

Strain hardening in bidisperse polymer glasses: Separating the roles of chain orientation and interchain entanglement

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The effects of entanglement and chain orientation on strain hardening in glassy polymers are separated by examining mixtures of chains with different lengths. Simulations show that the orientation of a molecule of a given chain length is the same in monodisperse systems and bidisperse mixtures, even when entangled and unentangled chains are mixed. In addition, the stress in mixtures is equal to the weighted average of the stresses in monodisperse systems. These results indicate that chains contribute independently to strain hardening, that chain orientation is determined by local interactions with the surrounding glass, and that entanglements play at most an indirect role in strain hardening in the range of strains typically studied. We discuss these results in the context of recent theories. © 2009 American Institute of Physics. [doi:10.1063/1.3276800]

I. INTRODUCTION

The mechanical performance and failure modes of glassy polymers are strongly affected by strain hardening; an increase in the stress needed to deform systems as the strain increases. There has been great interest in understanding the mechanisms of strain hardening so that it can be predicted and optimized for applications. Recent studies have challenged the traditional view that entanglements between polymer chains control strain hardening, and suggest that orientation of individual chains plays the dominant role. This paper uses simulations of polymer mixtures to separate the roles of entanglements and orientation.

The most widely used^{1,2} theories of strain hardening are based on rubber elasticity. They assume that entanglements between polymer chains act like chemical cross-links in a rubber and that strain hardening arises from the decrease in entropy of an affinely deforming entanglement network.³ The stress is written as

$$\sigma(\bar{\lambda}) \approx \sigma_{\text{flow}} + G_R g(\bar{\lambda}), \quad (1)$$

where σ_{flow} is the plastic flow stress, G_R the “strain hardening modulus,” $\bar{\lambda}$ the stretch tensor describing the macroscopic deformation, and g a dimensionless function that describes the reduction in chain entropy. This approach has had much success in fitting experimental stress strain curves, but the fits seem inconsistent with the underlying microscopic model, particularly in terms of the magnitude and temperature dependence of G_R .⁴ Another apparent difficulty in the approach of Refs. 1 and 2 is the separate, independent treatment of G_R and σ_{flow} , which ignores any potential contribution of plastic deformation to strain hardening.

A number of recent experiments and simulations have examined the origins of these difficulties.^{5–17} One realization is that the two terms on the right hand side of Eq. (1) are of

similar magnitude and must arise from similar mechanisms. Experiment, theory, and simulations all show that σ_{flow} and G_R are linearly related when pressure, T or strain rate is varied.^{10,15,16,18} This connection explains the large magnitude of G_R and the fact that it grows with decreasing temperature^{4,5} as is typical for the plastic flow stress. A direct connection between σ_{flow} and G_R has been established in the athermal limit ($T \rightarrow 0$), where both contributions to the stress are given by a single scaling factor times the rate at which interchain bonds break during local plastic rearrangements.^{12,13}

Simulations also show that strain hardening occurs in polymers that are too short to form the entangled network that is assumed in rubber elasticity theories.^{12–14,17} Moreover, the strain hardening in these unentangled systems can be mapped to that of entangled chains if the macroscopic deformation $\bar{\lambda}$ in Eq. (1) is replaced^{12,13} by an effective stretch tensor $\bar{\lambda}_{\text{eff}}$ that describes the orientation of individual chains,

$$\sigma(\bar{\lambda}) = \sigma_{\text{flow}} + G_R^0 g(\bar{\lambda}_{\text{eff}}), \quad (2)$$

where G_R^0 is the value of G_R in the long-chain limit. The orientation of entangled chains is consistent with an affine deformation, $\bar{\lambda}_{\text{eff}} = \bar{\lambda}$. For unentangled systems the orientation is consistent with a subaffine deformation by $\bar{\lambda}_{\text{eff}}$.

