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'Probing the phenomenon of superspreading at the nanoscale using GISAXS and XRR'

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1. Summary

1.1 Achievements

We obtained a set of encouraging experimental results using grazing incidence small angle x-ray scattering (GISAXS) on the superspreading of trisiloxane surfactant solutions over polypropylene substrates. We observed two characteristic types of signals in our GISAXS experiments:

(i) *Prominent flares whose angle changed as the droplet spread and then recoiled across the x-ray beam*

(ii)*Periodic banding structures relating to the ordering of molecular layers of superspreader.*

Both these signals are described in *section 2*. We compared solutions of a superspreader and a non-superspreading surfactant with similar molecular structure, and found that diffraction patterns of type (ii) were only observed for the superspreader solution. The results of our experiments seem to confirm the existence of an ordered precursor film ahead of the contact line, both during spreading and during evaporative recoil.

Based on our results we can begin to comment on the hypothesised models put forward to explain the phenomenon of superspreading [1]. We found no evidence for the existence of ordered micelle structures at the liquid/substrate interface, but interestingly our results do support a model consisting of ordered lamella.

1.2 Limitations encountered

The slow read-out speed of the MAR CCD was a limitation for our experiments. During the readout time, the leading edge of the droplet had advanced significantly across the x-ray beam making time-averaged measurements over a considerable flow of the droplet unavoidable. A larger-than-ideal beamstop was necessary which blocked lower-angle structure which was suggested to exist by the extrapolation of structures that we could see. However, we did obtain very useful data from these first experiments. We hope to build upon these data if an opportunity becomes available to exploit a detector with a faster response time.

XRR was not possible due to the need to keep the substrates absolutely horizontal to prevent any gravity-assisted spreading influencing the results. Thus, we focused on the GISAXS technique.

2. Preliminary Analysis of Results

Analysis is on-going, here we present some preliminary findings.

2.1 Flares

Figure 1 shows a summary of data obtained from one experiment involving the superspreading of 0.1% S240 over a polypropylene (PP) substrate. Images were taken continuously during the superspreading of the droplet across the x-ray beam. A prominent diagonal flare can be seen whose angle changes approximately linearly with time as the droplet advances across the x-ray beam. This angle is thought to be related to the angle between the droplets free surface and the horizontal - at the location on the droplet that is intersecting the x-ray beam at that particular time in its flow.

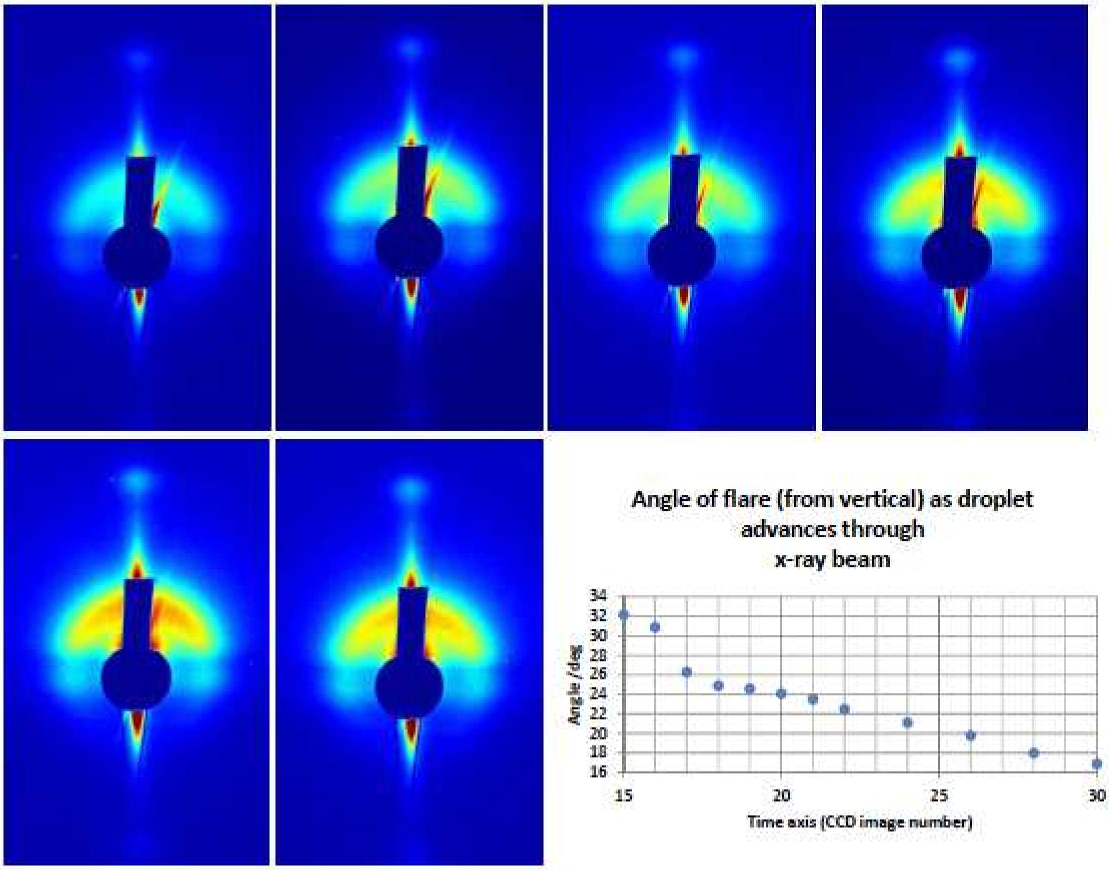

Fig. 1. In situ GISAXS data (preliminary) following the superspreading droplet advancing across the x-ray beam. The angle of the prominent flare is time dependent.

