull, Strain Stiffening in Synthetic and Biopolymer Networks, BioMacromolecules 11, 1358 (2011).

(14) J.-M. Carrillo, F. MacKintosh, and A. Dobrynin, Nonlinear Elasticity: From Single Chain to Networks and Gels, Macromolecules 46, 3679 (2013).

(15) T. Nakajima, Y. Fukuda, T. Kurokawa, T. Sakai, U. Chung, and J.P. Gong, Synthesis and Fracture Process Analysis of Double Network Hydrogels with a Well-Defined First Network, ACS Macro Lett. 2, 518 (2013).

(16) J.P. Gong, Y. Katsuyama, T. Kurokawa, and Y. Osada, Double-Network Hydrogels with Extremely High Mechanical Strength, Adv. Mater. 15, 1155 (2003).

(17) J.-Y. Sun, X. Zhao, W.R.K. Illeperuma, O. Chaudhuri, K.H. Oh, D.J. Mooney, J.J. Vlassak and Z. Suo, Highly stretchable and tough hydrogels, Science 489, 133 (2012).

(18) J. Li, W.R.K. Illeperuma, Z. Suo and J.J. Vlassak, Hybrid Hydrogels with Extremely High Stiffness and Toughness, ACS Macro Lett. 3, 520 (2014).

(19) X. Zhao, Multi-scale multi-mechanism design of tough hydrogels: building dissipation into stretchy networks, Soft Matter 10, 672 (2014).

(20) V. Rolón and M. Wagner, The damping function in rheology, Rheol. Acta 48, 245 (2009).

(21) K. Mayumi, A. Marcellan, G. Ducouret, C. Creton, and T. Narita, Stress-Strain Relationship of Highly Stretchable Dual Cross-Link Gels: Separability of Strain and Time Effect, ACS Macro Lett. 2, 1065 (2013).

(22) R.B. Bird, R.C. Armstrong and O. Hassager, Dynamics of Polymeric Liquids, 2nd ed. (John Wiley & Sons, New York, 1987).

(23) R.G. Larson, The Structure and Rheology of Complex Fluids, Topics in chemical engineering. Oxford University Press (1999).

(24) G. Bartenev and Y. Zuyev, Strength and Failure of visco-elastic materials (Pergamon Press, 1968), chap. 7, Dependence of Strength of elastomers on strain rate and type of filler, pp. 193–211.

(25) A.D. Freed and A.I. Leonov, The Bailey criterion: Statistical derivation and applications to interpretations of durability tests and chemical kinetics, Z. Angew. Math. Phys. 53, 160 (2002).

(26) J. Lucey, T. van Vliet, K. Grolle, T. Geurts, and P. Walstra, Properties of Acid Casein Gels Made by Acidification with Glucono-δ-lactone. 1. Rheological Properties, Int. Dairy J. 7, 381 (1997).

(27) B. O’Kennedy, J. Mounsey, F. Murphy, E. Duggan, and P. Kelly, Factors affecting the acid gelation of sodium caseinate, Int. Dairy J. 16, 1132 (2006).

(28) Rheological data were obtained with an ARES-LS strain-controlled rheometer (TA Instrument) using a homemade Plexiglas rotating cup of height 20.3 mm and diameter 25 mm with an inner Delrin fixed bob of radius 22.7 mm.

(29) A. Jaishankar and G.H. McKinley, Power-law rheology in the bulk and at the interface: quasi-properties and fractional constitutive equations, Proc. R. Soc. A 469, 20120284 (2013).

(30) C. Friedrich, H. Schiessel, and A. Blumen, Advances in the Flow and Rheology of Non-Newtonian Fluids, edited by D. A. Siginer, D. Kee, and R. P. Chhabra, (Elsevier, Amsterdam, 1999) pp. 429–466.

(31) We find similar results for the 8% wt. casein gel. The exponent $\alpha = 0.04 \pm 0.01$ and the prefactor $V = 640 \pm 5$ Pa. s$^a$ (see Fig. 1 in the Supplemental Material).
(32) R.S. Rivlin and K.N. Sawyers, Nonlinear continuum mechanics of viscoelastic fluids, Annu. Rev. Fluid Mech. 3, 117 (1972).

(33) Therefore independent step strain experiments, instead of traditional strain sweeps which accumulate larger total deformations, allow us to prevent the growth of cracks and to accurately measure the initial stiffening and subsequent softening behavior.

(34) M. Pouzot, T. Nicolai, L. Benyahia, and D. Durand, Strain hardening and fracture of heat-set fractal globular protein gels, J. Colloid Interface Sci. 293, 376 (2006).

(35) T. Gisler, R. C. Ball, and D.A. Weitz, Strain Hardening of Fractal Colloidal Gels, Phys. Rev. Lett. 82, 1064 (1999).

(36) \(h^*\) is defined as \(h^* = 1 + \sum_{j=1}^{2} \frac{b_{2j}}{50} \cdot \lambda_{2j}^{j}\), where \(\{b_{2j}\}_{j \in \mathbb{N}}\) are numerical coefficients defined in.\(^{34}\)

(37) M. Mellema, J.H.J. Opheusden, and T. Van Vliet, Categorization of rheological scaling models for particle gels applied to casein gels, J. Rheol. 46, 11 (2002).

(38) R.G. Larson, Constitutive Equations for Polymer Melts and Solutions (Butterworths, Boston, 1988).

(39) A. D. Freed and K. Diethelm, Fractional calculus in biomechanics: a 3D viscoelastic model using regularized fractional derivative kernels with application to the human calcaneal fat pad, Biomech. Model Mechanobiol. 5, 203 (2006).

(40) A. Jaishankar and G.H. McKinley, A fractional K-BKZ constitutive formulation for describing the nonlinear rheology of multiscale complex fluids, J. Rheol. 58, 1751 (2014).

(41) R.I. Tanner, From A to (BK)Z in Constitutive Relations, J. Rheol. 32, 673 (1988).

(42) S. K. Venkataraman and H. H. Winter, Finite shear strain behavior of a crosslinking polydimethylsiloxane near its gel point, Rheol Acta. 29, 423 (1990).

(43) E. Mitsoulis, 50 Years of the K-BKZ Constitutive Relation for Polymers, ISRN Polymer Science 2013, Article ID 952379 1 (2013).

(44) J. Bailey, An attempt to correlate some tensile strength measurements on glass: III, Glass Ind. 20, 95 (1939)

(45) A. Ya Malkin and C.J.S. Petrie, Some conditions for rupture of polymer liquids in extension, J. Rheol. 41, 1 (1997).
Fracture of a protein gel under a shearing deformation. Stress response $\sigma$ vs time $t$ (lower axis) and vs strain $\gamma = \dot{\gamma}_0 t$ (upper axis) of a 4% wt. casein gel to a constant shear rate $\dot{\gamma}_0 = 10^{-3} \text{s}^{-1}$ initiated at $t = 0$. Different lines correspond to model predictions from linear and nonlinear rheology that are introduced in this paper. Side-view images of the sample in the Couette cell at different strains recorded simultaneously to the experiment reported in the main graph. Paper: Nonlinear viscoelasticity and generalized failure criterion for polymer gels. Authors: B. Keshavarz, T. Divoux, S. Manneville, and G. H. McKinley.