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Extreme strain localization and sliding friction in physically associating polymer gels

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Model physically associating gels deformed in shear over a wide range of reduced rates displayed evidence of strain localization. The non-linear stress responses and inhomogeneous velocity profiles observed during shear rheometry coupled with particle tracking velocimetry were associated with the occurrence of rate-dependent, banding and fracture-like responses in the gel. Scaling law analysis from traditional sliding friction studies suggests that at the molecular level, deformation is confined to a shear zone with thickness comparable to the gel's mesh size, the smallest structurally relevant length scale in the gel.

1. INTRODUCTION

Shear deformation of soft materials and complex fluids often results in a wide variety of flow instabilities that manifest in a localized, planar fashion, *e.g.*, shear banding in micellar solutions¹ and ductile- and brittle-like fracture in fluids.²⁻⁴ In order to provide insight into the evolution and stability of these and other examples of localized deformation, the structural length scales and dissipative effects

such as frictional forces in the deformation zone need to be better understood. Knowledge of these length scales and forces has clear practical implications for the performance of self-healing and injectable materials⁵⁻⁷ and is relevant to recent experimental and theoretical work describing banding-to-fracture transitions.^{8,9}

In highly deformed materials, the overall strain energy of the system is often minimized by confinement of strain to a small region.¹⁰ In polymer gels, the smallest structurally relevant length scale for strain localization corresponds to the distance between neighboring junctions in the macromolecular network, commonly referred to as the ‘mesh size’, ξ of the gel (see Figure 1).

Figure 1. Schematic of the deformation-induced shear zone in a physically associating gel deformed at linear velocity, V . The network is composed of polymer strands spanning network junctions. A shear zone with thickness on the order of the mesh size, ξ , results from stretching and pull-out of network strands from their junctions, creating a plane of dangling strands and loops.

In appropriately designed gels and solutions (such as the model physically associating gel studied here), the network junctions are uniformly spaced such that the mesh size is fairly homogeneous throughout the bulk of the gel. This allows for determination of ξ by its relationship to the shear modulus, G ¹¹, *i.e.* $G \approx Ak_B T / \xi^3$. The factor A in this expression accounts for details of the macromolecular network structure, with A/ξ^3 describing the effective number density of Gaussian network strands. The network structure of the gel must be free from chain entanglements in order for the interpretation to be valid. The solvent-swollen gels studied here contained a relatively low concentration of polymer (4-6 vol.%) with strand molecular weights well below the predicted entanglement threshold at these concentrations¹¹ so entanglements don't need to be accounted for. In our analysis below we assume $A = 1$, defining ξ in the following simple way:

$$\xi = \left(\frac{k_B T}{G} \right)^{1/3}. \quad (1)$$

Previous investigations of the triblock copolymer gels that we use as model systems have shown that the value of ξ determined in this way corresponds closely to the average spacing between micelle cores that define the physical crosslinks of the gels.^{11,12}

Recently, we observed evidence of strain localization in model physically associating gels deformed to large values of strain over reduced shear rates spanning almost four orders of magnitude, $10^{-2} < \Gamma < 10^2$, where Γ is the product of the applied shear rate ($\dot{\gamma}$) and the gel relaxation time (τ).¹³ Flow curves predicted by a constitutive model assuming homogeneous deformation were non-monotonic, indicating that homogeneous flow will be unstable at high shear rates and consistent with the onset of flow instabilities.

In this article, we provide additional evidence to support the occurrence of *extreme* strain localization in the physically associating gels, where deformation is confined to a molecular shear zone of size comparable to the gel's mesh size, ξ . To inform our understanding of the microscopic structural rearrangements driving the gel's macroscopic mechanical behavior, the non-linear stress responses and flow fields observed by shear rheometry are combined with results from sliding friction scaling analysis and prior knowledge of the gel's well-defined structure and stress relaxation mechanisms. Instructive comparisons are made with results from traditional sliding friction experiments of gelatin gels and molecular dynamic simulations of opposing layers of polymer brushes in shear.

2. EXPERIMENTAL METHODS

The model physically associating gels were composed of acrylic triblock copolymer molecules (Kuraray, Co., Japan, used as received) with poly(methyl methacrylate) endblocks (PMMA; 8.9 kg/mol) separated by a poly(n-butyl acrylate) midblock (PnBA; 53 kg/mol), dissolved to a concentration of 4 to 6 vol.% in 2-ethyl-1-hexanol (Sigma-Aldrich, USA, used as received), a low volatility alcohol. Gels were deformed in a rotational rheometer (Anton-Paar Physica MCR 300, single-gap Couette cell, gap $h = 1.1$

mm, inner cylinder radius $r = 13.5$ mm). The main experimental results we present here (*i.e.*, non-linear stress-strain curves) were obtained from shear start-up experiments in which a gel sample was deformed in shear at a constant applied shear rate ($\dot{\gamma}$) and the resulting stress (σ) response was measured as a function of strain (γ) by the rheometer. A range of $\dot{\gamma}$ and temperatures were investigated. The concentration range investigated at each temperature was restricted by the torque limit of the rheometer.

