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Shear banding in simulated telechelic polymers

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ABSTRACT

The response of simulated telechelic polymers to shear is investigated. End groups of short polymeric chains form temporary junctions that are continuously broken and formed over time. As in experiments, two shear bands coexist for some shear rates. This allows us to study the microscopic differences between these shear bands. We find that the lifetime of a junction is lower in the high shear rate band. In addition, the average aggregate size is lower in this band since more dangling chains exist. Microstructural differences between the sheared and unsheared system are reported as well. Some of the chains, that bridge between two aggregates before shear is applied, form loops that connect with both ends to the same aggregate instead. In addition and more importantly, an increase of chains connecting the same two aggregates is observed. Such restructuring lowers the network connectivity and hence the stress needed to shear the system.

1. Introduction

Shear banding is a common phenomenon in many complex systems. When these systems are sheared at a rate that is higher than the inverse relaxation time, homogeneous flow becomes unstable. As a consequence two bands with different shear rates form. Although this effect has been observed in a wide variety of systems, such as emulsions, dispersions, granular materials, and foams, it has been most extensively studied experimentally in wormlike micelles [1–9]. A theoretical explanation for shear banding lies in the behavior of the underlying constitutive curve, relating shear stress σ to the shear rate $\dot{\gamma}$ [4,8,10]. In homogeneous flow, there is a range of shear rates for which the curve decreases, indicating a mechanical instability. Hence, it is predicted that the flow splits in two bands and the stress plateaus. This theory also predicts the width of the bands; the so-called lever rule states that the location of the interface between both bands changes gradually with the applied shear rate, while the local shear rates in both bands are constant. The interface is located such that

$$\dot{\gamma} = \alpha_1 \dot{\gamma}_1 + \alpha_2 \dot{\gamma}_2 \tag{1}$$

where α_1 and α_2 are the relative widths of the shear bands. Although some experiments confirm the lever rule [3,6], others indicate that the picture of two smooth bands separated by a stable interface is insufficient to explain the complex behavior at the interface [1,7,9,11]. The position of the interface seems to fluctuate and drift, long after the initial start of the shear.

Shear banding in associating telechelic polymers has been studied more recently [12–14]. From these studies, it is clear that shear banding is a complex problem that is still poorly understood. The behavior depends strongly on many parameters such as temperature, concentration, chemical structure, along with the details on how the flow curve was obtained [9,12]. Sometimes three bands are observed.

Simulations can help in shedding new light on some aspects of the problem. They allow us to study the structural properties at the microscopic scale in each shear band. We have employed a toy model of associating polymers. It consists of short polymer chains, whose end groups can aggregate together. Extensive studies of the equilibrium phase behavior of this model have been published [15,16]. Within the following, we will report on the topological changes of a polymer network, observed in a sheared system. If both end groups of the chain are part of the same aggregate, a loop is formed. If both end groups are part of different aggregates, the polymer chain forms a bridge. There are reports that the number of loops increases when shear is applied. The number of elastic active bridges decreases and as a result the stress decreases [3,15,17,18]. We investigate other topological differences as well. For example, aggregates could be linked by more than one chain. Such subtle structural features are hard to observe experimentally. Hence, we believe that our results provide new insight.

2. Simulation methods

The model used for simulating telechelic polymers is a hybrid model consisting of a molecular dynamics simulation (MDS) with

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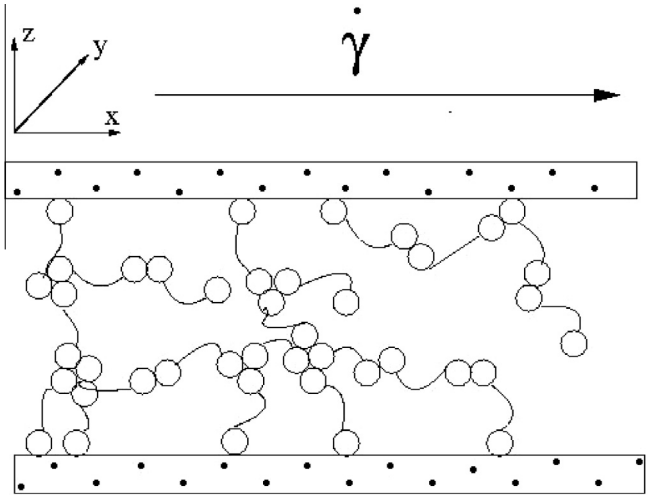

Fig. 1. Schematic of the simulation cell. The top wall is moved to the right at a constant rate. Stress is calculated from the interactions between the polymers and top wall. The junctions between the spheres can break and reform. The simulation is performed in 3 dimensions.

a Monte Carlo (MC) step and has been described in earlier work [15,16]. To model polymer chains, a standard bead-spring model [19] is used. Any two beads in the system experience a Lennard–Jones potential

$$U_{ij}^{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} - \left(\frac{\sigma}{r_c}\right)^{12} + \left(\frac{\sigma}{r_c}\right)^{6}\right] \quad \text{for } r_{ij} < r_c \tag{2}$$

that has been shifted and is purely repulsive ($r_c = 2^{1/6}$). All units in this paper are expressed in terms of the Lennard–Jones units: length (σ), energy (ε), and time $\tau = \sigma(\frac{m}{\varepsilon})^{1/2}$. Neighboring beads within the polymer chain experience a strong anharmonic FENE spring potential

$$U_{ij}^{\text{FENE}} = -\frac{1}{2}kR_0^2 \ln\left[1 - \left(\frac{r_{ij}}{R_0}\right)^2\right] \quad \text{for } r_{ij} < \mathrm{R}_0 \tag{3}$$

with $k = 30$ and $R_0 = 1.5$. This standard bead-spring model has been extended to include a MC step which models the associative properties of the polymer chains [15,20]. During a MC step, junctions between end groups of chains can either be formed or broken. A junction between end groups is modeled as the FENE potential from Eq. (3) and a negative association energy equal to −22. Each attempt to break and form junctions is accepted or rejected based on the energy difference between the old and new configuration. Note that if the FENE bonds are stretched, they are more likely to break in an MC attempt.

