Experimental report

25/01/2024

Proposal: 9-11-2139 **Council:** 4/2023

Title: A transient SANS study of the structure of complex fluids during extensional flow

Research area: Materials

This proposal is a new proposal

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Samples: 35 kDa polyethylene oxide (0.05 wt%) and 2 kDa deuterated polyethylene oxide (40 wt%) in D2O
35 kDa polyethylene oxide (0.05 wt%) and 2 kDa polyethylene oxide (40 wt%) in D2O
35 kDa polyethylene oxide (0.1 wt%) and 2 kDa polyethylene oxide (40 wt%) in D2O
35 kDa polyethylene oxide (0.1 wt%) and 2 kDa deuterated polyethylene oxide (40 wt%) in D2O

Instrument	Requested days	Allocated days	From	To
D22	3	2	13/11/2023	15/11/2023

Abstract:

This proposal aims to explore the structural changes that occur during uniaxial extensional flow and develop structure-property relations between the transient microstructural evolution of a model extensional flow material and its macroscopic extensional flow behavior. A total of four samples will be tested using a home-built CaBER-SANS sample environment in the D-22 beamline. Samples will consist of two concentrations of 35 kDa PEO (0.05 and 0.1 wt%) mixed with protonated and deuterated 2 kDa PEO (40 wt%) dispersed in D2O. The deuterated 2 kDa PEO will be contrast matched with the surrounding D2O, thus allowing us to capture the structural dynamics of the 35 kDa PEO and identify how each component of the solution contributes to the its extensional flow properties. Time-resolved SANS techniques will be employed to resolve how the structure of these polymers evolves during capillary formation and breakup. A bin size of 0.1 s will be used to capture these structural changes. For this study, we propose to use 3 days of time on the D-22 beamline to carry out these transient CaBER-SANS studies.

The work carried out as part of proposal 9-11-2139 saw the commissioning of a capillary extensional breakup rheometer (CaBER) sample environment for use on SANS beamlines. The installation of the instrument on the D22 beamline can be seen in figure 1 it was where secured to a translation table.

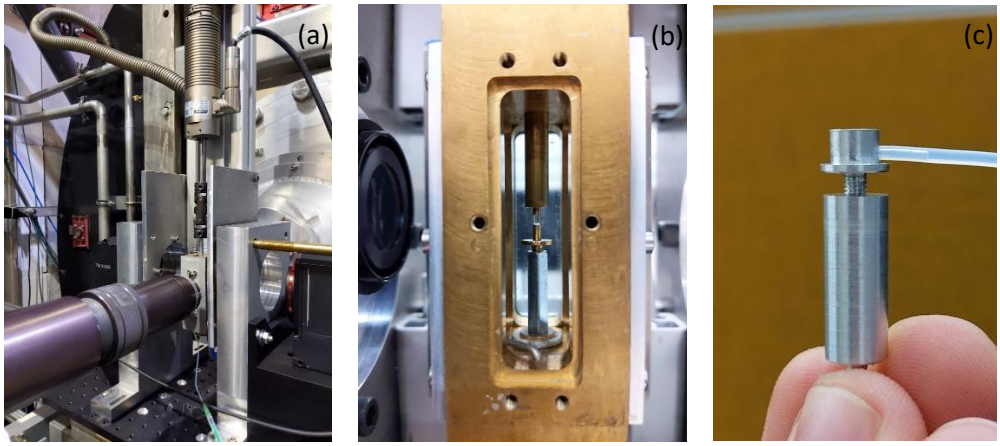

Figure 1. a) The CaBER sample environment installed on the D22 SANS beamline. b) A close-up of the sample chamber viewed along the direction of the neutron beamline. The front panel is removed to demonstrate the easiest way to access the sample, upper pin, and lower pin when the CaBER is not installed on the beamline. c) The bottom pin used during the experiment showing how it was modified to allow for easier loading. A hole in the top of the pin is connected to the PTFE tube, which is in turn routed out of the sample chamber and connected to a syringe.

During commissioning, several challenges were noted with the setup. Solutions have since been identified and will be implemente d by the next time this sample environment is used. The issues are as follows:

1) Complete automation of the CaBER measurement was not possible due to limitations of the software used to control the optical micrometer. A work around has been identified using a parallel I/O port on the optical micrometer. The automation software has been updated to support this additional connector.
2) Accessing the sample chamber for loading and cleaning of evaporated material was more challenging than anticipated due to limited space around the CaBER once it was installed on the beamline. This resulted in significant time loss when loading new material into the sample chamber. A redesign is in the works to allow for easy access to the interior of the sample chamber.

