The Need for Rheo-Physical Experiments of Complex Fluids Erk 2020

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Shear flow curves (examples in Fig. 1) are routinely used by industrial researchers as a screening tool when optimizing a new complex fluid formulation. For example, if shear thinning is a performance target, new compositions that exhibit strong shear thinning behavior and display similar viscosity to existing data sets from commercialized products will typically be selected for further development. However, as recently reported by Erk and Lindberg[1], the most common features of shear flow curves obtained from concentrated complex fluids – including shear thinning behavior – can actually result from a wide variety of **inhomogeneous material responses** in which strain is localized to a particular region or interface within the system (*e.g.*, wall slip, plug flow, shear banding). That is, *shear flow curve tests are anything but routine,* to the detriment of existing industrial models that utilize flow curve data to predict processing parameters. This also complicates direct comparisons with prior studies and historical data sets which may measure, *or merely assume,* homogeneous flow behavior.

This disconnect – between measured rheological data and true material response – is a major issue when characterizing complex fluids. Commercial rheometers are effectively "blind" to **nonaffine, strain localizing instabilities** that can occur within a sample, such as interfacial wall slip and plug flow and bulk shear banding. Strain localization can only be confirmed by directly quantifying the local velocities within a sample as it is being deformed. The shape of the measured velocity profile across the thickness of the sample indicates the flow behavior (see inset plots in Fig. 1b). Of the lab-scale, flow visualization techniques that are used to quantify local velocities, particle-based velocimetry by optical or ultrasonic methods provides the best spatial and temporal resolution (1-10 microns, 2.5 ms-0.1 s per profile).[2] When a flow visualization method is coupled with shear rheometry, the resulting **"rheophysical" technique** will have the required resolution to correlate the true physical behavior of the sample with its measured stress response. At Purdue, optical and ultrasonic rheophysical tools have been custom built by the Erk group to study shear-induced fracture and sliding friction in physically associating polymer solutions[3,4] and wall slip in model cement pastes.[5]

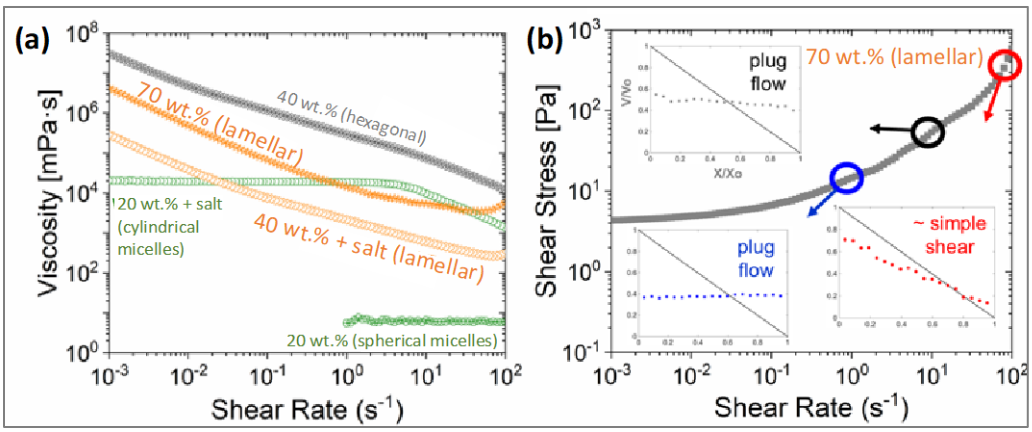

Figure 1: (a) Viscosity response for different concentrations (phases) of sodium laureth sulfate surfactant in water, including the 70 wt.% lamellar phase. (b) Stress response of the 70 wt.% SLE_1S lamellar sample, with inset plots showing the normalized velocity profiles measured by ultrasound-based flow velocimetry. Caicedo, Lindberg, and Erk, *et al.*, *Rheo Acta*, 2019. Ref. 1

In recent experiments by Erk and Lindberg with lamellar-structured surfactant solutions,[1] signatures of shear thinning were present in the rheometry data as shown in Fig. 1a. However, upon closer investigation with ultrasound-based flow velocimetry measurements (Fig. 1b), shear thinning corresponded to plug-flow behavior for low and moderate shear rates and pseudo-simple shear at high shear rates. Thus, the measured shear thinning response was the direct result of *inhomogeneous* flow and was hypothesized to result from lamellar domains that progressively orient and slip within the high-shear regions surrounding the plug. The relationship between microstructure and rheology has important implications on the processing of concentrated surfactant materials, where wide variations in solution properties (*e.g.*, viscosity) would require greater input energy.