Local velocity profiles of the sheared gel samples were obtained separately by a custom particle tracking velocimetry (PTV) set-up coupled with a stress controlled rheometer (Anton-Paar Physica MCR 500; see Ref. ¹⁴ for schematic of the set-up). To obtain the velocity profiles, a sheet of laser light was used to illuminate a cross sectional area of the sample in the velocity gradient direction, *i.e.*, across the gap of a transparent Couette cell ($h = 0.5$ mm, $r = 17$ mm). The samples were seeded with hollow glass beads ($d = 9.18 \pm 0.19$ μm), the in-plane motion of which was captured by a high speed camera. The measured stress response of samples was independent of the presence of the beads. At the fastest shear rates investigated ($\dot{\gamma} = 2$ s⁻¹), images were captured at a frame rate of 10 Hz, providing a temporal resolution of 0.1 s and a minimum spatial resolution of 100 μm (*i.e.*, the maximum displacement between consecutive images of the fast moving beads near the inner rotating cylinder of the Couette cell, equivalent to ~ 75 pixels of the 450 x 500 pixel image). The finest spatial resolution was fixed by the size of the glass beads, $O(10$ $\mu\text{m})$. A program was written in IDL (Research Systems, Inc.) to extract the local velocity profiles from the acquired images.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Self-assembly of the macromolecular network in the gels was driven by the temperature dependence of the interaction parameter between the solvent and the PMMA endblocks – a dependence which is unusually strong in the experimentally accessible temperature range.¹⁵ As a result, the structure and mechanical properties of the gels were a strong function of temperature as shown in Table 1 and described in detail elsewhere.^{11,13} In summary, at elevated temperatures ($> 50^\circ\text{C}$) the gels behaved as low-viscosity liquids with $\tau < 1$ s. As the temperature was reduced, the endblocks assembled into

spherical aggregates in order to minimize their interaction with the solvent and causing τ to increase dramatically. At the temperatures of interest (20° to 28°C), the gels effectively became viscoelastic materials, composed of endblock aggregates acting as the network junctions interconnected by flexible and unentangled midblock strands (see Figure 1).¹¹ Since these gels are composed of a thermoreversible, physically crosslinked, macromolecular network, stress relaxation occurs by the exchange of endblock segments between neighboring aggregates (termed chain “pull-out”¹⁶) and can be characterized by a relaxation time, τ , approximated from stretched-exponential fits to linear stress relaxation data.¹³ Values of the mesh size calculated from Eq. (1) range from 20-50 nm.

Table 1. Temperature-dependent mechanical properties.^a

Polymer Concentration (vol.%)	20°C		25°C		28°C	
	τ (s)	G (Pa)	τ (s)	G (Pa)	τ (s)	G (Pa)
4.0	45	65	3.5	40	-	-
4.5	100	150	8	95	-	-
5.0	120	260	10	200	2.4	110
5.5	-	-	25	330	5	250
6.0	-	-	37	500	8	390

^a G was determined from high frequency oscillatory measurements ($\gamma_0 = 5\%$, $\omega = 100 \text{ rad s}^{-1}$), yielding values equivalent to shear moduli extrapolated to zero time in stress relaxation experiments (see Ref. ¹³ for details).

During shear start-up experiments, the gels displayed non-linear strain stiffening and softening behavior over a wide range of reduced shear rates, $\Gamma = 0.048$ to 120. We have reported and discussed similar non-linear stress responses previously^{13,17}; thus, only the most relevant characteristics of these responses are summarized here. Representative stress-strain curves are shown in Figure 2a for a 5 vol.% gel deformed at 28°C. Strain stiffening (*i.e.*, upturn in the stress response due to increasing shear modulus with increasing strain) was observed at small values of strain. This behavior was previously found to correspond to non-linear stretching of the triblock copolymer molecules in the macromolecular network.¹⁷ The strain-softening behavior resulting in the stress maxima at intermediate values of strain in Figure 2a is believed to be due to damage accumulation in the deformed network and ultimately, localized failure of the gel – a manifestation consistent with the non-monotonic flow curves predicted in

previous work.¹³ Such an extreme reduction in the stress response as the gel is deformed to larger values of strain is reminiscent of ‘fluid fracture’ in telechelic polymer solutions.^{3,18}

