Creep and brittle failure of a protein gel under stress

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Biomaterials such as protein or polysaccharide gels are known to behave qualitatively as soft solids and to rupture under an external load. Combining optical and ultrasonic imaging to shear rheology we show that the failure scenario of a protein gel is typical of brittle solids: after a power-law creep regime fully accounted for by linear viscoelasticity and homogeneous deformation, fractures nucleate and grow logarithmically perpendicularly to shear up to sudden rupture. A single equation accounting for those two successive processes nicely captures the full rheological response. The failure time follows a decreasing power-law with the applied shear stress strongly reminiscent of the Basquin law of fatigue for solids. These results are in excellent agreement with recent fiber-bundle models that include damage accumulation on elastic fibers and exemplify protein gels as model brittle soft solids.

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So far huge effort has been devoted to designing protein gels with specific properties and textures at rest \[1\,1\,1\]. However, their mechanical behavior deep into the nonlinear regime has only been partially addressed \[1\,2\,3\] and several fundamental issues remain unexplored such as the spatially resolved rupture scenario or the physical relevance of the analogy with brittle failure in hard solids.

In this Letter we report on stress-induced fracture in protein gels by means of creep experiments coupled to optical and ultrasonic imaging. Gels formed by slow acidification of a sodium caseinate solution \[1\,4\] display fractures under large strain at fixed low pH values \[1\,2\,3\], which makes them perfect candidates to quantify brittleness in soft solids and tackle the above-mentioned issues. We demonstrate that under an external load, these casein gels display brittle-like failure that results from two successive physical processes: a reversible primary creep regime characterized by a homogeneous strain field and the irreversible nucleation and fracture growth leading to gel failure. Our results are in full agreement with the predictions of some recent fiber-bundle models and hint to universal features of brittle failure common to both soft and hard solids.

Gels are prepared by dissolving sodium caseinate powder (Firmenich) at 4% wt. in deionized water under gentle mixing at 35°C and 500 rpm. To induce gelation, 1% wt. glucono-δ-lactone (GDL) is dissolved in the solution and its hydrolysis progressively lowers the pH over the course of 8 hours [Fig. 1(a) in the Supplemental Material]. While still liquid, the solution is poured into the gap of a polished Plexiglas Couette cell immersed into a temperature-controlled water tank at 25.0±0.1°C \[1\,5\]. Rheological data are recorded during gel formation by a stress-controlled rheometer through small amplitude oscillatory shear at frequency \( f = 1 \) Hz (Fig. 1 in the Supplemental Material \[1\,5\]). Gelation is complete when the elastic \( (G') \) and viscous \( (G'') \) moduli reach a plateau with \( G' \gg G'' \). A constant stress \( \sigma \) is
then applied to the sample from time $t = 0$ and the subsequent strain response $\gamma(t)$ is monitored. Images of the gel are recorded simultaneously to the rheology (Logitech Webcam Pro 9000). The local velocity and strain fields can also be imaged in the gradient–vorticity plane $(r, z)$ simultaneously to rheology by a custom-made ultrasonic scanner detailed in [16]. In this case, prior to acidification, the sodium caseinate solution is seeded with acoustic tracers here 3% wt. polyamide spheres (Orgasol 2002 ES3 NAT 3, Arkema, diameter 30 $\mu$m, density 1.02) that do not modify the final gel properties [Fig. 1(b) in the Supplemental Material]. Failure being irreversible, each creep experiment requires to prepare a fresh sample in situ.

Under a constant applied shear stress $\sigma$, the global strain $\gamma(t)$ displays a robust time dependence (Fig. 1): $\gamma(t)$ slowly grows with time up to $\gamma \sim 1$ then accelerates until the gel fails at a well-defined time $\tau_f$. These three successive steps are better highlighted in Fig. 2 by focusing on the global shear rate $\dot{\gamma}(t)$. Figures 3 and 4 gather the results from local measurements and are discussed below together with each of the successive regimes inferred from global data. Note that these failure dynamics do not qualitatively depend on geometry nor on system composition (see Movie 1 in the Supplemental Materials).

