Instrument & technical upgrades

Effect of branching on shear banding in worm-like micelles (WLMs) under large amplitude oscillatory shear (LAOS)

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Structured surfactant solutions such as worm-like or polymer-like micelles (WLMs/PLMs) are commonly used in applications ranging from consumer products to oil and energy recovery fluids [1,2]. Linear WLMs tend to exhibit shear banding flow instabilities under steady shear deformation, phenomena where the flow organises into macroscopic bands with high shear rate (low viscosity) and low shear rate (high viscosity). These instabilities may compromise the quality of the applications; however, branching in WLMs can minimise or eliminate shear banding instability [1]. Research has primarily focused on steady-state shear banding; however, WLMs may also shear band under dynamic deformations that are more likely to be seen in industrial applications. Shear banding under large amplitude oscillatory shear (LAOS) deformation has been widely predicted [3], but experimental corroboration has been limited.

A newly designed, magnetically driven 1-2 (flow-gradient) plane shear cell developed in the ILL Large-Scale Structures group in collaboration with the NIST Center for Neutron Research has enabled microstructure measurements of a wide array of complex fluids under time- and spatially-dependent flows [4]. Spatially-resolved measurements are a capability unique to the 1-2 shear cell, now available to all ILL users, as rheo-SANS or other current flow cell configurations do not provide spatial information. By taking measurements at multiple positions across the gradient of the flow in the 1-2 shear cell, spatially heterogeneous flow profiles such as shear banding under LAOS can be identified [5]. Further advances in SANS data collection at the ILL have increased the temporal resolution of SANS responses by orders of magnitude, enabling continuous dynamic responses to be measured. The WLM solutions investigated consist of 1.5 % wt mixed cationic/anionic surfactants (97:3 wt ratio of CTAT/SDBS) prepared in D_2O. Sodium tosylate is added to induce branching, where 0.01, 0.05 and 0.10 % wt NaTos correspond to low, mild, and high degrees of branching, respectively. The degree of branching is determined via SANS, cryo-TEM and rheo-optical methods [1,2]. Steady shear and LAOS conditions are reported using the dimensionless frequency and shear rate, or Deborah (De) and Weissenberg (Wi) number. In the mildly branched solution, steady shear banding is observed between 1< Wi <100. Steady shear SANS results can be observed in figure 1a, where significant decreases in the scattering anisotropy from the inner (r/H=0.15) to outer wall (r/H=0.85) indicate shear banding (Wi =25, 75). This scattering anisotropy is used to calculate a segmental alignment factor at each gap position (figure 1b). The sharp decreases in A_f with increasing r/H are similar to the discontinuous velocity profiles measured in shear banding fluids. When A_f>0.2 at all gap positions, the material no longer shear bands (Wi >100).

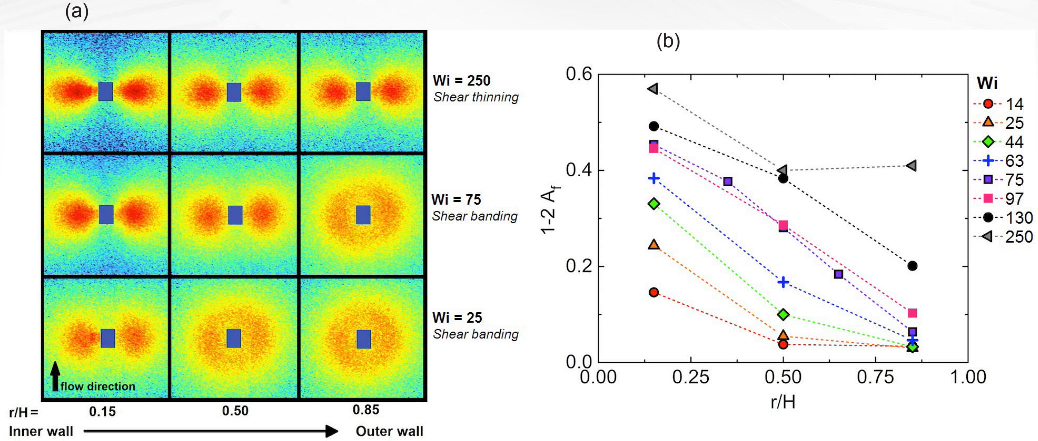

Figure 1: 1-2 plane scattering patterns and alignment factor as a function of gap position, r/H, and Wi. At Wi=25 and 75, the system shear bands, whereas only shear thinning is observed at Wi = 250. Significant decreases in A_f from the inner (r/H=0.15) to outer (r/H=0.85) wall are indicative of shear banding.