Following the maximum in the observed stress-strain curves, the stress approached a plateau at large values of strain for all investigated gel concentrations, temperatures, and applied shear rates. A plateau stress (σ_{pl}) was quantified for each stress-strain curve from the intersection of tangents to the strongly negative slope of the stress maximum and the weakly negative slope of the stress plateau at large strain (see inset of Figure 2a). As seen in Figure 2b for the representative 5 vol.% gel deformed at 28°C, a unique value of σ_{pl} was observed for each applied shear rate. The resulting apparent viscosities, η_{app} (calculated by dividing σ_{pl} by the applied shear rate, $\dot{\gamma}$), displayed power-law shear thinning behavior (see inset of Figure 2b). Power-law shear thinning was observed at all investigated concentrations (4 to 6 vol.%), temperatures (20°, 25°, and 28°C) and shear rates ($\Gamma = 0.048$ to 120).

Figure 2. (a) Shear stress response as a function of strain for 5 vol.% gel deformed at 28°C and reduced rates of $\Gamma = 0.072$ to 2.4, corresponding to applied shear rates of $\dot{\gamma} = 0.03$ to 1.0 s^{-1} . Inset: intersection of the dashed tangent lines used to determine σ_{pl} for $\Gamma = 0.24$. (b) Value of plateau stress as a function of applied shear rate for 5 vol.% gel at 28°C ($G = 110 \text{ Pa}$). Inset: apparent viscosities at 28°C for ($\circ$) 5, ($\square$) 5.5, and ($+$) 6 vol.% gel; the solid line represents $\eta_{app} \approx \Gamma^{-0.7}$. Error bars represent the standard deviation of σ_{pl} or η_{app} from experiments using different batches of gel.

The hypothesis that we seek to prove here is that the experimentally observed stress plateaus can be attributed to localized frictional stresses within a narrow shear zone within the gel. To uncover direct evidence of strain localization in the deformed gels, local velocity profiles were obtained by particle tracking velocimetry (PTV). Figure 3 displays two series of velocity profiles obtained from PTV experiments of gels deformed at relatively low ($\Gamma = 0.2$, Figure 3a) and high ($\Gamma = 2.4$, Figure 3b) shear rates. At both rates, linear velocity profiles were observed prior to the maximum in the stress-strain curve, indicative of homogeneous shear flow in the gel. At strains beyond the stress maximum, the velocity profile became sharply inhomogeneous (see closed symbols in Figure 3a and b) – macroscopic evidence of shear-induced flow instabilities. For the gel deformed at a relatively low rate (Figure 3a), the velocity profiles displayed clear evidence of a shear banding response (*i.e.*, separation of the flow field into regions of different shear rates, signified by a kink in the measured velocity profile^{19,20}) and was immediately followed by elastic recoil resulting in negative velocities. In the gel deformed at a relatively high shear rate (Figure 3b), evidence was observed of a different type of flow instability manifestation at $y/h \approx 0.3$, what we define here as a ‘fracture-like’ response occurring at the interface between regions of the sample moving in opposite directions.

Figure 3. Normalized velocity as a function of position (y) in the gap (moving wall at $y/h = 0$ and stationary wall at $y/h = 1$) for a 5 vol.% / 28°C gel deformed at: (a) $\Gamma = 0.2$ with

PTV at $\gamma = 5$ ($\circ$), 19.6 ($\blacksquare$), 20.6 ($\diamond$), and 21.6 (+); and (b) $\Gamma = 2.4$ with PTV performed at $\gamma = 4.6$ ($\circ$), 7.4 ($\blacksquare$), 8.2 ($\diamond$), and 13.8 (+). Insets display the simultaneously measured stress response with symbols corresponding to PTV data.

As seen in Figure 3, the velocity profile at large values of strain was similar in appearance to profiles that typically result from macroscopic wall slip (*i.e.*, adhesive failure at the sample/wall interface). However, the presence of wall slip is inconsistent with the preceding mid-gap banding and fracture-like responses observed at intermediate values of strain and greater stress magnitudes. Since velocity profile measurements cannot be obtained within a distance of $O(10\text{ }\mu\text{m})$ normal to the rheometer fixture walls (due to the inherent resolution limit of PTV with micron-size particles), the near-wall deformation behavior of the gel cannot be directly resolved. In the future, shear rheometry coupled with a sophisticated fluorescence-based technique (*e.g.*, near-field laser velocimetry^{21–23}) could be employed to determine the local velocity profiles within length scales comparable to macromolecular sizes, $O(10\text{--}100\text{ nm})$. Contrary to the appearance of the data at large strain, we argue that wall slip is not taking place here but instead, the stress-relaxing instability responsible for the banding and fracture-like responses has propagated towards the moving wall, driven in that direction by the inherent stress gradient of the Couette rheometer cell.¹⁴