As seen in the inset of Fig. 4 the failure time $\tau_f$ sharply decreases as a power-law of $\sigma$ with an exponent $\beta \approx 5.5$. $\tau_f$ further allows us to rescale all the shear rate data $\dot{\gamma}(t)$ onto the single master curve of Fig. 2(a) by plotting $\dot{\gamma}/\dot{\gamma}\text{min}$ vs $t/\tau_f$, where $\dot{\gamma}\text{min}$ is the minimum shear rate reached at a time $\tau\text{min}$ [see also Fig. 2 in the Supplemental Material for the original $\dot{\gamma}(t)$ data]. On about four decades for $t \lesssim 0.1\tau_f$, the shear rate decreases as a power-law $\dot{\gamma}(t) \sim t^{-\alpha}$ with $\alpha \approx 0.85 \pm 0.02$. This is strongly reminiscent of the primary creep observed in solids and referred to as Andrade creep [17, 19]. Interestingly, here, this scaling can be fully accounted for by linear viscoelasticity without invoking any irreversible plasticity. Indeed casein gels display a power-law rheology $G'\left(f\right) \sim G''\left(f\right) \sim f^{0.15}$ [inset of Fig. 2(a)], which corresponds to a compliance $J\left(t\right) \equiv \dot{\gamma}(t)/\sigma \sim t^{0.15}$ in the linear deformation regime [20]. This nicely corresponds to the observed $\dot{\gamma}(t) \sim t^{-0.85}$ and suggests that primary creep is purely reversible without unrecoverable plastic events. Homogeneity and linear response are further confirmed, at least up to the available spatial ($\sim 10 \mu$m) and temporal ($\sim 1$s) resolutions, by direct visualization which shows no sign of crack or fracture [Fig. 3(a)] and by ultrasound imaging which reveals velocity and strain fields averaged over the vertical direction $z$ that linearly decrease with the radial position $r$ within the gap [Fig. 3(a–b)] with insignificant $z$-dependence [Fig. 3(a, left)] and no slippage at the Plexiglas walls.

For $0.1 \lesssim t/\tau_f \lesssim 0.9$, $\dot{\gamma}(t)$ departs from power-law behavior and goes through a minimum value at time $\tau\text{min} = (0.56 \pm 0.04)/\tau_f$ independently of the applied stress [Fig. 2(b) and inset] as similarly reported for metals [21], solid composite materials [19] and fiber-bundles models (FBMs) [22, 23]. This linearity between $\tau\text{min}$ and $\tau_f$, also known as the Monkman-Grant relation [24], allows one to “predict” the failure time from the intermediate-time response. During this secondary creep regime, regularly-

FIG. 2: (color online) Normalized shear rate responses $\dot{\gamma}(t)/\dot{\gamma}\text{min}$ corresponding to the data of Fig. 1 and plotted so as to emphasize the three successive regimes. $\dot{\gamma}\text{min}$ is the minimum shear rate reached at $\tau\text{min}$ (see text and Suppl. Fig. 2). The yellow line shows the master curve inferred from fitting $\dot{\gamma}(t)$ by Eq. 1 with $\alpha = 0.85$, leading to $\lambda = 0.378 \pm 0.002$ and $\mu = 0.187 \pm 0.002$. (a) Primary creep: $\dot{\gamma}(t)/\dot{\gamma}\text{min}$ vs $t/\tau_f$ in logarithmic scales. Inset: Linear viscoelastic moduli $G'$ (top) and $G''$ (bottom) as a function of frequency $f$ for a strain amplitude of 0.1%. Red lines are power laws $G' \sim G'' \sim f^{0.15}$. (b) Secondary creep: $\dot{\gamma}(t)/\dot{\gamma}\text{min}$ vs $t/\tau_f$ in logarithmic scales. Gray dashes show the minimum of Eq. 1 reached at $\tau\text{min} = 0.556\tau_f$. Inset: $\tau\text{min}$ vs $\tau_f$. The red line is $\tau\text{min} = 0.56\tau_f$. (c) Tertiary creep: $\dot{\gamma}(t)/\dot{\gamma}\text{min}$ vs $(\tau_f - t)/\tau_f$ in logarithmic scales with a reversed horizontal axis.
spaced cracks nucleate from the top and bottom edges of the Couette cell and start growing perpendicular to the applied stress [Fig. 3b], see also Movie 2 in the Supplemental Material]. These macroscopic fractures are invaded with water expelled from the surrounding gel matrix. Although fractures have not yet entered the ultrasonic region of interest, velocity maps become heterogeneous along the z direction [Fig. 3b, left] and display intermittent fluctuations [Fig. 3c,d]. The level of these fluctuations, which can also be seen on the global response for the same applied stress [▼ in Fig. 2b], is poorly reproducible and stress-dependent. We propose that such intermittency arises from microscopic cracks ahead of the fracture tip. Since heterogeneity is much smaller along the radial direction [compare red and black lines in Fig. 3d], these “precursors” either extend across the full 2-mm gap or induce long-range displacements that span the gap. In any case, such noisy features are typical of slow crack growth in solids \[25, 26\] and more generally of avalanche behavior \[27\].

