

Stress Enhancement in the Delayed Yielding of Colloidal Gels

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Networks of aggregated colloidal particles are solidlike and can sustain an applied shear stress while exhibiting little or no creep; however, ultimately they will catastrophically fail. We show that the time delay for this yielding decreases in two distinct exponential regimes with applied stress. This behavior is universal and found for a variety of colloidal gel systems. We present a bond-rupture model that quantitatively describes this behavior and highlights the role of mesoscopic structures. Our result gives new insight into the nature of yielding in these soft solid materials.

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Networks of weakly aggregated colloidal particles, or colloidal gels, exhibit a solidlike behavior [1]: their elastic modulus G' is nearly independent of frequency ω and significantly larger than their viscous modulus G'' . Interestingly, G'' exhibits a feature common to many soft materials; it is largely frequency-independent but nevertheless displays a weak but noticeable increase at the lowest ω typically measured [2]. This rise suggests the presence of an ultraslow relaxation mechanism in the material. Such relaxation could reflect the ultimate fluidlike behavior of the gel at frequencies so low they cannot be probed with oscillatory rheology. Alternatively it could result from aging, which leads to irreversible fluidization of the gel [3] that cannot even be correctly measured with oscillatory rheological measurements. Instead, the mechanics of such soft solid materials can be probed with creep measurements. At low applied stress σ , the creep response of colloidal [4,5] and polymeric gels [6,7] typically displays the characteristics of a mechanically stable solid, with the deformation reaching a time-independent plateau that reflects the elasticity of the material. However, this solidlike stability persists only for a finite time, whereupon the gel suddenly and catastrophically yields. For polymer networks, the time between the application of a load and the time of yield, τ_d , exhibits an exponential dependence on the applied stress; this results from stress-enhancement of the thermal relaxation of individual bonds within the network [6,7]. The yielding of colloidal gels also exhibits a strong dependence on stress [4,5], but the origin of this behavior has never been fully established. An understanding of its origins is essential as it would provide new insight into the underlying nature of colloidal gels and their stability. This demands careful experiments and new theoretical interpretations.

In this Letter we report the results of a study of delayed yielding of colloidal gels subjected to shear stresses. We show that the delay time of presheared gels exhibits two distinct exponential regimes with applied stress. This behavior is universal; it is observed in colloidal gels with completely different gelation mechanisms and vastly

different elastic moduli. We present a model which fully accounts for this behavior and elucidate the mechanisms of the catastrophic failure. It also accounts for the observed strong dependence on the morphology of the gel.

Rheological experiments are carried out on a stress-controlled rheometer (MCR501, Anton Paar) in a concentric cylinder geometry. We study a strong gel of carbon black particles (Cabot Vulcan XC72R) in tetradecane at 8 wt%. Its elastic modulus is $G_0 = 7690$ Pa, measured before each experiment to confirm that the sample has not evolved due to evaporation or particle migration. To establish reproducible initial conditions, they are presheared for 60 s at a strain rate $\dot{\gamma} = 500$ s⁻¹ and left to recover for 15 min before starting the measurement. Unless stated otherwise, all samples are subjected to a preshear treatment prior to the creep experiments.

For very low σ , the initial creep response is purely elastic: γ increases linearly with time, followed by an inertial ringing reflecting the elasticity of the sample [8] after which γ becomes nearly independent of time [Fig. 1(a)] and $\dot{\gamma}$ tends to zero [1(b)]. Virtually no creep is observed over the full length of the experiment [dashed line in Fig. 1(a)]. However, as σ is increased, the initial response remains the same, but the time-independent creep persists only for a finite time, whereupon the sample fails catastrophically and both γ and $\dot{\gamma}$ increase sharply [Figs. 1(a) and 1(b)]. This occurs after a delay τ_d , which we take to be the point where the increase in $\dot{\gamma}$ is maximal, as shown by the arrows in Fig. 1(b). As σ is increased τ_d decreases [Fig. 1(a)]. Ultimately, the range over which the creep is time independent becomes very small and failure is nearly instantaneous. Directly after yielding, the linear elastic modulus is essentially unchanged, but the gel yields at significantly shorter times, unless it is rejuvenated by a strong preshear treatment.