A 1 mm wide by 1.7 mm tall beam was selected for these measures and was situated 3 mm above the bottom pin (figure 2.a). Based on these dimensions, deadtime at the start of each CaBER measurement was identified, during which the beam was blocked by the aluminum upper pin. This resulted in high background scattering and artifacts in the vertical and horizontal directions (figure 2.c) and limited access to short time scales. At longer times, reflections from the air-filament interface were observed as the filament thinned (figure 2.d). For this reason, a narrow beam was selected that fit within the standing capillary for a significant portion of the measurement. A slight misalignment of the beam relative to the capillary resulted in the reflection appearing first on one side.

Reducing the deadtime at short times requires the center of the sample to remain at a constant height and would involve dropping the lower pin while raising the upper pin. Implementing this solution would involve a redesign of the sample environment and is beyond the scope of the current intended measures. Extending the time window before air-filament reflections begin to dominate the

sample requires a sample with a larger extensional viscosity and longer elongational relaxation time to slow the dynamics of the material.

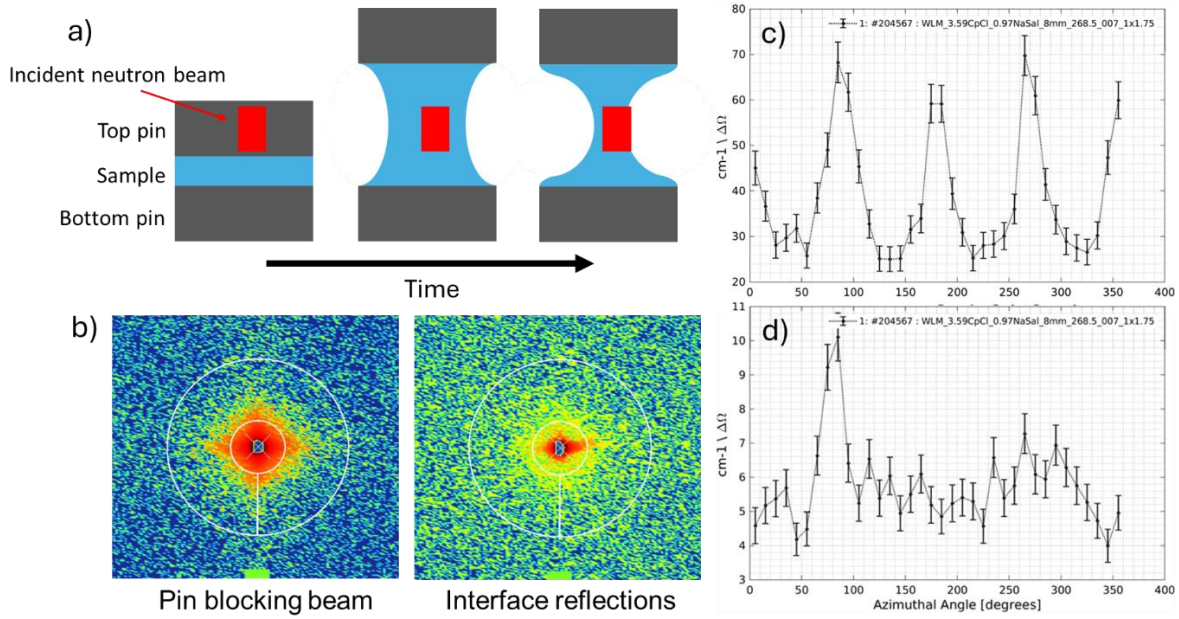

Figure 2. a) A cartoon depicting the pins (gray) and sample (blue) relative to the beamline (red) as a function of time. b) 2D scattering data from the start of the experiment when the pin blocks the beam (c) and from the end of the experiment when the reflection from the air-filament interface becomes prominent (d).

Experiments on the bogar fluid/polymer blends:

Two polymer solutions composed of a mixture of 1M hPEO + 9k dPEO and 250k hPEO + 250k dPEO were tested. Both showed very rapid filament thinning and capillary break up, such that long times were not accessible, leaving a small time window to observe the stretching of the polymers. Upon analysis of these measures, we observe isotropic scattering from the 1M hPEO sample and hints of anisotropy in the 250k PEO sample as shown in figure 3. One should however consider that the q-range did not allow detection of the plateau for either material and hence the experiment was not highly sensitive to morphological changes of the molecule. Improving upon these measurements would require a beam line dedicated to ultra-small angles. In the case of the 250k PEO sample, the appearance of a peak around 270˚is promising but due to the rapid dynamics of the material, requires longer scattering times to improve the signal to noise ratio.