This perspective can be explained by considering the following: in a deforming gel, the relative strength of the bulk gel (cohesive) interactions compared to the gel/wall (adhesive) interactions will ultimately prescribe *where* the instability-driven stress relaxation mechanisms will nucleate. The mid-gap banding and fracture-like responses observed at values of strain corresponding to the stress overshoot strongly suggest that the bulk cohesive interactions are weaker than the adhesive interactions at the wall and that localized cohesive failure – occurring by chain pull-out followed by solvent-filled void formation and coalescence^{16,24} – is ultimately responsible for the observed non-linear stress response during shear. Indeed, adhesive wall slip and cohesive failure are simply two stress relaxation mechanisms that can become active at some local critical stress (the competition between these relaxation mechanisms was directly addressed recently in micellar solutions²⁵). Once the stress has

relaxed in the bulk gel due to localized cohesive failure, the energetic drive for additional adhesive failure at the walls is diminished. The data in Figure 3 clearly show that wall slip is not occurring at the stress maximum, and we see no reason to expect that it occurs subsequently at lower shear stresses.

In the data displayed in Figure 3, the banding and fracture-like responses occur near the middle of the gap, allowing for clear visualization. In repeated experiments, the inhomogeneous responses were found to more frequently appear close to the walls of the rheometer fixture, consistent with profiles observed by Berret, *et al.*³ In the cases where instability nucleation was near the wall, the velocity profiles exhibited similarities with wall-slip behavior, again indicating the resolution limitation of PTV experiments. However, for intermediate and high Γ , the first few PTV images captured immediately following the stress maximum typically displayed evidence of secondary flows in the bulk gel (*i.e.*, flow in the vorticity or gradient directions), yielding incoherent velocity profiles. Incoherence through the thickness of the sample would not be expected if simple adhesive slip were occurring at the walls; instead, this behavior is consistent with planar instabilities propagating through the bulk of the gel. Additionally, visual inspection of the inner and outer walls of the Couette cell immediately following the experiments was consistent with cohesive failure: after disassembling the fixture, a layer of gel (variable thickness) remained adhered to both surfaces.

4. THEORETICAL ANALYSIS AND DISCUSSION

Since we are now confident that the non-linear stress responses observed via shear rheometry are due to cohesive failure and subsequent strain localization occurring within the bulk of the deformed gel, it follows that the stress plateau experimentally observed at large values of strain is most likely a measure of the frictional stress within the localized shear zone. To evaluate this hypothesis, the experimental results were analyzed within the physical framework depicted in Figure 1. In this physical model, cohesive failure of the deformed gel results in an intact portion of gel moving at a constant linear velocity V across a stationary portion of gel. At the molecular level, deformation is localized into a shear zone with thickness on the order of the gel's mesh size, ξ . Above some threshold velocity,

network strands crossing the shear zone would be pulled out from their respective network junctions^{16,26} and would dangle freely or form loops as shown in Figure 1. At lower velocities, the dangling chains would re-associate across the shear zone, and the failure interface would effectively ‘heal’. A similar argument was constructed by de Gennes to describe the formation and stability of slip planes in entangled polymer melts.²⁷

To test the validity of the physical model in Figure 1 as applied to our experimental data, we followed a scaling law approach employed by Baumberger, *et al.*²⁸ in a traditional sliding friction experiment to describe the frictional stress response of gelatin gels sliding on a glass substrate. In this approach, the apparent viscosity, η_{SZ} , of the deformation-induced shear zone in Figure 1 is a function of the experimentally observed plateau stress at each applied shear rate:

$$\eta_{SZ} = \frac{\sigma_{pl}(\dot{\gamma})}{\dot{\gamma}_{SZ}} ; \quad \dot{\gamma}_{SZ} = \frac{V}{\xi} = \frac{\dot{\gamma}h}{(k_B T / G)^{1/3}} . \quad (2)$$

In Eq. (2), the effective deformation rate within the shear zone, $\dot{\gamma}_{SZ}$, is approximated by the linear velocity divided by the shear zone thickness, *i.e.*, the elastic estimate for the mesh size.