We observe these flares for both superspreading and non-superspreading droplets and a full analysis of the angle data is on-going. There is likely to be a significant difference in flare angle as a function of time, and therefore spreading rate, between superspreading and non-superspreading droplets. This local and dynamic measurement of these angles gives interesting insight into the dynamics of spreading droplets.

2.2 Periodic banding structure

Figure 2 shows some images of the periodic banding structures observed for the superspreading droplets (0.1% Evonik Break-Thru S240) on PP substrates. Analysis of the periodicity of the banding of Fig. 2a results in a spacing of the order of 10 nm, which is consistent with the molecular dimensions of the superspreader trisiloxane molecules. Such structures were not observed for droplets of a non-superspreading surfactant with similar molecular structure (Evonik Break-Thru S233) on the same substrate. Fig. 2c shows that banding was also occasionally seen on the diagonal flare structures, at particular times towards the start or end of the droplet intersecting the x-ray beam.

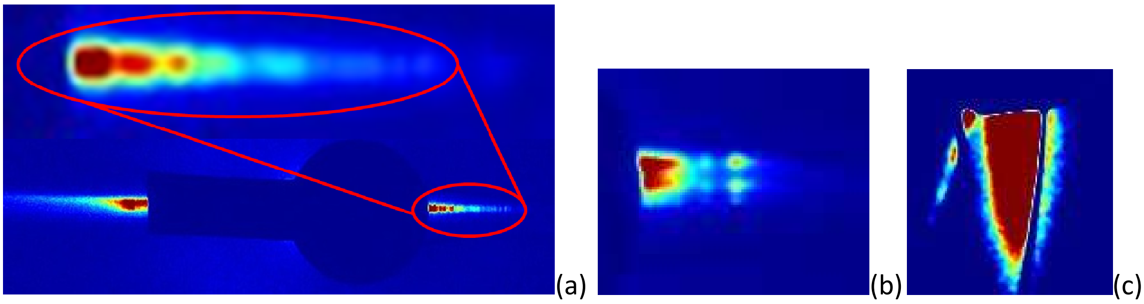

Fig. 2. XMaS data (using MAR CCD) showing evidence of molecular layering near (a) the receding contact line and (b,c) the advancing droplet edge, of a 0.1% S240 solution on polypropylene.

Before our beamtime, there was little evidence on the state of the superspreader/substrate interface at the molecular scale. A qualitative model had been proposed that attempted to explain the difference between superspreading and non-superspreading surfactants, which can appear chemically to be very similar, in terms of either micelle crystallisation or mono/bi-layer formation [1,2]. However, no direct experimental evidence is available, although it is known that ordered macromolecular structures near a moving contact line can significantly affect the wetting behaviour of other systems, such as dilute solutions of flexible polymers [3]. Our GISAXS results suggest the formation of a molecular layer at the interface between a superspreading droplet and the PP substrate. The compact structure of the trisiloxane molecules may allow their adsorption and self-assembly into densely-packed two-dimensional lamella at the solid substrate, promoting droplet spreading. Thus, preliminary analysis of our results supports the model of Fig. 3B.

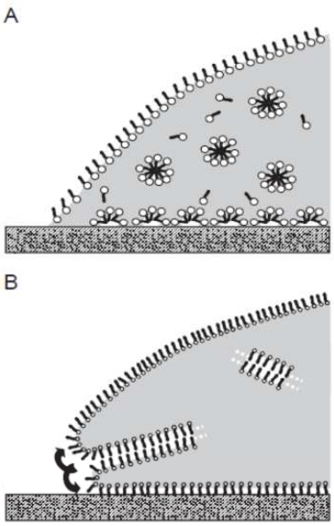

Fig. 3. Two proposed models for the leading edge: (A) non-superspreading surfactant, (B) superspreading surfactant. From Ref. [1]

Conclusions and the next steps

Our main conclusions to date are listed in section 1. We have contributed a short article on these experiments to the XMaS newsletter 2014 [4].

Due to recent developments at XMaS it is now possible to obtain an improved data set exploiting the new Pilatus 300K detector. This new detector will be of great benefit to us for two main reasons:

(i) the faster time response of the detector will allow us to better track the dynamics of the superspreading droplets and their evaporative recoil leading to an increased understanding of the dynamics of the system,

(ii) the larger dynamic range of the Pilatus will allow smaller sized beamstops to be used, allowing us to acquire scattered signal at smaller momentum transfer values.

We will request a second period of beamtime for new measurements on superspreading at higher time resolution. This would enable a greater understanding of the phenomenon in terms of the dynamics and structures formed. With a more detailed understanding, a higher impact factor for our publication would be possible. If we are unsuccessful in gaining further beamtime, we will publish the data that we have as best we can.

We thank the staff at the XMaS beamline for their help, particularly Oier for his collaboration in these GISAXS experiments.

References

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[2] R.M. Hill, *Current Opinion in Colloid and Interface Science* 3, 247 (1998).
[3] M.I. Smith and V. Bertola, *Phys. Rev. Lett.* 104, 154502 (2010).
[4] D.S. Martin et al., *XMaS Newsletter* (2014).