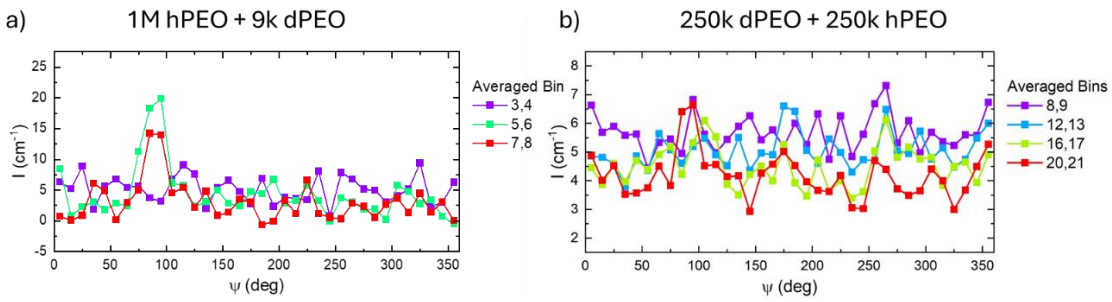

Figure 3. a) Azimuthal data for the 1M hPEO + 9k dPEO sample immediately after the upper pin was out of the beam. Note that the data were isotropic in the one data set before the air-filament appears. b) Azimuthal data for the 250k dPEO + 250k hPEO sample immediate after the upper pin was out of the beam. In both plots, the peak around 90˚ is due to the air-filament interface.

Experiments on the wormlike micelles:

Using the polymers as a basis for possible changes that can be captured with CaBER-SANS, we turned to CPCL wormlike micelles, an alternative system with slower dynamics that has a great track record for use in Rheo-SANS. CPCL and similar systems are also of great industrial importance due to their extreme shear thinning behavior. Despite thorough characterization in shear, most industrial processes involve applying extensional flow set to these systems, for which much less is known.

The advantage of the system is that flow-induced anisotropy is known to appear in the 0.1 to 0.01 $Å^{-1}$ q range and that the relaxation times of Kuhn segments, which is what one observes in the scattering, are relatively slow. Moreover, the thinning of the filament occurs on a longer time scale, thus extending the viable time window for collecting scattering data. We observed an initial alignment that fades out over 1 to 2 seconds as shown figure 4.a. At longer times, the air-filament reflection is observed, but it is still possible to extract alignment information by using the other half of the azimuthal profile. Analysis is ongoing to obtain absolute orientational ordering and to link this time-dependent ordering with the filament diameter as measured in-situ with the optical micrometer (figure 4.c).

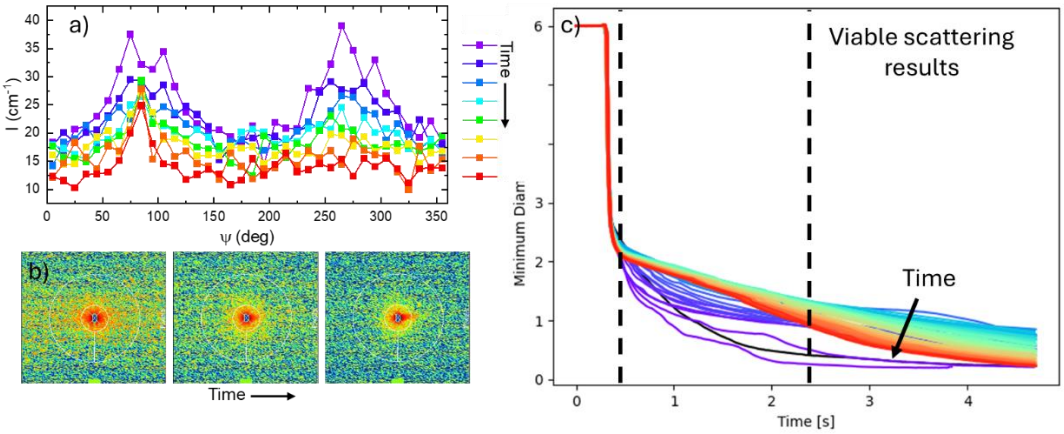

Figure 4. a) Azimuthal profiles showing the transition from anisotropic features at short times to isotropic scattering at long times. b) Snapshots of the 2D scattering data spanning the same time range as (a). c) Capillary diameters measured as a function of time using the optical micrometer from the CaBER. The vertical lines indicated the accessible time window for SANS.

While the majority of instances where the filament did not form were filtered out, there are several instances where the material failed to re-wet the upper pin at the start of the scattering measurement. Examples of this issue are highlighted in figure 4.c in purple and blue. Ongoing efforts are being made to remove these data sets. Collecting the data shown in figure 4.a and 4.b, took a total of about 3 hours of active scattering time. From the data collected, we can identify that main thinning in a standing capillary formed during CaBER occurs after alignment of the Kuhn segments has already relaxed. This observation leads to broader questions as to the structural contributions that affect extensional flow dynamics.

It is known that the addition of salt greatly affects the rheology of CPCL worm-like micelle systems. Therefore, the last hours of this proposal were spent measuring a CPCL sample with 0.5 M NaCl added to it. Data for this system are still being processed and will be available shortly. However, fully describing the impacts of this additive on the structural changes in CPCL micelles and their macroscopic extensional characteristics requires a more complete sweep of salt concentrations. This study is planned as the next set of measurements with this novel sample environment.