Seven LAOS conditions were examined for this composition, and shear banding was observed in four of the conditions (De=0.17, Wi =75; De=0.33, Wi =75; De=0.58, Wi =75; De=0.5, Wi =64). Shear banding was not observed in three conditions (De=0.5, Wi =113; De=0.67, Wi =85; De=0.75, Wi =96) despite the fact that this sample exhibits shear banding under steady shear at Wi =85 and 96. The results are in excellent agreement with recent VCM model predictions of LAOS shear banding [3]. Two distinct forms of dynamic shear banding were identified. In figures 2a and b, the alignment factor is shown at multiple gap positions, r/H, and times throughout the oscillation, t/T, for De=0.17, Wi =75. The maximum alignment during the LAOS cycle and the alignment profiles are similar to that of the steady shear case (figure 2b). The shear-banded structure is persistent through much of the oscillation cycle. As the oscillation period is long, the material can relax during the cycle, leading to alignment similar to that of steady shear. A different form of shear banding is seen for De=0.58, Wi =75 (figure 2c-d), where the material is trapped in a metastable shear-banded state. The material exhibits 'hyper-alignment,' a phenomenon where

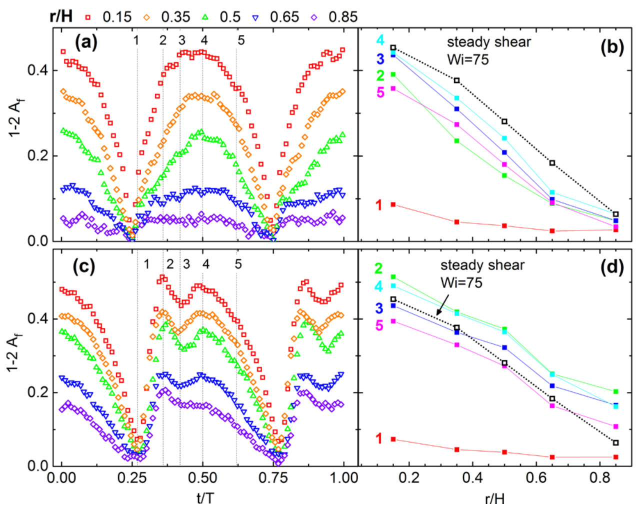

Figure 2: 1-2 alignment factor as a function of gap position, r/H, and time during oscillation, t/T for De=0.17, Wi =75 (a-b) and De=0.58, Wi =75 (c-d). When De=0.17, the material has time to relax during the oscillation cycle, leading to a shear banding that is similar to that of steady shear. When De=0.58, the material is trapped in a metastable, hyper-aligned state that distinctly differs from the steady shear case.

the maximum alignment under LAOS is larger than that of steady shear. The hyper-alignment observed during this faster oscillation period is a consequence of incomplete material relaxation during the cycle. The alignment factor profiles shown in figure 2d are of greater magnitude than those observed under steady shear, but still show a distinct banded structure. Hyper-alignment was also observed in the non-shear banding conditions at higher Deborah numbers, indicating that shear banding is not a requirement for hyper-alignment.

Shear banding under LAOS was also identified in the low branching solution at De=1, Wi =225 (figure 3a) and De=1, Wi = 321, where steady shear banding is observed between 1<Wi <600. In both cases, little hyper-alignment was observed at r/H=0.25, and no hyper-alignment was observed at r/H=0.75. Conversely, no shear banding was observed in the highly branched solution under steady shear or LAOS at De=1, Wi=25 (figure 3b). Despite the order of magnitude lower Weissenberg number, significant hyper-alignment was observed. No alignment is observed in the low branched solution at Wi=25. The results suggest that shear banding under steady shear is necessary, but not sufficient to observe shear banding at comparable Weissenberg numbers under LAOS. Further, branching appears to inhibit steady and dynamic shear banding, while magnifying hyper-alignment. These results can aid in the formulation of WLMs/PLMs for specific applications where both steady and dynamic flows are relevant, as well as provide data necessary for critically testing modern, microstructure-based constitutive equations. ■