The above findings support the notion that entanglements play an indirect role and that strain hardening is produced by the increased rate of local plastic rearrangements that are needed to maintain chain connectivity as chains orient.^{12,13,19} In contrast, other recent experiments^{5,20} suggest that entanglements play a central role. They find that G_R is directly proportional to the entanglement density ρ_e in both pure systems and polymer mixtures. However, there are other explanations for this correlation. For example, an increase in chain stiffness increases ρ_e (Ref. 21) but also straightens the chains, so that more plastic rearrangements are required to maintain chain connectivity.^{13,17,22}

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In this paper we examine strain hardening of polymer mixtures. Using polymers with different chain lengths but the same interactions, stiffness, etc. allows us to isolate the roles of entanglements and orientation. The simulation results show that the orientation of chains plays the dominant role and that the response of mixtures has a surprisingly simple mean-field form. The variation in chain orientation with macroscopic stretch is nearly independent of the length of surrounding chains. In addition, the stress in mixtures is a simple weighted average of results for pure systems. These results suggest that strain hardening can be modeled as a sum of contributions from individual chains as they are deformed by interactions with the surrounding glass and produce local plastic rearrangements in the glass to maintain their connectivity.

II. POLYMER MODEL AND METHODS

Molecular dynamics (MD) simulations are performed using a coarse-grained bead-spring polymer model.²³ All monomers have mass m and interact via the truncated and shifted Lennard-Jones potential

$$U_{LJ}(r) = 4u_0[(a/r)^{12} - (a/r)^6 - (a/r_c)^{12} + (a/r_c)^6], \quad (3)$$

where $r_c = 1.5a$ is the cutoff radius and $U_{LJ}(r) = 0$ for $r > r_c$. Covalent bonds between adjacent monomers on a chain are modeled using the finitely extensible nonlinear elastic (FENE) potential

$$U(r) = -0.5kR_0^2 \ln(1 - (r/R_0)^2), \quad (4)$$

with the canonical²³ parameter choices $R_0 = 1.5a$ and $k = 30u_0/a^2$. The equilibrium covalent bond length is $l_0 = 0.96a$. We consider semiflexible chains with an angular potential $U_{\text{bend}} = k_{\text{bend}}(1 - \cos(\theta))$, where θ is the angle between consecutive bond vectors along a chain. All quantities are expressed in units of the molecular diameter a , binding energy u_0 , and characteristic time $\tau_{LJ} = \sqrt{ma^2/u_0}$. Periodic boundary conditions are imposed, with periods L_i along directions $i = x, y$, and z .

Simulations are performed using the same protocols as in Refs. 11–13. A rapid quench with cooling rate $0.002\epsilon/(k_B\tau_{LJ})$ is applied to well-equilibrated melts,²⁴ producing glasses at the desired temperature T . The rapidity of the quench suppresses aging and strain softening at small strains. As in experiments,²⁵ we find that the strain hardening regime of interest here is not affected by changes in quench protocol or extended aging near T_g (over times $> 10^4\tau_{LJ}$). The simulations presented here are performed at $T = 0.2u_0/k_B$ and $T = 0.275u_0/k_B$. Both values are well below the glass transition temperature $T_g \approx u_0/3k_B$,²⁶ yet sufficiently high to observe significant thermally activated rate-dependent relaxation.¹¹ Uniaxial compression is performed at constant strain rate $\dot{\epsilon} \equiv \dot{L}_z/L_z$. The volume stays nearly constant during compression. In this case the function describing the entropy loss in Eq. (1) can be written as $g(\lambda) = 1/\lambda^2 - \lambda$, where $\lambda = L_z/L_z^0$ is the stretch relative to the initial size L_z^0 .

The strain rates used range from $10^{-6}/\tau_{LJ}$ to $10^{-4}/\tau_{LJ}$. Mappings to real polymers²³ give τ_{LJ} of the order of 10–100 ps, so our lowest strain rate corresponds to

$\sim 10^4 - 10^5 \text{ s}^{-1}$. This is within the range probed by experiments (e.g., up to 10^5 s^{-1} in Ref. 27). Previous simulation studies in this range of $\dot{\epsilon}$ and T have been shown to capture many aspects of experiments, including logarithmic rate dependence,²⁶ creep,²⁸ and a linear relationship between flow and hardening modulus.¹⁵ Our lowest rate is also orders of magnitude slower than those obtainable with more computationally intensive united atom models (e.g., Ref. 17). At the higher rates studied with these potentials, unentangled chains deform significantly more affinely on the end-to-end scale because there is insufficient time for activated retraction along their length. This motion is particularly important for the chain length dependence of strain hardening considered here [i.e., Fig. 1(c)].