To uncover the scaling behavior, the shear zone viscosity is normalized by the solvent viscosity ($\eta_s = 0.011, 0.009, 0.008$ Pa-s for 2-ethyl-1-hexanol at 20°, 25°, and 28°C, respectively) and plotted as a function of the effective Weissenberg number, W_{SZ} , which is a measure of the relative deformation rate within the localized shear zone. Assuming the shear zone can be treated as a solution of ideal linear chains of size ξ , a conservative estimate for the controlling relaxation timescale in the shear zone is the longest Rouse relaxation time, τ_R ²⁹:

$$\tau_R \approx \frac{2\eta_s \xi^4}{b\pi k_B T} \quad \therefore \quad W_{SZ} = \dot{\gamma}_{SZ} \tau_R \approx \frac{2\eta_s V}{b\pi G} . \quad (3)$$

The statistical segment length, b , is assumed to be 0.5 nm. This simple treatment utilizing the Rouse model assumes random-walk, Gaussian statistics and an incompressible system. To take into account hydrodynamic interactions, the Zimm relaxation time, $\tau_Z \approx \eta_s \xi^3 / k_B T$, can be used in place of τ_R .²⁹

The calculated relative viscosity of the shear zone as a function of W_{sz} is shown in Figure 4a. The data over the complete range of concentration, temperature, and Γ collapse onto a single curve, well fitted by the following empirical power law with slope n ,

$$\frac{\eta_{sz}}{\eta_s} = \left(\frac{W_{sz}}{W_0} \right)^n; \quad n = -0.64 \pm 0.08, \quad W_0 = 172. \quad (4)$$

Replacing τ_R with τ_Z results in a similar data collapse and power-law scaling (see Figure 4b), with $n = -0.69 \pm 0.08$ and $W_0 = 3.8$.

Figure 4. Relative viscosity in the shear zone as a function of W_{sz} for 4 to 6 vol.% triblock copolymer gels at 20 to 28°C (Γ ranges from 0.048 to 120) assuming (a) Rouse relaxation and (b) Zimm relaxation. The solid lines indicate the power-law fit from Eq. (4) with (a) $n = -0.64 \pm 0.08$ and $W_0 = 172$ and (b) $n = -0.69 \pm 0.08$ and $W_0 = 3.8$. Solid points in (a) for collapsed gelatin data are from Ref. ²⁸.

At very large shear rates, the shear zone would be expected to become rich in solvent and potentially grow in thickness due to hydrodynamic effects and gel syneresis.³⁰ In our analysis, an increase in shear zone thickness would result in an over-estimation of $\dot{\gamma}_{sz}$ as calculated from Eq. (2) and would explain the observed values of relative viscosity that fall below unity at the highest shear rates in Figure 4.

Interestingly, as seen in Figure 4a, the data for our triblock copolymer gels behave in a strikingly similar fashion to the collapsed data obtained by Baumberger, *et al.*²⁸ for gelatin gels sliding on glass.

In their study, a power-law dependence was observed with a slope of -0.60 ± 0.07 ($\Gamma \gg 1$, $G \sim 10^3$ Pa). This shear-thinning response was believed to result from dangling gelatin chains moving through a solvent-rich shear zone of thickness ξ between the bulk gelatin network and the glass substrate.

However, in their study it is difficult to assign a true structural length scale to ξ due to the inherent randomness of gelatin's physically crosslinked structure.³¹ By design, our triblock copolymer gels have a very homogeneous, well-defined macromolecular network structure, where the network junction spacing is controlled by the molecular weight of the unentangled midblock and the overall copolymer concentration in the gel.¹¹ Thus, the primary result of our study is that the thickness of the molecular shear zone can now be directly related to the smallest structurally relevant length scale in the gels. The collapse of the data onto a single master curve and the similarity in scaling with traditional sliding friction experiments supports our hypothesis that the experimentally observed values of σ_{pl} are measures of the friction within a localized shear zone with thickness on the order of the gel's mesh size.

The similarity in power-law scaling observed here with results from Baumberger, *et al.*²⁸ may imply some interesting universality for sliding friction of gels (note: see recent work by Cohen, *et al.*³² for another example of similar scaling) but at the moment, the actual significance of the power-law behavior and shear-thinning slope of Figure 4 remains unclear. Experimental and theoretical results from studies of tethered polymer chains on opposing, sliding plates provide some insight into the shear-thinning behavior.^{33–38} Tethered chains attached to a sliding plate are typically observed to stretch and tilt in response to increasing velocity of the shear flow, a phenomenon referred to as ‘physical thinning’ of the polymer layer.³⁹ In recent molecular dynamics simulations by Galuschko, *et al.*³⁷, tethered linear polymer chains became elongated in the direction of the applied shear force for $W > 1$, and interestingly, the deformation ratio of the tethered chains was shown to be a universal function of W . This physical thinning response led to universal shear-dependent viscosity decreases as $\eta \sim W^{-0.43}$. Similar power-law, shear-thinning responses at $W > 1$ were also observed by Carrillo, *et al.*³⁸ in molecular dynamic simulations of charged and neutral tethered bottle-brush chains; shear thinning was found to be universal