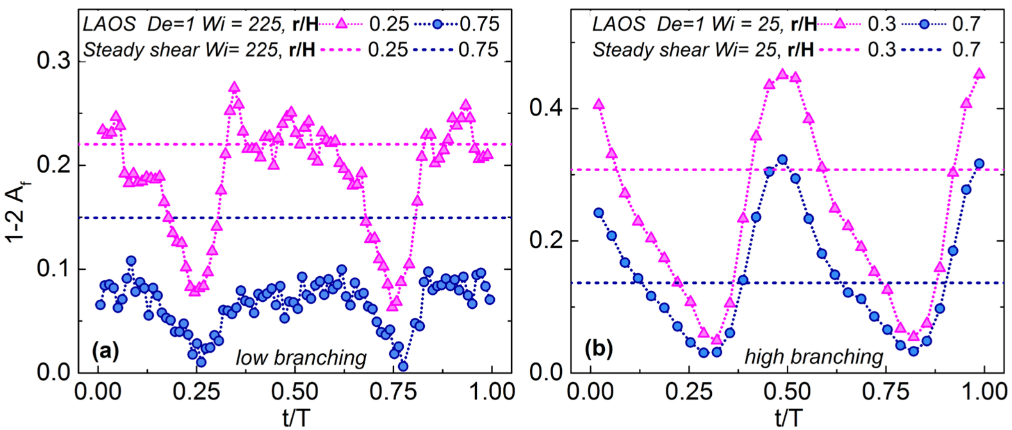

Figure 3: 1-2 A_f as a function r/H and t/T for the (a) low branching solution, De=1, Wi =225 and (b) high branching solution, De=1, Wi =25. Steady shear A_f is shown with dotted lines. Little hyper-alignment is seen in the low branching solution, whereas hyper-alignment is significant in the high branching solution.

References:

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[2] B.A. Schubert, E.W. Kaler and N.J. Wagner, Langmuir 19(10) 2003
[3] L. Zhou, L.P. Cook, and G.H. McKinley, Journal of Non-Newtonian Fluid Mechanics 165(21) 2010
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[5] M.A. Calabrese, S.A. Rogers, L. Porcar and N.J. Wagner, submitted to Journal of Rheology 2015

The new RAINBOWS reflectometry technique is successfully tested

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Up to now we have only three techniques available to us to measure the wavelength of the neutrons we use in our experiments: Choppers, monochromators and selectors.
They have two things in common, they are very expensive and extremely wasteful in the sense they cannot use all of the available neutron beam. For example the choppers on D17 have such a tiny opening that the beam can be said to be truly open for only about 8 minutes a day.
The idea of using a prism to measure the wavelength is no different from how different colours of light are deflected different amounts by a prism.
The great advantage of this technique is not only its simplicity and its low price but the fact that most of the available neutrons are used, with only those absorbed, reflected and scattered by the prism lost. Figure 1 shows the measured cold source spectrum on D50 measured by a specially shaped MgF_2 prism. The two dips correspond precisely to the wavelengths removed from the beam by the upstream instruments D16 and Super ADAM and the ripples to the left of them are the neutrons scattered out by aluminium in the beam such as the safely membranes. The fact that these features are readily resolved shows the wavelength resolution will be adequate for experiments. Figure 2 shows the results of a reflection from a 100 nm thick Ni layer on glass which subsequently passes through the prism.
The peak to the right are neutrons that reflected from the prism surface and the remaining signal are the varying reflectivity of the sample as a function of increasing wavelengths towards the left. Data analysis is ongoing but we are confident the technique works and will be useful not only for conventional reflectivity on D50 but the very fast kinetics on D17 and FIGARO as part of the endurance program will open up many new scientific possibilities.
We would like to thank everyone who contributed to developing this new technique. ■

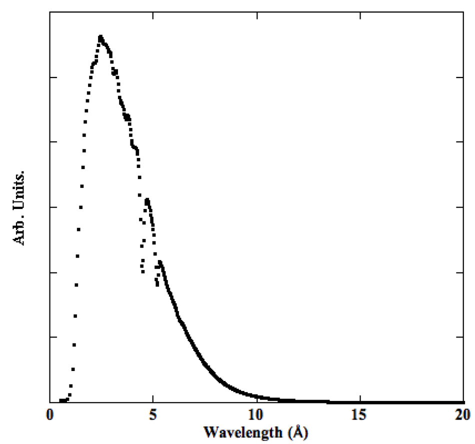

Figure 1: The incoming neutron spectrum.

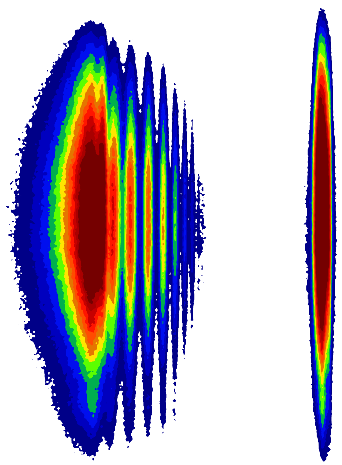

Figure 2: Raw data image of a sample reflection through the prism.