Systems contain short and long chains with N_{short} and N_{long} monomers, respectively. The total number of monomers is N_{tot} and the weight fraction of short chains is f . We present results for $N_{\text{long}} = 350$, $10 \leq N_{\text{short}} \leq 25$, and $k_{\text{bend}} = 0.75\epsilon$, but equivalent results were obtained for a range of other values. For this k_{bend} , the entanglement length is $N_e \sim 40$ monomers.²⁹ In experiments, unentangled glasses with $N \leq N_e$ typically exhibit brittle fracture, but fracture is suppressed in simulations,^{11,14} perhaps because of the small system size and periodic boundary conditions.

III. RESULTS

Panels (a) and (b) of Fig. 1 show the stress as a function of $g(\lambda)$ for mixtures with $N_{\text{short}} = 25$ and 10, respectively. Results for $f = 0.5$ lie directly between the results for pure systems with $f = 0$ and 1. Also shown is the weighted average of the pure system results

$$\sigma_{\text{ave}} = (1 - f)\sigma_{\text{long}} + f\sigma_{\text{short}} \quad (5)$$

for $f = 0.5$. Within our statistical accuracy, the stress in the mixtures is equal to this weighted average. We have verified that this “stress superposition principle” holds for different k_{bend} , chain lengths, temperatures, and f . When $N_{\text{short}} < 10$ there is almost no strain hardening of short chains and G_R rises linearly with $(1 - f)$ as found in Ref. 11.³² The only discrepancies from stress superposition are observed at large $g(> 3.5)$ when chains in entangled systems have stretched nearly taut and significant energy is stored in the covalent bonds. Experiments only reach such large stretches when special sample preparation procedures are used.^{2,25}

Equation (1) would predict a linear increase in stress with g . The systems in Fig. 1 were chosen to exhibit deviations from this straight line behavior, but still obey stress superposition. Deviations from linearity in experiments are often fit by including non-Gaussian (finite chain length) corrections to the network entropy.² Previous simulations are not consistent with this interpretation.^{12,13} They show that the upturn in stress for entangled systems reflects energy stored in the glass, while the downward curvature for unentangled systems results from subaffine deformation of the chains ($|\ln(\lambda_{\text{eff}})| < |\ln(\lambda)|$). Despite the different curvatures for the long and short chains in Fig. 1, their contributions to the stress in mixtures are simply additive.