In the tertiary creep regime, for \(t \gtrsim 0.9 \tau_f\), the shear rate increases by more than four orders of magnitude and diverges as \((\tau_f - t)^{-1}\) [Fig. 2c)]. This finite-time singularity corresponds to the final growth of the fractures along the vorticity direction \(z\) as they accelerate and eventually meet in the middle of the Couette cell at time \(\tau_f\) [Fig. 3c-d)]. Ultrasonic velocity maps directly correlate with the crack growth and reveal the complex structure of the displacement field at the tip and around the fracture. In particular, Fig. 3d, left) suggests that the fracture is initiated at the inner cylinder at \(r = 0\) and the presence of large positive and negative velocities in the vicinity of the crack tip is indicative of strong compression and recoil of the gel matrix. Finally, the fracture length \(\ell(t)\) is observed to grow logarithmically with \((\tau_f - t)\) upon approaching \(\tau_f\) [Fig. 3d)]. In other words one has \(d\ell/dt \sim \gamma(t) \sim (\tau_f - t)^{-1}\), which indicates that the global shear rate is linked to fracture-induced displacements.

Finally, we emphasize that the (reversible) Andrade-like creep and the (irreversible) crack growth are two physical processes that effectively superimpose to yield the global rheological response. Indeed, as seen from the yellow line in Fig. 2 the master curve \(\dot{\gamma}(t)/\gamma_{\text{min}}\) vs \(t/\tau_f\) is perfectly fitted by:

\[
\frac{\dot{\gamma}(t)}{\gamma_{\text{min}}} = \lambda \left( \frac{t}{\tau_f} \right)^{-\alpha} + \frac{\mu}{1 - t/\tau_f},
\]

with only two adjustable parameters \(\lambda\) and \(\mu\) once \(\alpha = 0.85 \pm 0.02\) is fixed. The remarkable collapse of the whole data set to such a simple equation allows us to interpret the secondary creep regime as a mere crossover from creep to crack growth.

Let us now summarize and discuss the most prominent results of this Letter. First we have shown that casein gels display a remarkable failure scenario similar to that of brittle solids and characterized by the same three successive creep regimes. Here, the primary creep and its power-law exponent \([\gamma(t) \sim t^{-\alpha}\) with \(\alpha = 0.85 \pm 0.02\] are fully accounted for by linear viscoelasticity and local measurements consistently display a homogeneous bulk deformation. Such a link between creep and viscoelasticity is shared by other biopolymer gels with power-law rheology \[28, 29\] as well as hard-sphere-like colloidal glasses \[4\]. Protein gels thus appear to remain purely elastic and reversible throughout primary creep, a hallmark of brittle materials. By contrast primary creep in solids is irreversible and has been attributed to dislocation interactions in the case of crystalline materials \[18\] or to localized plastic rearrangements in amorphous materials \[30\].

The logarithmic fracture growth in the tertiary creep regime constitutes our second important result. Such an evolution is also commonly reported in disordered solid materials displaying brittle rupture and interpreted in the framework of Griffith-like models based on global or
local energy barriers. However these approaches all predict exponential scalings for $\tau_f(\sigma)$ while our data are best fitted by the decreasing power-law $\tau_f \sim \sigma^{-\beta}$ with $\beta = 5.45 \pm 0.05$ (inset of Fig. 1). This last key result suggests that thermally activated crack growth is not relevant to the present soft solid. Rather the power-law scaling is strikingly reminiscent of the Basquin law of fatigue found for a variety of heterogeneous or cellular materials under cyclic deformation. Basquin law has also been recently predicted by FBMs that combine elastic fibers with a local yield strain and take into account damage accumulation. Interestingly assuming damage accumulation to be proportional to $\sigma^\gamma$ directly leads to Basquin law with $\gamma = \beta$ and large values of $\gamma$, typically larger than 5 as found here for $\beta$, lead to macroscopic cracks due to the simultaneous rupture of a large number of fibers. More generally FBMs under compressive or elongational load predict three successive creep regimes exactly alike Fig. 2 with similar proportionality between $\tau_{\text{min}}$ and $\tau_f$ and finite-time singularity. This highlights the relevance of FBMs in the context of creep in protein gels, whose microstructure indeed appears to be formed of strands, but also urges to study FBMs in shear geometries to check whether they would be able to predict fracture growth as observed here.