for the charged brushes, $\eta \sim W^{-0.53}$. While the results from these simulations are qualitatively consistent with each other and the universal shear-thinning behavior we observe in Figure 4, the magnitude of the power-law slope varies in each case. Carrillo, *et al.*³⁸ attribute this variation in scaling exponent to differing interactions between the tethered chains and surrounding solvent, an idea consistent with our observation in Figure 4a and 4b of the scaling exponent's dependence (though slight) on the characteristic relaxation time in the shear zone.

The choice of the controlling relaxation timescale depends on the nature of the polymer-solvent interaction. In terms of polymer concentration, the Rouse model is more appropriate to describe the dynamics of concentrated solutions and polymer melts (where drag forces are localized along the chain length and hydrodynamic interactions can be ignored) while the Zimm model better describes the dynamics of dilute polymer solutions where long-range forces are important.⁴⁰ Here, scaling analysis utilizing both models is presented in Figure 4 for completeness and allows for direct comparison with data from Baumberger, *et al.*²⁸ where Rouse relaxation was assumed. Future investigation is required to determine if one model is more relevant than the other for the shear zone described here.

In our gels, σ_{pl} / G ranged from 1 to 6; for comparison, $\sigma / G \sim 0.5$ for gelatin sliding on glass.²⁸ The main implication of the relatively large frictional stresses in the shear zone of our gels compared to the shear modulus of the bulk gel is that additional non-linear deformation of the gel is expected to take place at large values of strain (*i.e.*, preventing observation of a steady-state stress response). These 'secondary instabilities' are most likely the origin of the weakly negative slope of the observed stress plateau for the highest applied shear rates (*e.g.*, $\Gamma = 2.4$ in Figure 2a). Indeed, sample break-up was observed at the top of the Couette rheometer cell at very large strain for the highest applied shear rates. A second implication of the large frictional stresses in our gels is that the only feasible way to probe the sliding friction response of these relatively weak gels is to utilize a shear-induced, fracture-like instability as we have done in these experiments. When a more traditional sliding friction experiment was attempted utilizing rotating parallel plates⁴¹, numerous issues were encountered from the outset such as extreme deformation and sample destruction upon loading.

Recently, the macroscopic zone of failure in telechelic polypeptide solutions was directly observed to be much wider than the estimated distance between crosslinks.¹⁸ This was interpreted as evidence of a ‘fluidization’ zone in the vicinity of a microscopic fracture plane that grew in thickness with increasing shear rate, possibly corresponding to localized fracture of the gel into smaller fragments. Indeed, this hypothesized transition from microscopic instabilities to macroscopic deformation is consistent with the observations reported here: shear zones of thickness comparable to the bulk mesh size $O(nm)$ manifest macroscopically as the inhomogeneous velocity profiles displayed in Figure 3, which occurred over $O(100\ \mu m)$ length scales and ultimately allowed for the responses to be resolved with PTV.

5. OVERALL IMPLICATIONS

Recent experimental studies have sought to characterize a distinction between strain localization manifestations (*e.g.*, shear banding, fluid fracture) in sheared viscoelastic gels and complex fluids.^{2,4,9} The observed macroscopic responses are found to be strongly affected by only slight changes in deformation rate and material structure, resulting in transitions sometimes referred to as brittle-to-ductile⁴ or failure-mode transitions.⁸ Though the macroscopic signatures are becoming clearer through sophisticated experimentation, the microscopic stimulus remains poorly understood in many systems.

Similar to previous studies, here we experimentally observe two distinct macroscopic responses to strain localization as the gels were deformed in shear: shear banding at relatively low shear rates and fracture-like responses at higher shear rates. Interestingly, the power-law shear thinning rheology of the hypothesized shear zone in the gel (captured by the scaling law in Figure 4) remained constant across the full range of investigated shear rates, $\Gamma = 0.048$ to 120 . Thus, this rate-independent scaling suggests that the two different strain localization manifestations ultimately stem from the same microscopic phenomenon – the instability-driven formation of molecularly thin shear zones containing dangling network strands and loops in a solvent-rich environment. In this light, fracture can be simply viewed as a special case of shear banding, where a very high shear rate is obtained across a very thin shear plane.