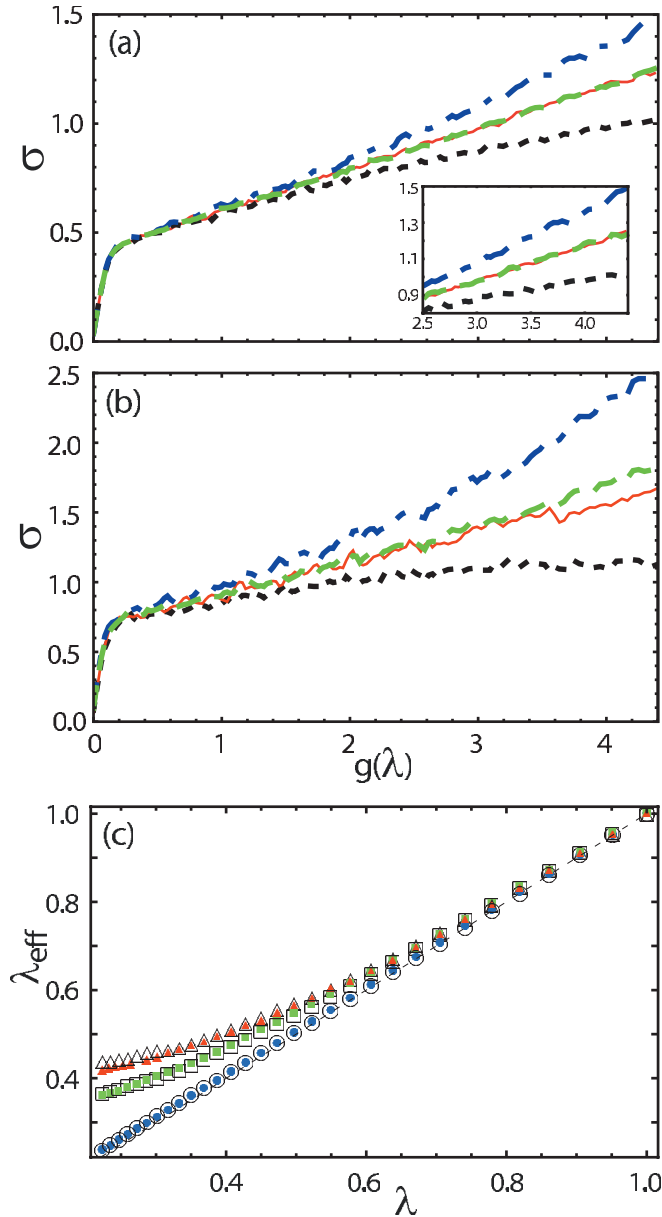


FIG. 1. [(a) and (b)] Stress plotted against $g(\lambda)$ for uniaxial compression of monodisperse glasses with length N_{long} (dashed-dotted) or N_{short} (dotted) and of 50/50 mixtures of the two lengths (dashed). The solid curves show the average of the two monodisperse systems. Here $k_{\text{bend}}=0.75u_0$ ($N_e=39$). (a) $N_{\text{short}}=25$, $T=0.275u_0/k_B$, and $|\dot{\epsilon}|=10^{-5}/\tau_{\text{LJ}}$ (Ref. 30). The inset shows a blowup of the data at large g . (b) $N_{\text{short}}=10$, $T=0.2u_0/k_B$, and $|\dot{\epsilon}|=10^{-4}/\tau_{\text{LJ}}$. (c) Variation in λ_{eff} with λ for pure systems with $N=350$ (solid circles), $N=25$ (solid squares), and $N=10$ (solid triangles). Open symbols of the same shape show results for chains of each length in $f=0.5$ mixtures.

These results do not conflict with experiments that found G_R was proportional to ρ_e .^{5,20,31} For the specific polymers studied, the entanglement density of mixtures is a weighted average of pure systems. Thus these systems also obey stress superposition. It would be interesting to perform similar experiments on polymer mixtures whose entanglement density was a nonlinear function of weight fraction. The relation between ρ_e and f is nonlinear for the systems considered here because they are mixtures of entangled and unentangled chains. In these systems G_R is not linear in ρ_e .³²

To understand why the contribution of chains to stress is additive, we examined the changes in molecular conforma-

tions during shear. As in Ref. 12, the orientation was quantified by the effective stretch λ_{eff} . This is defined as the mean stretch of chains along the compression direction; $\lambda_{\text{eff}} = \langle R_z/R_z^0 \rangle$, where R_z is the rms z -component of the end-to-end vector of a chain and R_z^0 the value before strain. Panel (c) shows $\lambda_{\text{eff}}(\lambda)$ for the same systems shown in panels (a) and (b). In mixtures, values of λ_{eff} for short and long chains are obtained from separate averages over chains of the same length at each value of the macroscopic strain. No time averaging is performed. Remarkably, $\lambda_{\text{eff}}^{\text{long}}$ and $\lambda_{\text{eff}}^{\text{short}}$ do not themselves depend on f . In other words, the orientation of the long (short) chains is not dependent on whether they are in a pure system or mixed with a fairly high fraction of short (long) chains. This f -independence of λ_{eff} holds over the same broad range of conditions as the stress superposition principle.

How can we understand the apparent f -independence of λ_{eff} ? The simplest qualitative picture is that interchain interactions in the glass tend to enforce an affine deformation of the chains, but that this is opposed by intrachain bonds. Chains cannot deform affinely at small scales because this would stretch the stiff covalent bonds along the chains. Instead, chains are observed to straighten over an effective persistence length l_p that increases with g .^{11,17} This straightening is independent of chain length until the associated stress becomes large enough to force relaxation of the chain along its length. For the systems considered here, the friction with neighboring chains is large enough that significant relaxation does not occur until unentangled chains are stretched to a substantial fraction of their fully extended length. Straightening chains while maintaining their connectivity requires local rearrangements of the surrounding monomers. The number of rearrangements grows with the persistence length and this was found to correlate directly with the strain hardening at low temperatures.^{12,13}