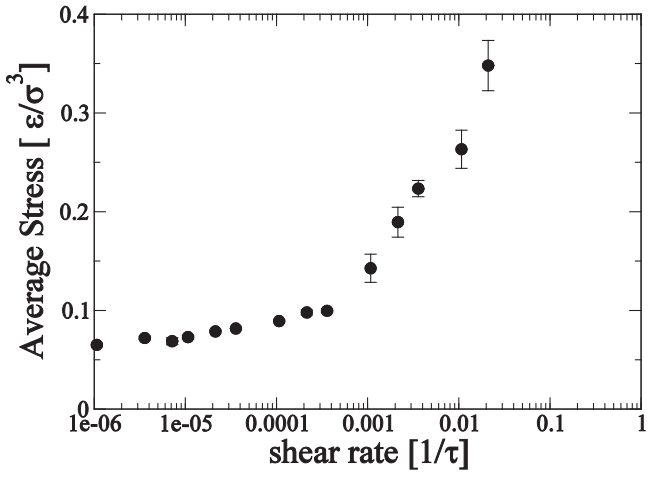

Fig. 2. Average stress in the steady state as a function of shear rate. Error bars are obtained from the standard deviation of different runs, independently cooled from $T = 1.5$.

The equations of motions are integrated using a fifth-order Gear predictor–corrector algorithm with $\delta t = 0.005\ \tau$. The temperature is controlled by coupling the system to a heat bath. All results shown in this work are at a temperature $T = 0.35$ in the gel state [15]. The system is initially cooled at a rate of 2500 τ per $\Delta T = 0.1$ from a high sol state at $T = 1.5$. The system is always equilibrated for 5000 τ at $T = 0.35$ before shear is applied. Results are averaged over several shear runs, obtained using initial states that resulted from cooling different high temperature states. The simulation cell has dimensions $23.69 \times 20.54 \times 27.84$ and contains 1000 chains. Each chain is 8 beads long. Hence, the volume fraction of the simulation cell that is occupied equals 0.31. A schematic of the system is shown in Fig. 1. It is confined by two solid walls in the z-direction and has periodic boundary conditions in the other two directions. 5% of the end groups are permanently grafted to the walls. This allows us to perform shear experiments in which the top wall is

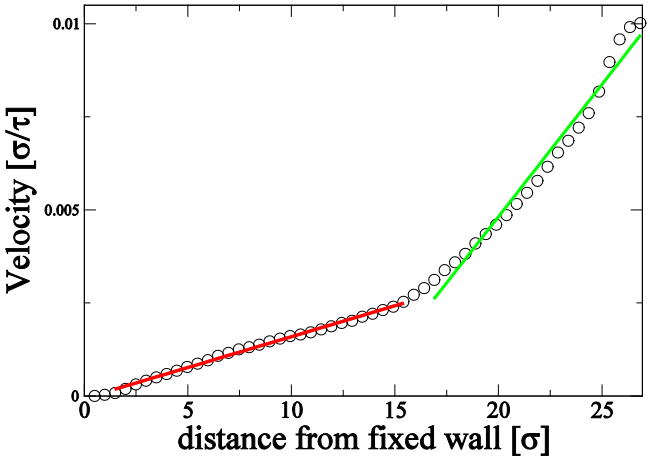

Fig. 3. Velocity profile for an applied shear rate of $\dot{\gamma} = 3.59 \times 10^{-4}\tau^{-1}$. The slopes for both shear rate bands are shown as bold lines and indicate shear rates of $1.6 \times 10^{-4}\,\tau^{-1}$ and $7.11 \times 10^{-4}\,\tau^{-1}$.

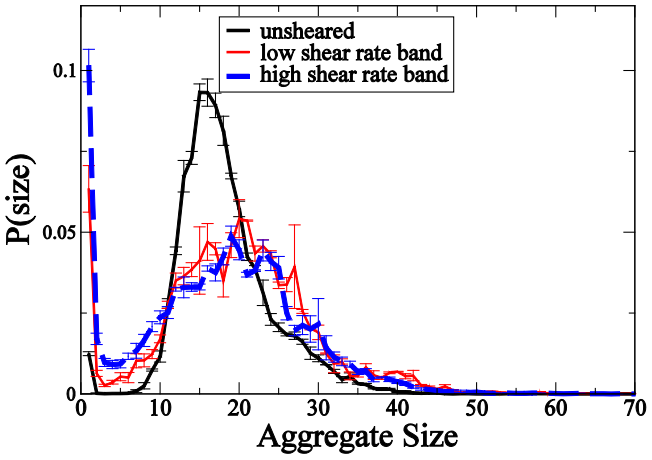

Fig. 4. Aggregate size distribution for the unsheared system (dotted), the high shear rate band (solid), and the low shear-rate band (dashed).