Similar behavior is observed for polymer gels, where it is understood quantitatively as the result of an activated process with an energy barrier originating from the breaking of physical bonds that provide the cross-links in the network. Transition-state theory predicts that this barrier

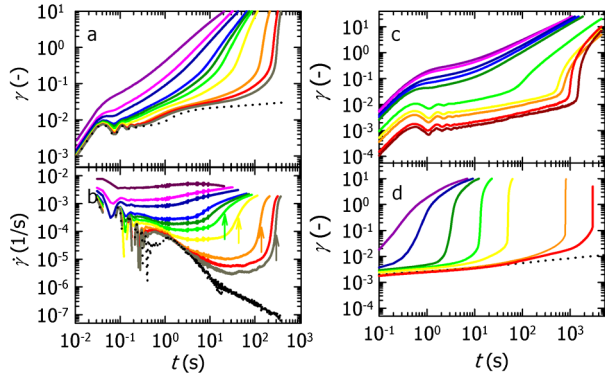


FIG. 1 (color online). (a) Creep response of carbon black gels at 8 wt% for $\sigma = 50.0$ – 15.0 Pa, decreasing from left to right and (b) corresponding shear rate $\dot{\gamma}$, arrows illustrate the choice for τ_d as the maximum in $d\dot{\gamma}/dt$. (c) Creep curves for weak gel of polystyrene particles depleted with dextran ($\sigma = 0.6$ – 0.01 Pa) and (d) for thermoreversible stearylated-silica gels ($\sigma = 12.0$ – 6.3 Pa).

decreases linearly with σ [9]; this manifests as an exponential dependence of τ_d on σ , which is indeed observed for polymeric networks loaded in shear [7] or bending [6]. To test whether this microscopic prediction holds for colloidal gels, we plot τ_d as a function of σ on a semilogarithmic plot, where the error bars represent the standard deviation across at least three independent measurements (triangles, Fig. 2). Surprisingly, rather than the single exponential decay, we observe two distinct exponential regimes for our presheared gels.

To account for the more complex behavior observed for colloidal gels, we generalize the bond-rupture model [7]. Within this model τ_d is approximated by the time required for the rupture of a single bond due to thermal fluctuations. The rate of this rupture is increased by the applied stress. However, this picture is based on the behavior of a single

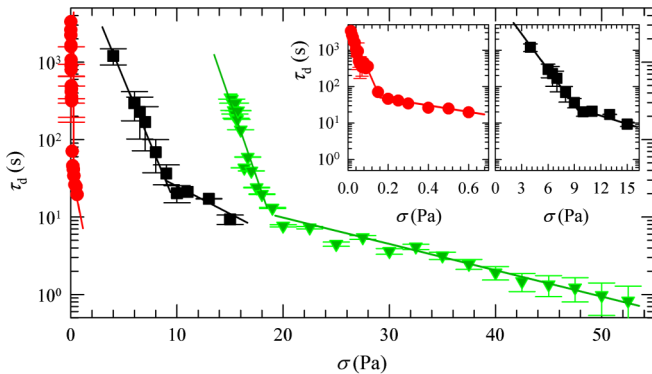


FIG. 2 (color online). Delay time τ_d between the application of the shear stress σ and the moment of yield, for gels of strong gel of carbon black at 8 wt% (triangles), depletion gel of polystyrene colloids and dextran ($\phi = 0.3$, $c_p = 50$ mg/ml circles), and thermoreversible gel of pNIPAM-grafted colloids at $\phi = 0.075$ (squares). Drawn lines are exponential fits, according to Eq. (3). Insets show magnifications of the data for weak depletion and thermoreversible gels.

bond; it ignores the actual structure of a colloidal gel. In contrast to the structure of a polymeric gel, colloidal gels are highly heterogeneous: particles aggregate into a network of mesoscopic strands which form a mechanically stable, percolating network. These strands can be many particles wide; therefore, they do not break directly when only a single bond ruptures. Instead, their integrity is maintained by the adjacent bonds, and thermal fluctuations can lead to reformation of a broken bond. Catastrophic failure of a strand occurs only when all bonds across the strand break simultaneously.

At sufficiently high σ , interparticle bonds rupture at a higher rate than they reform, then the breaking of entire strands occurs at approximately the same rate as the breaking of single bonds. We expect that catastrophic failure of the network occurs very rapidly; this reduces to the behavior predicted by the single-bond-rupture model leading to the exponential dependence observed at high σ . By contrast, in the limit of low σ , the bond-breaking rate is smaller than the bond-reforming rate; thus, the rupture of a strand is much more unlikely and occurs only in the rare event of *simultaneous* dissociation of all bonds in its cross section. This also leads to an exponential dependence of τ_d on σ but with a different characteristic stress. This accounts for the two distinct regimes of delayed yield observed experimentally (triangles in Fig. 2): a rapid, catastrophic rupture of the structure at high stresses, and a slow, stochastic erosion of the structure at low stresses.