Note that entanglements do not enter directly in this picture. Since entangled and unentangled chains behave in the same manner at small $|g|$, the constraints on their rearrangements must be determined by very local interactions with the surrounding matrix. Entanglements only become relevant when g is so large that l_p reaches a significant fraction of the separation between entanglements.^{12,13,17} In this limit entanglements become more effective than friction from the matrix in enforcing an affine displacement of the chain. The associated tension in the chains grows as l_p approaches $N_e l_0$ and contributes significant energetic terms to the strain hardening at large $|g|$.^{13,14,25,33}

It is worth considering under which conditions this mean field picture should break down. For the reasons described above, the range of validity in very densely entangled systems will be limited to small strains. Fortunately, few synthetic polymers are so densely entangled that superposition would break down in the experimentally accessible³⁴ range of strains. The mean field picture should also break down for extremely short chains where the high density of chain ends changes the density, friction, and other properties significantly. Stress superposition will be particularly sensitive to changes in the relaxation rate of chains on the end-end scale τ_{relax}^{-1} with f . These are known to be significant for T above

T_g , where τ_{relax} for short chains is increased when they are mixed with longer chains, leading to greater orientation at a given shear rate.^{35,36} Our results show that such coupled-orientation effects are small deep in the glassy state.

IV. DISCUSSION AND CONCLUSIONS

The simulations presented here provide further evidence that strain hardening in polymer glasses depends primarily on chain orientation rather than entanglement. They also provide new insight into the factors that control the degree of orientation. The local coupling to the glassy matrix enforces an affine deformation of the chains ($\lambda = \lambda_{\text{eff}}$) at small $|g|$. Hardening arises primarily from the plastic rearrangements needed to maintain intrachain connectivity as chains orient and are straightened over greater lengths. As the associated stress on the chains grows, there is an increasing tendency for them to relax along their length, leading to subaffine deformation ($\lambda \neq \lambda_{\text{eff}}$). The observation that the value of λ_{eff} for a given chain length is independent of f and that the stress due to plastic rearrangements obeys the superposition principle implies that chains relax nearly independently. The degree of relaxation depends on a competition between the intrachain tension caused by alignment and friction with the glassy matrix. Entanglements only enter at very large $|g|$ where they prevent relaxation of chains that are much longer than N_e .

To our knowledge, no microscopic theory that predicts the functional form of λ_{eff} in glasses has been published. Constitutive models which employ a viscoelastic or viscoplastic description of glassy strain hardening (e.g., Refs. 37 and 38) typically decompose $\bar{\lambda}$ into rubber elastic and plastic parts (or use other internal state variables), but do not explicitly account for $\lambda \neq \lambda_{\text{eff}}$ or the N -dependence of nonaffine relaxation.³⁹ It would be interesting to see if a first principles theory like that of Ref. 18 could be generalized to predict $\lambda_{\text{eff}}(\lambda)$. The qualitative ingredients that must enter such a microscopic theory are evident from the results shown here and in Refs. 12, 13, and 17. Simply put, λ_{eff} falls behind λ when the stress in the material is insufficient to further affinely orient the average chain.

Fortuitously, λ_{eff} can now be accurately measured in scanning near-field optical microscopy experiments,⁴¹ which can discriminate values for different chain lengths in a bidisperse system. Reference 41 showed λ_{eff} falls behind λ for entangled chains deformed slightly above T_g ; similar studies on a variety of chain lengths below T_g would be of great interest. These might prove that λ_{eff} is one of the “mesoscale” quantities⁴² whose understanding will improve modeling of the deformation of amorphous materials. Other recent experiments⁴³ have shown that segmental dynamics and larger-scale polymer dynamics are nontrivially coupled below T_g . Further developments along these lines would be welcome, as would extension of the recently improved understanding of the relation⁴⁴ between linear viscoelastic behavior and structural relaxation to the nonlinear regime.

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- primitive path analysis (Ref. 29). The correct value of ρ_e scales as $(1-f)^2$ and is not linearly related to G_R in mixtures. We thank Alexei E. Likhman and Daniel J. Read for pointing out an inconsistency that led to this discovery.
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