References

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(2) Manneville, S. Recent Experimental Probes of Shear Banding. *Rheol. Acta* **2008**, *47* (3), 301–318. https://doi.org/10.1007/s00397-007-0246-z.

(3) Thornell, T. L.; Helfrecht, B. A.; Mullen, S. A.; Bawiskar, A.; Erk, K. A. Fracture-Healing Kinetics of Thermoreversible Physical Gels Quantified by Shear Rheophysical Experiments. *ACS Macro Lett.* **2014**, *3* (10), 1069–1073. https://doi.org/10.1021/mz500524d.

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(5) Murray, L. R.; Bice, J. E.; Soltys, E. G.; Perge, C.; Manneville, S.; Erk, K. A. Influence of Adsorbed and Nonadsorbed Polymer Additives on the Viscosity of Magnesium Oxide Suspensions. *J. Appl. Polym. Sci.* **2018**, *135* (3), 45696. https://doi.org/10.1002/app.45696.

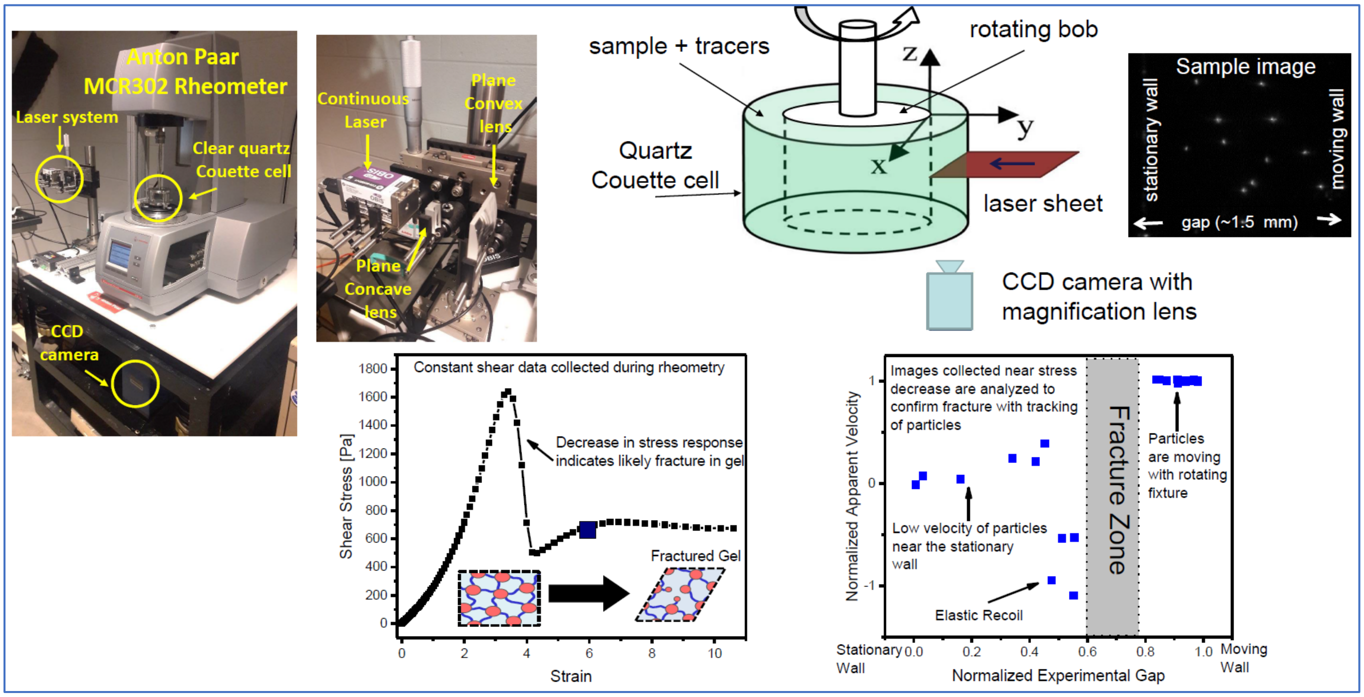
Technical Details: Rheo-physical instruments at Purdue University to visualize flow fields