6. CONCLUSIONS

Results from shear rheometry experiments of physically associating, triblock copolymer gels coupled with scaling law analysis supported the occurrence of extreme strain localization in the deformed gels with a molecular shear zone of thickness comparable to the bulk mesh size, ξ . The shear-thinning stress response of the gels at large deformation was strikingly similar to the behavior of gelatin gels sliding on glass in traditional sliding friction experiments and to results from molecular dynamic simulations of opposing polymer brush layers in shear. Together, these results indicated that the shear bands and fracture planes that spontaneously formed as a result of a molecular strain localization process were structurally equivalent to the free surface of the gel.

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REFERENCES

1. Helgeson, M.E.; Porcar, L.; Lopez-Barron, C.; Wagner, N.J. Direct observation of flow-concentration coupling in a shear-banding fluid, *Phys. Rev. Lett.* **2010**, *105*, 084501.
2. Gladden, J.R.; Belmonte, A. Motion of a viscoelastic micellar fluid around a cylinder: Flow and fracture, *Phys. Rev. Lett.* **2007**, *98*, 224501.
3. Berret, J.F.; Srro, Y. Evidence of Shear-Induced Fluid Fracture in Telechelic Polymer Networks, *Phys. Rev. Lett.* **2001**, *87*, 048303.
4. Ramos, L.; Laperrousaz, A.; Dieudonn, P.; Liguore, C. Structural Signature of a Brittle-to-Ductile Transition in Self-Assembled Networks, *Phys. Rev. Lett.* **2011**, *107*, 148302.

5. Cordier, P.; Tournilhac, F.; Soulie-Ziakovic, C.; Leibler, L. Self-healing and thermoreversible rubber from supramolecular assembly, *Nature* **2008**, *451*, 977-980.
6. Henderson, K.J.; Zhou, T.C.; Otim, K.J.; Shull, K.R. Ionically cross-linked triblock copolymer hydrogels with high strength, *Macromolecules* **2010**, *43*, 6193-6201.
7. Olsen, B.D.; Kornfield, J.A.; Tirrell, D.A. Yielding Behavior in Injectable Hydrogels from Telechelic Proteins, *Macromolecules* **2010**, *43*, 9094-9099.
8. Sprakel, J.; Spruijt, E.; Gucht, J. van der; Padding, J.T.; Briels, W.J. Failure-mode transition in transient polymer networks with particle-based simulations, *Soft Matter* **2009**, *5*, 4748-4756.
9. Tixier, T.; Tabuteau, H.; Carrière, A.; Ramos, L.; Ligoure, C. Transition from “brittle” to “ductile” rheological behavior by tuning the morphology of self-assembled networks., *Soft Matter* **2010**, *6*, 2699.
10. Shull, K.R. Fracture and Adhesion of Elastomers and Gels: Large Strains at Small Length Scales, *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 3436-3439.
11. Seitz, M.E.; Burghardt, W.R.; Faber, K.T.; Shull, K.R. Self-assembly and stress relaxation in acrylic triblock copolymer gels, *Macromolecules* **2007**, *40*, 1218-1226.
12. Bras, R.E.; Shull, K.R. Self-Consistent Field Theory of Gelation in Triblock Copolymer Solutions, *Macromolecules* **2009**, *42*, 8513-8520.
13. Erk, K.A.; Shull, K.R. Rate-Dependent Stiffening and Strain Localization in Physically Associating Solutions, *Macromolecules* **2011**, *44*, 932-939.
14. Hu, Y.T.; Lips, A. Kinetics and mechanism of shear banding in an entangled micellar solution, *J. Rheol.* **2005**, *49*, 1001.
15. Drzal, P.L.; Shull, K.R. Origins of mechanical strength and elasticity in thermally reversible, acrylic triblock copolymer gels, *Macromolecules* **2003**, *36*, 2000-2008.

