Advances in measuring time-resolved neutron scattering from flowing complex fluids

S. A. Rogers, M. A. Calabrese, and N. J. Wagner

Soft materials can undergo time-dependent flows during their production, processing and transportation, as well as during use. The microstructure of soft materials may be significantly different under flow than that at rest. Such flow-induced changes in microstructure may be beneficial, such as reducing the viscosity during the pouring of liquid detergents or transporting fluids while drilling oil and gas wells, or detrimental, such as the degradation of product stability during shipping. Therefore, there is a fundamental need for accurate, time-resolved measurements of microstructure under flow to aid in understanding and controlling the properties of flowing complex fluids.

This report presents new methods for probing microstructural changes on the nanoscale during dynamic deformations using time-resolved small-angle neutron scattering (SANS). Traditional SANS methods provide the necessary structural information on relevant length scales, but are typically averaged in time. With increases in neutron flux on the SANS instruments at the NCNR and through developing more efficient and accurate algorithms for analyzing data from temporally-resolved SANS experiments, we can now uncover previously unknown dynamic behaviors of materials whose static and steady-state flow properties may have been well-understood for decades.

As an example of the new information accessible using time-resolved SANS, we explore the effects of branching on the flow properties of self-assembled micellar solutions. The issue of branching in polymer science is a significant and long-standing scientific and technological challenge and worm-like, or polymer-like micelles are often used as model systems for understanding this class of complex fluids. Time dependent flows, such as flow startup and large amplitude oscillatory shear (LAOS), have been proposed as methods to characterize branching in such systems. We recently developed SANS techniques involving transient flows for the purpose of linking microstructural transitions to the macroscopic flow behavior [1-6].

The branched micellar solutions of interest are composed of the mixed cationic and anionic surfactant cetyltrimethylammonium tosylate (CTAT) and sodium dodecyl benzene sulfonate (SDBS) with sodium tosylate (NaTos) added to induce branching [7]. Under shear flow, segmental alignment of the micelles is observed in the flow direction and is quantified here by the scalar alignment factor, A_f, which varies from 0 for isotropic to 1 for full alignment. Material behavior is especially interesting under LAOS deformations [2, 4], where temporal resolution of ≈ 100 ms can be achieved.

Reported here is an example from our recent study of the alternating state of a branched WLM under LAOS (Fig. 1). Time stamping and triggering capabilities allow the alignment factor to be measured throughout the course of the applied oscillation [4]. A new analysis method that employs signal-processing techniques is applied to the neutron scattering data. We compare the values of A_f obtained from the standard stroboscopic method using binning techniques in Fig. 1a, where 15 discrete points were collected per half period against the same data but analyzed using the new procedure shown in (b). This new analysis provides a nearly continuous curve (b) revealing fine details in the time evolution of A_f (circled region) that closely mimic similar features observed in the rheology, overlaid in Fig 1(b). These microstructural changes are not evident in the data obtained using traditional binning (a). The method also decreases the total measurement time required to achieve a given level of precision as compared to binning methods. Ongoing and future work will use these techniques to quantify the effects of branching on WLM rheology and should find numerous applications in broader studies of the time-dependent behavior of complex fluids and soft materials.

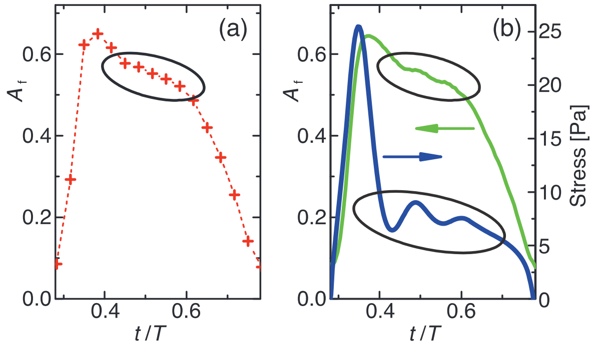

FIGURE 1: The alignment factor for a branched WLM during part of a LAOS cycle: (a) measured using standard binning methods and (b) using the new methods. The new technique (b) resolves features (circled regions) that are not apparent in (a) but that are evident in the rheological stress measurements during LAOS at 0.2 rad/s and 225 strain amplitude.

References

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Center for Neutron Science, Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716