To date, my team's most significant contribution to the polymer science community is our research on the **development of flow instabilities in viscoelastic solutions and polymer gels utilizing rheometry-based measurement techniques**. To accurately study the formation and evolution of shear-induced flow instabilities, we successfully constructed *two flow visualization systems that are coupled to our commercial Anton Paar rheometer*: an optics-based, particle tracking velocimetry system for transparent samples and an ultrasonic speckle velocimetry system for opaque samples. This unique instrument allows our team to quantify the rheological behavior of almost any soft material or complex fluid – from polymer hydrogels to cement slurries – while simultaneously collecting velocity profile measurements with millisecond temporal and microscale spatial resolution. Thus far, we have:

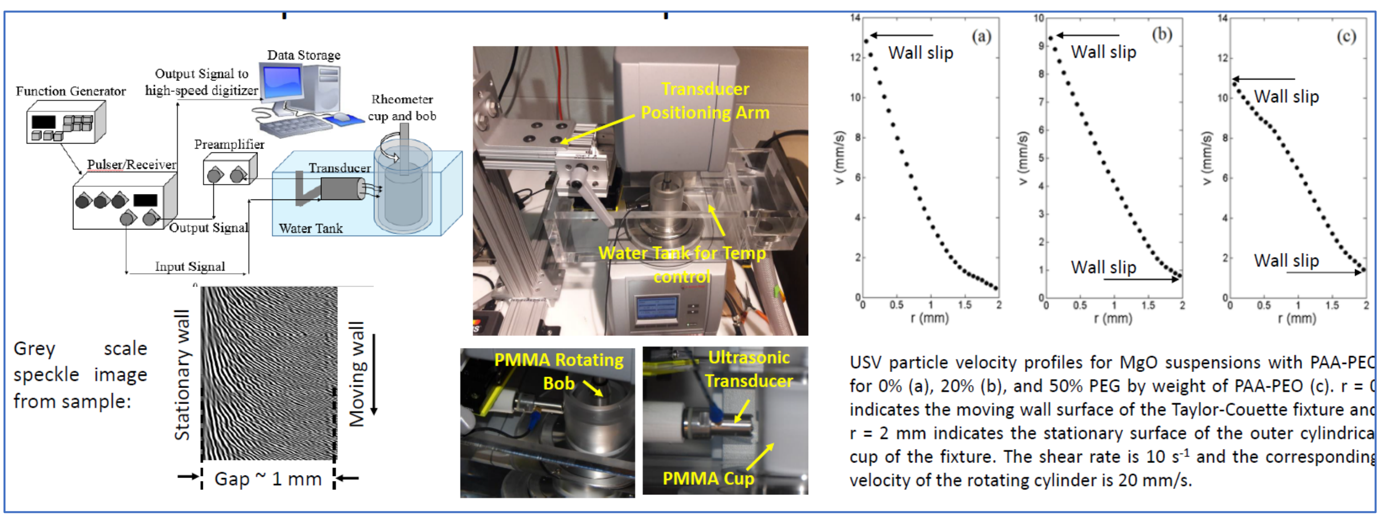
- Observed shear-induced fracture behavior and quantified the temperature-dependent healing kinetics of model physically associating polymer gels (**Ref 3. - *ACS Macro Letters* 2014**; **Ref. 4 - *J of Polymer Science Part B: Polymer Physics* 2016**) – also see images & data on next page
- Related changes in viscosity to structural rearrangement within model cementitious suspensions of solid oxide particles stabilized by polymer (**Ref. 5 - *J of App Poly Science* 2018**) – also see images & data on next page
- Discovered that shear thinning of surfactant pastes can result from both uniform and nonuniform material responses, including plug flow and shear banding (**Ref. 1**, invited article in ***Rheologica Acta* 2019**; in collaboration with engineers at The Procter & Gamble Company) – images & data in Figure 1 on prior page

<u>Custom-built flow visualization equipment at Purdue</u> allows for rheometry data to be collected and directly correlated with a sample's macroscale deformation response.

1. **Particle tracking velocimetry** (for transparent samples), used to detect shear banding and fracture in self-assembled polymer solutions. (images & data from Ref. 3)



2. **Ultrasonic speckle velocimetry** (for opaque samples), used to detect wall slip in model cement slurries. (images & data from Ref. 5)



USV particle velocity profiles for MgO suspensions with PAA-PEO for 0% (a), 20% (b), and 50% PEG by weight of PAA-PEO (c). r = 0 indicates the moving wall surface of the Taylor-Couette fixture and r = 2 mm indicates the stationary surface of the outer cylindrical cup of the fixture. The shear rate is 10 s^{-1} and the corresponding velocity of the rotating cylinder is 20 mm/s.