Investigating the Structural Mechanisms of Shear Banding Using Spatially-resolved Flow-SANS

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Shear banding is a flow-induced phenomenon observed in a wide variety of materials, including highly entangled polymers, self-assembled surfactants, colloidal suspensions, and pastes. Its rheological and macroscopic signatures have been well-studied for over a decade, yet surprisingly little is known about the underlying microstructural mechanism(s) that give rise to shear banding in soft matter. In this report, we demonstrate the capabilities of a new shear cell for spatially-resolved small angle neutron scattering (SANS) measurements in the flow-gradient (1-2) plane to elucidate the microstructural mechanisms by which shear banding occurs in a model wormlike micellar surfactant solution.

Perhaps the most well-studied fluids that exhibit shear banding are viscoelastic wormlike micelle (WLM) solutions, comprised of long, entangled threadlike aggregates of amphiphilic molecules [1]. Shear banding in these systems was originally observed visually as birefringent bands near the rotating wall of a Couette flow geometry [2]. The signature of banding is segregation of the flow field into two fluid layers, one at a high shear rate and one at a low shear rate, that span the flow geometry. These bands coincide with a stress plateau in steady state shear rheological measurements, (Fig. 1).

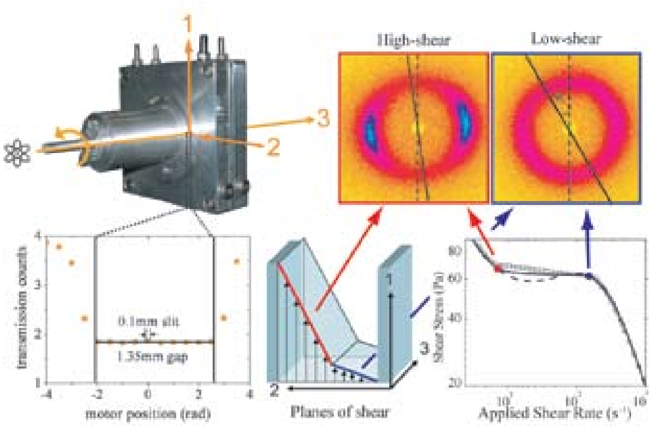

FIGURE 1: Diagram of the 1-2 plane flow-SANS shear cell. A plot of the neutron transmission demonstrates the gap resolution obtainable. The illustration shows the ability to probe gap-resolved structure in the two different shear bands.

Rheological theories that explain this behavior assume a non-monotonic constitutive stress-rate relationship, similar to a van der Waals loop equation of state for first order phase transitions [3]. This has led many investigators to propose that shear banding coincides with an underlying shear-induced phase transition. For example, the cationic surfactant CTAB in D_2O is known to shear band in the vicinity of an equilibrium isotropic-nematic (I-N) transition [4]. However, rigorous validation of this mechanism remains elusive, due to challenges in measuring separately the surfactant aggregate microstructure in both the high-shear and low-shear bands.

Recently, we have developed the ability to measure spatially-resolved microstructure under shear via SANS by using a short gap Couette cell and collimating the incident neutron beam down the gap (vorticity axis). A slit aperture enables collecting SANS from slices in the flow-gradient (1-2) plane of shear [5]. These 1-2 plane flow-SANS measurements provide several capabilities lacking in other techniques to measure structure under shear, namely: (1) the size ranges accessible by SANS cover the relevant microstructural scales of WLM solutions (e.g., micelle radius, persistence length, mesh size, etc.); (2) measurements in the 1-2 plane allow quantification of both the segmental orientation and degree of alignment, whereas more common measurements in the 1-3 plane measure only a projection of the segmental alignment [4]; (3) the slit aperture provides gap-resolved measurements of the structure, which allows discrimination between the high-shear and low-shear bands. Figure 1 shows a diagram of the shear cell and demonstration of these capabilities.

In this highlight, we report results for a model shear banding WLM of the cationic surfactant CTAB at 0.49 mol/L (490 mM) and 32 °C, for which the rheology and shear banding are well-characterized [6]. Flow-SANS measurements are performed at seven positions across the 1.35 mm Couette gap using a 0.1 mm slit. Figure 2 displays a visual summary of the results, where the intensity ring is a correlation peak due to segment-segment interactions. Anisotropy in this ring indicates segmental flow alignment, with high alignment typical for a nematic phase. A significant difference in scattering anisotropy is observed between positions in the low-shear and high-shear bands (also shown in Fig 1.)

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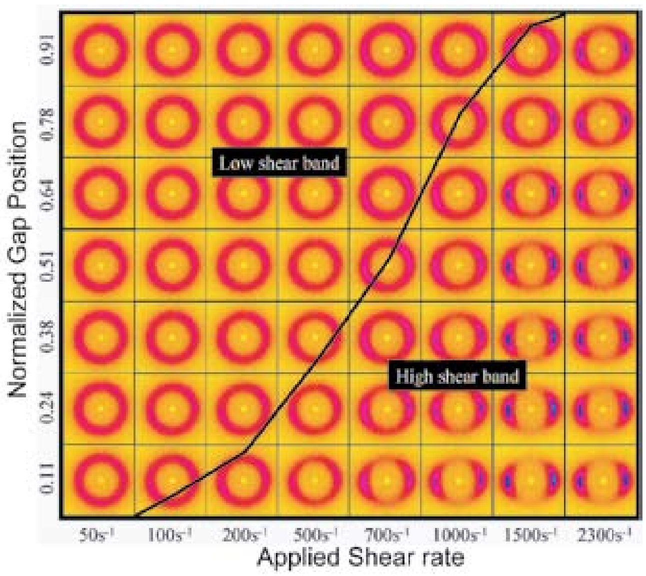

FIGURE 2: Two-dimensional scattering plots for nominal applied shear rates and normalized gap positions spanning the shear banding transition for the CTAB sample. The black line indicates the measured location of the interface between the high-shear and low-shear bands.