This conceptual picture can be made quantitative by first considering the microscopic scale of the bonds between individual colloids. These can both rupture and heal by thermal fluctuations at rates k_D and k_A , respectively. The activated process of dissociation is enhanced by a force f across the bond induced by a macroscopically applied stress: the stress-dependent dissociation rate is $k'_D = k_D \exp(f\delta/k_B T)$ [9], with δ the range of the attraction. It is this stress-enhanced bond rupture that explains delayed failure in polymeric gels [7]. To understand the yielding dynamics of colloidal gels, we must also consider structures at scales larger than individual particles.

For large applied stresses, the dissociation rate increases substantially and becomes much greater than the association rate: $k'_D \gg k_A$. To calculate the dissociation rate of a strand we assume that the average strand has a cross section composed of n bonds. The survival probability of a single bond is $p_1(t) = \exp(-k'_D t)$; consequently, the probability that a strand is intact at a given time is $p_n(t) = 1 - [1 - p_1(t)]^n$, where we assume that the force per bond within a strand remains constant as individual bonds are broken. When a strand becomes weaker, part of the load it carries is redistributed to neighboring strands. To find the average lifetime of a strand τ_D , we integrate over its survival probability, yielding the strand dissociation rate

$$K_D = \frac{1}{\tau_D} = \left(- \int_0^\infty t' \frac{dp_n}{dt'} dt' \right)^{-1} = \frac{k'_D}{S_n} \approx \frac{k'_D}{\epsilon + \ln n}, \quad (1)$$

where $S_n = \sum_{j=1}^n 1/j$ and $\epsilon = 0.5772\dots$ is Euler's constant. Thus, the gel strands dissociate at almost the same rate as single bonds as σ is sufficiently large.

For small applied stress, bond rupture is followed almost immediately by its reassociation $k'_D \ll k_A$; only when all n bonds in the strand break within a time $\mathcal{O}(1/k_A)$ can a strand rupture. The probability that one bond of the cross section is broken is $P_1 = k'_D/k_A$; thus the probability that all bonds are broken is $P_n = P_1^n$. When a strand is broken, the reassociation of any one of the n bonds across the fracture plane restores the integrity of the strand; thus the average time a strand remains broken is $1/nk_A$. The failure of a single strand is therefore a Poisson process with rate $K_D \approx nk_A P_n = nk_A (k'_D/k_A)^n$. Consequently, strand rupture at low stresses is cooperative, making it significantly slower than the rupture of individual bonds. Moreover, this rate has a different stress scaling than that for high stresses [Eq. (1)]; this gives rise to two regimes for delayed yielding.

To extend these results for single strands to the macroscopic scale of our experiments, we assume that the gel is statistically homogeneous at larger length scales with a total area density of strands ρ . Thus for an applied stress σ , the force on each strand is σ/ρ and the force per bond becomes $f = \sigma/n\rho$. Upon application of σ the structure begins to erode, which we assume to be distributed over the entire sample volume, thus preserving statistical homogeneity of the network. Consequently, the strand density decreases,

$$\frac{d\rho}{dt} = -\rho K_D + (\rho_0 - \rho)K_A, \quad \rho(t=0) = \rho_0, \quad (2)$$

where K_A denotes the association rate of entire strands. The strand dissociation rate increases exponentially with increasing stress; moreover, as the material starts to erode, the forces on the remaining strands grow as ρ decreases, thereby exacerbating the increase of K_D . The structural erosion is thus a self-enhancing process. The ultimate failure of the gel requires the formation of a localized, macroscopic yield plane; this short and final stage of the failure is not captured by Eq. (2). However, it is the slow erosion of the structure that determines the delay time as predicted by Eq. (2).

