Experimental report

23/10/2019

Proposal: 9-11-1874 **Council:** 4/2018

Title: Influence of substrate and shear on adsorption at solid / liquid interfaces: Towards stability prediction in lubricants.

Research area: Materials

This proposal is a resubmission of 9-11-1837

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Experimental team: Richard THOMPSON
James HART

Local contacts: Philipp GUTFREUND

Samples: poly(butadiene)
squalane, d-squalane (C30H62, C30D62)

Instrument	Requested days	Allocated days	From	To
FIGARO	3	3	20/06/2019	23/06/2019

Abstract:

The combination of neutron reflectometry with rheology is relatively new, but is extremely important to understand fundamental processes of lubrication where adsorption from solution to a solid interface and the nature of the adsorbed layer will dictate the properties of the lubricant. Here we which to exploit this setup to study the adsorption of a model polymer addtive (polybutadiene) as a function of shear rate, bulk composition and temperature. We have deliberately chosen an extremely simple system in order to focus on the effect of substrate on NR. This will provide important insights into the nature of deposition of actives in lubricants and provide unprecedented detail on the relationship between polymer dynamics, phase behaviour and adsorption. We have calculated the reflectivity for the adsorption of a polymer layer of order of the polymers dimensions and shown that this technique is sufficiently sensitive, when using a deuterated squalane model oil, to characterise the quantity and nature of the adsorbate. Ultimately we propose to implement models based on these studies to provide robust tools for predicting failure mechanisms in structured products such as lubricants.

Influence of substrate and shear on adsorption at solid / liquid interfaces: Towards stability prediction in lubricants.

9-11-1874

Experimental team: James Hart, Richard Thompson, Philipp Gutfreund

Polymers are added to lubricants in order to deliver required tribological characteristics, and minimise contact between surfaces in engines. However, their presence contributes to viscosity and hence energy dissipation, which is undesirable. We aim to understand how shearing can modify the distribution of polymers near surfaces in order to better understand and optimise the use of polymers in lubricants. In this first rheo-NR experiment, specular reflectivity on FIGARO was used to explore adsorption of hydrogenous polybutadiene from perdeuterated hydrocarbon solutions under shear at a silicon-oxide interface. The experimental setup is shown in schematic form in figure 1.

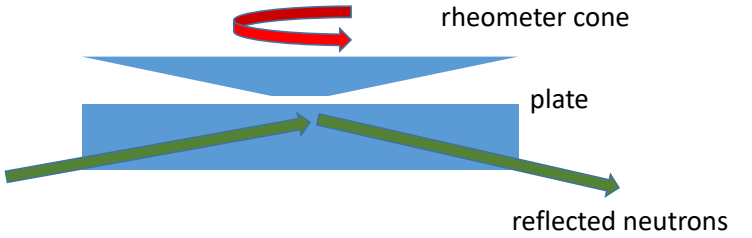

Figure 1. Sketch of "rheo-NR" setup to study interfacial segregation under a well-defined flow field.

Our reflectivity data (Figure 2, left) gave a clear critical edge for the reflection at the interface between the silicon oxide surface of the silicon block (s.l.d. 2.07×10-6 $Å^{-2}$) and deuterated squalene (s.l.d. 6.06×10^{-6} $Å^{-2}$). When this region is normalized to R(*Q*)=1, it is clear that there is a subtle, but statistically significant reduction in R(*Q*) in the intermediate *Q* range when the sample is sheared. Careful fitting of the data shows that this drop in reflectivity corresponds to an increase in the adsorption of the hydrogenous polymer at the substrate interface (figure 2, right).

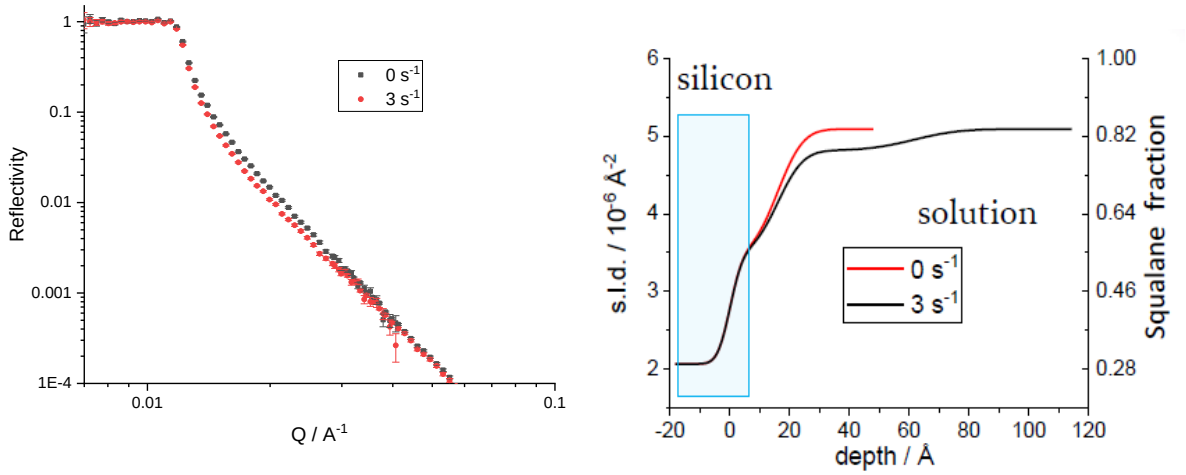

Figure 2. (left) Specular R(Q) of PBd in d-squalane under quiescent conditions and under imposed shear rate of 3.0 s-1. (right) scattering length density and composition profiles derived from fits to R(Q).

We have explored this behavior for a range of shearing conditions and compositions and established that there appears to be a critical shear rate, below which the impact of shear on adsorption is negligible. This may correlate with a characteristic relaxation time of the polymer solution e.g. the reputation time. We postulate that orientation effects (expected when the shear rate exceeds the inverse reptation time) may be significant to the measured adsorption.

Finally, we noted that the background seen in the raw detector data is quite unusual when or after high shear has been applied (figure 3). In addition to the specular reflectivity (the horizontal stripe), the FIGARO detector revealed significant scattering in the transmitted beam (the large patch towards the upper left). This appears to suggest that some bulk ordering, possibly a shear banding effect is also significant and induced by shearing. Curiously, this part of the signal appears to persist long after the shearing has stopped and the specular reflectivity has recovered to its quiescent behavior.

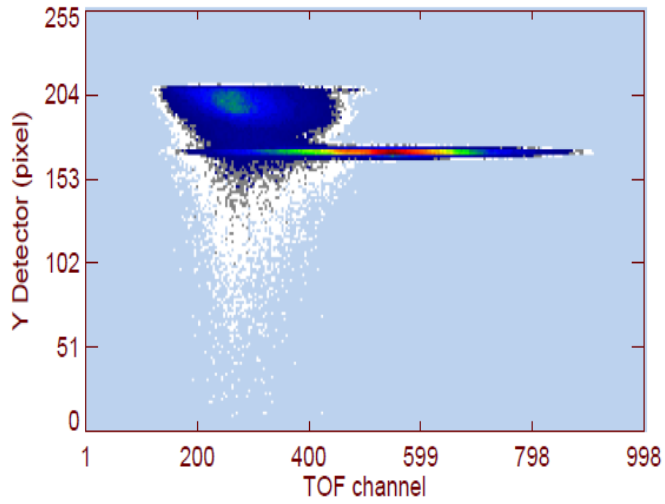

Figure 3. Raw detector data for 20% PBd in d-squalane under shear.