The average segmental orientation, φ_o, of the micelles relative to the flow direction is defined in Fig. 1, where $0° < \varphi_o < 45°$. Similarly, the net segmental alignment is given by the alignment factor, A_f, which characterizes the orientational order in the fluid [6]. As the average shear rate at each gap position is known from independent velocimetry measurements [6], all of the data can be plotted as master curves of φ_o and A_f versus the local shear rate (Fig. 3). Doing so demonstrates a clear transition at $\varphi_o \approx 10°$ and $A_f \approx 0.15$, where a jump in orientation and alignment occurs between the low-shear and high-shear bands. Predictions from a constitutive model that couples the fluid's rheology and micellar orientation order are in excellent quantitative agreement in both low and high shear states.

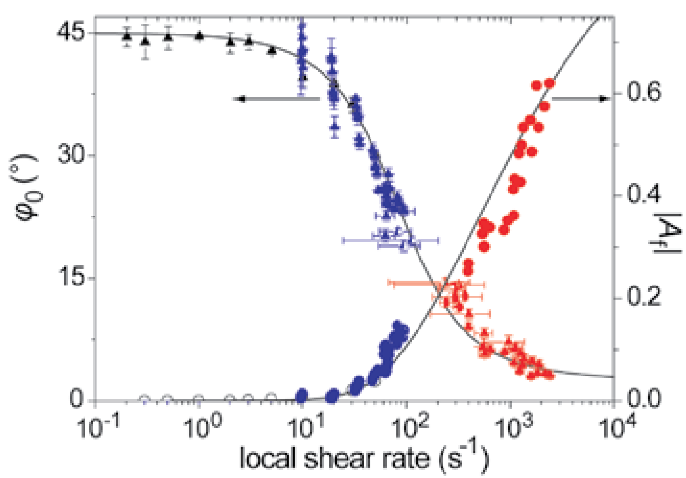

FIGURE 3: Orientation angle (closed) and alignment factor (open) versus local shear rate measured by velocimetry in the high-shear (red) and low-shear (blue) bands. Half filled symbols are for measurements with contributions from both bands. Data are augmented at low shear rates using flow-birefringence measurements (black). Lines give predictions from the Giesekus model (solid).

The high degree of microstructural order observed at the highest shear rates is consistent with a flow-aligned nematic order, significantly less order is observed for non-banding WLM solutions at comparable shear rates [6]. This is further confirmed through sector-averaged plots of the intensity in the flow-aligned direction (Fig. 4), which show that the low shear band has a nearly identical structure to the fluid at rest, whereas the high-shear band shows an increase in sharpness and location of the structure peak similar to what is observed for an equilibrium nematic phase (shown for reference.) This confirms the hypothesis that shear banding results from a shear-induced I-N transition for CTAB. This is in contrast to some other surfactant systems that show a transition to a biphasic network structure [5]. Nonetheless, in both systems, the underlying thermodynamic phase behavior plays a critical role in determining how and when a fluid will exhibit shear banding.

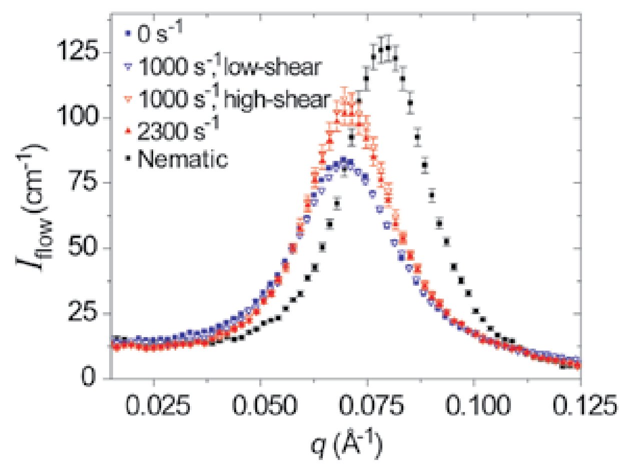

FIGURE 4: Sector-averaged intensity in the flow direction for the shear rates indicated. Open symbols show structure in the high-shear (red) and low-shear (blue) bands. The sharpening of the peak at high rates is similar to what is observed for a flow-aligned nematic phase at rest (black).

In conclusion, spatially-resolved 1-2 plane flow-SANS measurements enable direct measurement of the mesophase microstructure and orientational order of WLMs in each shear band under flow. The results provide critical information that is being used to test and refine microstructure-based models of shear banding [6]. This technique is unique in its ability to resolve local structure in non-homogeneous flows and as such is a powerful tool for quantitative interrogation of the nonlinear behavior of soft matter under shear.

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