By deriving approximate analytic solutions to Eq. (2) we identify the two regimes for τ_d . We assume that the reassociation of entire strands is negligibly slow $K_A = 0$:

$$\tau_d \approx \begin{cases} \frac{1}{n^2 \sigma C k_A} \left(\frac{k_A}{k_D}\right)^n e^{-n\sigma C}, & k'_D \ll k_A, \\ \frac{S_n}{\sigma C k_D} e^{-\sigma C}, & k'_D \gg k_A. \end{cases} \quad (3)$$

where $C = \delta/n\rho_0 k_B T$, having the units of compliance, and σC reflects the elastic energy per bond at yield. This yields two distinct exponential regimes for the delay time, allowing our essential experimental observation (Fig. 2) to be rationalized. Moreover, the ratio of the characteristic

stresses for each regime is determined by the number of bonds across a strand n .

The two stress regimes of τ_d are separated by a critical stress $\sigma_c = C^{-1} \ln(k_A/k_D)$ at which bond rupture and healing occur at the same rate $k'_D = k_A$. The microscopic parameter C sets the order of magnitude for the relevant stresses for the delayed yield. All parameters can be obtained directly from the slopes and intercepts of the two exponential regimes (triangles, Fig. 2) without adjustable parameters [Eq. (3)]. The slope of the high stress regime directly yields $C = 4.5 \times 10^{-2} \text{ Pa}^{-1}$, and thus the slope nC of the low stress regime yields $n = 25$. From the extrapolation of τ_d to σ_0 for each regime, we find $k_D = 2.6 \times 10^{-1} \text{ s}^{-1}$ and $k_A = 7.5 \times 10^{-1} \text{ s}^{-1}$. Thus $\sigma_c = 24 \text{ Pa}$, in excellent agreement with the crossover observed experimentally $\sim 20 \text{ Pa}$ (triangles, Fig. 2).

This behavior should be intrinsic to all gels. To explore the generality of our description we investigate a very weak gel formed by polystyrene particles ($d = 480 \text{ nm}$, $\phi = 0.35$) suspended in a mixture of $\text{H}_2\text{O}/\text{D}_2\text{O}$, for buoyancy matching, and with a depletion attraction induced through the addition of 50 mg/ml dextran of 200 kg/mol . This gel is much weaker with $G_0 = 203 \text{ Pa}$. The delayed yielding response is similar in form [Fig. 1(b)]. Moreover, τ_d again exhibits two distinct exponential regimes (circles in Fig. 2). We also study a gel formed with polystyrene colloids ($d = 430 \text{ nm}$) onto which the thermoresponsive polymer pNIPAm is grafted. These are suspended in a mixture of $\text{H}_2\text{O}/\text{D}_2\text{O}$ at $\phi = 0.075$. They can be made adhesive by increasing the temperature above the lower critical solution temperature of the polymer, causing them to gel [10]. For $\phi = 0.075$ the gel exhibits $G_0 = 2689 \text{ Pa}$ and displays two clear exponential regimes (squares in Fig. 2). These results confirm the universal nature of the delayed yielding response of colloidal gels.

A critical component of our explanation is the structure and thickness of individual strands. To explore these effects we modify the strand structure while keeping the attraction energy and ϕ constant. For this purpose we use thermoreversible gels made from stearyl-ated-silica particles ($d = 160 \text{ nm}$) suspended in dodecane. These systems undergo a fluid-gel transition when cooled below 29°C [4] but can be rejuvenated prior to each new measurement by heating to 40°C . A fine-stranded structure is formed by rapidly cooling to 5°C ; for $\phi = 0.25$ the as-formed gel has $G_0 = 6233 \text{ Pa}$ and exhibits a single exponential regime (circles in Fig. 3) indicative of $n \approx 1$. A single exponential regime was also observed in other colloidal gels [4,5]. After gelation, the structure can be coarsened by applying a mild preshear [11]. Application of a linear prestrain γ_{pre} , at constant $\dot{\gamma} = 10^{-2} \text{ 1/s}$, results in a gel whose linear viscoelastic properties are unchanged. However, the gel becomes dramatically less resilient to yielding; for a given σ , τ_d decreases by many orders of magnitude. For weak colloidal gels, application of a prestrain induces a thickening of the strands [11]. Interestingly, upon application of a