To conclude, the present time- and space-resolved study shows that protein gels qualify as model, brittle soft solids. Prompted by the remarkable simplicity of Eq. (1) that encompasses Andrade creep, the Monkman-Grant relation and finite-time singularity within a single equation, future modeling will undoubtedly focus on the microscopic ingredients needed to predict quantitatively the Monkman-Grant prefactor and the Basquin exponent $\beta$. The next experimental step consists in a statistical study of the fluctuations associated to crack nucleation and growth as well as a systematic investigation of other systems in order to check for universality in the irreversible creep rupture of soft solids in general and of biogels such as actin, alginate or agar gels in particular. Such a study is expected to have important implications in understanding the behavior of biomaterials under extreme stress conditions.

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Supplemental material

Supplemental movies

Supplemental Movie 1 shows the failure of a 4% wt. casein gel acidified with 4% wt. GDL in a plate-plate geometry for an imposed shear stress \( \sigma = 120 \) Pa. The plate diameter is 50 mm and the gap width is 1 mm. Fractures grow parallel to the vorticity direction, i.e. along the radial direction in this case. The global rheological response is fully similar to that measured in the Couette geometry.

Supplemental Movie 2 shows the creep experiment analyzed in Figs. 3 and 1 and performed under \( \sigma = 300 \) Pa on a 4% wt. casein gel seeded with 3% wt. polyamide spheres and acidified with 1% wt. GDL. The gap width of the Couette cell is 2 mm and its height is 60 mm. Images recorded by a standard webcam (Logitech Webcam Pro 9000) are shown in the top left panel. Velocity maps \( v(r, z, t) \) inferred from ultrasonic imaging by averaging over 4 s are shown in the top right panel using linear color levels. The vertical position \( z = 0 \) on the ultrasonic images corresponds to about 20 mm below the top of the Couette cell. The two bottom graphs show the global shear rate response \( \dot{\gamma}(t) \) (left) and the strain response \( \gamma(t) \) recorded by the rheometer (AR G2, TA Instruments) simultaneously to optical and ultrasonic imaging.

Supplemental figures

Supplemental Figure 1 illustrates the gelation process of a 4% wt. sodium caseinate solution seeded with 3% wt. polyamide spheres through time-resolved measurements of the elastic and viscous moduli, respectively \( G' \) and \( G'' \), under small amplitude oscillatory shear. GDL contains an ester function which, once added to the solution at time \( t = 0 \), hydrolyzes spontaneously and leads to a slow decrease of the pH [Fig. 1(a)] towards the casein isoelectric point (pH \( \approx 4.6 \)) at which casein particles aggregate. Gelation actually starts earlier at pH \( \approx 5 \) as shown by gray dashed lines and as already discussed in Ref. 1. At this point the elastic and viscous moduli display a sudden increase then overshoot and converge towards their steady-state values where \( G' \gg G'' \) [Fig. 1(b)]. Note that the maximum of the overshoot is reached around the isoelectric point. The decrease of both moduli at lower pH is usually attributed to the over-acidification which enhances the repulsive electrostatic interactions between casein particles of net positive charge 2.

Supplemental Figure 2 shows the shear rate \( \dot{\gamma}(t) \) obtained by differentiating the raw strain of Fig. 1 in the main text. For \( 0.1 \lesssim t/\tau_f \lesssim 0.9 \), i.e. in the secondary creep regime, \( \dot{\gamma}(t) \) is smoothed using a moving average over \( \delta t \approx 0.01 \tau_f \) in order to remove high-frequency noise due to differentiation at very small shear rates. The same data normalized by its minimum value \( \dot{\gamma}_{\text{min}} \) is plotted in Fig. 2(a) as a function of \( t/\tau_f \) leading to a nice collapse onto a single curve whatever the imposed shear stress.
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