16. Baumberger, T.; Caroli, C.; Martina, D. Solvent control of crack dynamics in a reversible hydrogel, *Nature Materials* **2006**, *5*, 552-555.
17. Erk, K.A.; Henderson, K.J.; Shull, K.R. Strain Stiffening in Synthetic and Biopolymer Networks, *Biomacromolecules* **2010**, *11*, 1358-1363.
18. Skrzyszewska, P.J.; Sprakel, J.; de Wolf, F.A.; Fokkink, R.; Stuart, M.A.C.; van der Gucht, J. Fracture and Self-Healing in a Well-Defined Self-Assembled Polymer Network, *Macromolecules* **2010**, *43*, 3542-3548.
19. Manneville, S. Recent experimental probes of shear banding, *Rheologica Acta* **2008**, *47*, 301-318.
20. Hu, Y.T.; Palla, C.; Lips, A. Comparison between shear banding and shear thinning in entangled micellar solutions, *Journal of Rheology* **2008**, *52*, 379-400.
21. Migler, K.B.; Hervet, H.; Leger, L. Slip transition of a polymer melt under shear stress, *Phys. Rev. Lett.* **1993**, *70*, 287.
22. Hervet, H.; Léger, L. Flow with slip at the wall: from simple to complex fluids, *Comptes Rendus Physique* **2003**, *4*, 241-249.
23. Léger, L.; Hervet, H.; Bureau, L. Friction mechanisms at polymer-solid interfaces, *Comptes Rendus Chimie* **2006**, *9*, 80-89.
24. Tabuteau, H.; Mora, S.; Porte, G.; Abkarian, M.; Ligoure, C. Microscopic Mechanisms of the Brittleness of Viscoelastic Fluids, *Phys. Rev. Lett.* **2009**, *102*, 155501.
25. Lettinga, M.P.; Manneville, S. Competition between Shear Banding and Wall Slip in Wormlike Micelles, *Phys. Rev. Lett.* **2009**, *103*, 248302.
26. Baumberger, T.; Caroli, C.; Martina, D. Fracture of a biopolymer gel as a viscoplastic disentanglement process, *Eur. Phys. J. E* **2006**, *21*, 81-89.
27. de Gennes, P.-G. Melt fracture of entangled polymers, *Eur. Phys. J. E* **2007**, *23*, 3-5.

28. Baumberger, T.; Caroli, C.; Ronsin, O. Self-healing slip pulses and the friction of gelatin gels, *Eur. Phys. J. E* **2003**, *11*, 85-93.
29. Doi, M.; Edwards, S.F. *The theory of polymer dynamics*, (Oxford University Press: Oxford, 1986)
30. Du, M.; Maki, Y.; Tominaga, T.; Furukawa, H.; Gong, J.P.; Osada, Y.; Zheng, Q. Friction of Soft Gel in Dilute Polymer Solution, *Macromolecules* **2007**, *40*, 4313-4321.
31. Ross-Murphy, S.B. Structure and rheology of gelatin gels: recent progress, *Polymer* **1992**, *33*, 2622-2627.
32. Cohen, C.; Restagno, F.; Poulard, C.; Léger, L. Incidence of the molecular organization on friction at soft polymer interfaces, *Soft Matter* **2011**, *7*, 8535-8541.
33. Kreer, T.; Müser, M.H.; Binder, K.; Klein, J. Frictional Drag Mechanisms between Polymer-Bearing Surfaces, *Langmuir* **2001**, *17*, 7804-7813.
34. Schorr, P.A.; Kwan, T.C.B.; Kilbey, S.M.; Shaqfeh, E.S.G.; Tirrell, M. Shear Forces between Tethered Polymer Chains as a Function of Compression, Sliding Velocity, and Solvent Quality, *Macromolecules* **2003**, *36*, 389-398.
35. Grest, G.S. Interfacial Sliding of Polymer Brushes: A Molecular Dynamics Simulation, *Phys. Rev. Lett.* **1996**, *76*, 4979.
36. Eiser, E.; Klein, J.; Witten, T.A.; Fetters, L.J. Shear of Telechelic Brushes, *Phys. Rev. Lett.* **1999**, *82*, 5076.
37. Galuschko, A.; Spirin, L.; Kreer, T.; Johner, A.; Pastorino, C.; Wittmer, J.; Baschnagel, J. Frictional Forces between Strongly Compressed, Nonentangled Polymer Brushes: Molecular Dynamics Simulations and Scaling Theory, *Langmuir* **2010**, *26*, 6418-6429.
38. Carrillo, J.-M.Y.; Russano, D.; Dobrynin, A.V. Friction between Brush Layers of Charged and Neutral Bottle-Brush Macromolecules. Molecular Dynamics Simulations, *Langmuir* **2011**,

39. Doyle, P.S.; Shaqfeh, E.S.G.; Gast, A.P. Rheology of Polymer Brushes:□ A Brownian Dynamics Study, *Macromolecules* **1998**, *31*, 5474-5486.
40. Colby, R.H.; Rubinstein, M. *Polymer Physics*, (Oxford University Press Inc.: New York, 2003)
41. Gong, J.; Osada, Y. Surface friction of polymer gels, *Progress in Polymer Science* **2002**, *27*, 3-38.