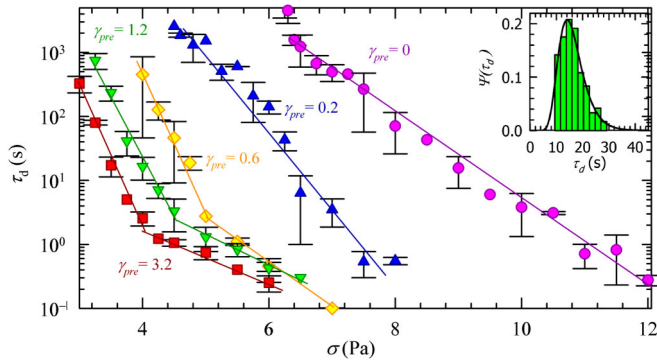


FIG. 3 (color online). τ_d versus σ for thermoreversible gels of stearylated silica after the application of various γ_{pre} . Inset shows the distribution of breaking times at $\phi = 0.25$ and $\sigma = 8$ Pa, drawn line is the predicted log-normal distribution.

prestrain to thermoreversible silica gels the initial single exponential regime transforms into two distinct regimes in τ_d (Fig. 3). The ratio of the slopes of the two exponential regimes increases from $n \approx 1$ at $\gamma_{pre} = 0$ to $n \approx 6$ for $\gamma_{pre} = 3$. This reflects the increasing thickness of the strands. These data highlight the pivotal role of mesoscopic structures.

An essential assumption of our model is the stochastic nature of structural erosion at low σ ; we take the rupture of a single strand to be a Poisson process. As macroscopic failure is the result of many strand ruptures, τ_d must be log-normally distributed. To test this we repeat 150 identical creep experiments. The breaking times between the individual runs are uncorrelated, confirming that the pretreatment generates history-free conditions. The distribution of delay times $\Psi(\tau_d)$ indeed shows the expected log-normal distribution (inset, Fig. 3), confirming the stochastic nature of the erosion mechanism.

The remarkable dynamic nature of yielding in these gels can be probed using an alternate methodology: rather than applying a constant stress we instead apply a constant strain rate $\dot{\gamma}$ to the thermoreversible silica gels. Initially, σ increases linearly with γ , reflecting the behavior of an elastic solid; the gel yields at γ between 0.35 and 0.70%, whereupon the stress reaches a maximum σ_{max} [Fig. 4(a)]. This is reached at time $t_{max} = \sigma_{max}/G_0\dot{\gamma}$, which must be of the same order as τ_d . Thus, solving $t_{max} = \tau_d$ reveals that σ_{max} is a linear function of $\ln\dot{\gamma}$, when neglecting $\mathcal{O}(\ln\sigma_{max})$ terms. This is indeed observed for three different values of ϕ [Fig. 4(b)].

Our data provide new insight into the failure mechanisms of weakly aggregated colloidal gels. Two distinct exponential regimes in the delay time reflect the heterogeneous and multiscale structure of these soft solid materials. Our data also address the intriguing question of the nature of gels as a true zero-frequency solid. Extrapolating τ_d to $\sigma = 0$ suggests the gels will ultimately yield even in the absence of an applied stress. The resulting zero-stress yield time depends on the strength of the gel, ranging from 2 h

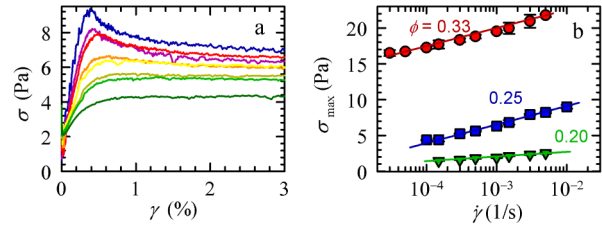


FIG. 4 (color online). Left: Stress-strain response at various imposed shear rates for the same system as in Fig. 3 at $\phi = 0.25$; from bottom to top $\dot{\gamma} = 1.5 \times 10^{-4}$, 3×10^{-4} , 5×10^{-4} , 1×10^{-3} , 1.5×10^{-3} , 3×10^{-3} , 5×10^{-3} , 1×10^{-2} 1/s. Right: Yield stress σ_{max} as a function of shear rate at different volume fractions. Drawn lines are logarithmic fits.

for the weakest gels (circles in Fig. 2) to nearly infinite time scales (10^{15} s or 30×10^6 years) for the strongest gels (triangles in Fig. 2), making direct determination of these times difficult if not impossible. If the ultralow-frequency fluidization of the gel results from equilibrium relaxation of the network, as is the case for polymer networks, it is unlikely that the zero-stress relaxation time would be determined by the extrapolation of the stress-dependent yield data for τ_d . Instead, the large observed range of the exponential stress dependence of τ_d , and the nonequilibrium nature of these colloidal gels, suggests that the ultimate fluidization of the gel at $\sigma = 0$ results from irreversible aging.

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