Experimental Report

12/03/2015

Proposal: **9-11-1683** **Council:** 4/2014

Title: Stick-Slip transition of polymer solutions on polymer brushes

This proposal is continuation of: 9-11-1557

Researh Area: Physics

Main proposer: **KOROLKOVAS Airidas**

Experimental Team: AKGUN Bulent
WOLFF Maximilian
KOROLKOVAS Airidas
ADLMANN Franz

Local Contact: GUTFREUND Philipp

Samples: Si
diethylphtalate
polystyrene

Instrument	Req. Days	All. Days	From	To
FIGARO User-supplied	5	4	16/11/2014	20/11/2014

Abstract:

From rheology it is known that entangled polymer melts or solutions do not obey the stick boundary condition at a solid wall when exposed to high shear stress. This may display an interfacial stick-slip transition (SST) where the apparent flow rate jumps discontinuously due to a massive wall slip. Although this phenomenon is frequently observed in polymer tribology and several theoretical models exist to describe it, a direct experimental observation of its origin is still lacking. In our experiment we will use in situ shear neutron reflectometry to record the theoretically proposed structural change during SST.

Experimental report

FIGARO No. 9-11-1683

Sample preparation. 0.704 grams of deuterated polystyrene (dPS), molecular mass M=600 kg/mol, purchased from Polymer Source, was dissolved in 1.446 grams of hydrogenated diethyl phthalate (hDEP), and an abundant amount (10 grams) of tetrahydrofluran (THF). The THF was then removed in a rotary evaporator under reduced pressure at 40°C. The final sample was a 32.7% wt solution of dPS in hDEP, with a presumably negligible amount of THF.

Sample environment. A clean virgin silicon (100) slab of size 7x7x1 cm was fixed on the stage of the Anton Paar Rheometer. The polymer solution was transferred on the silicon, and closed with the rheometer plate, leaving a 60 µm gap. Temperature was maintained at (45±1)°C throughout the experiment.

Measurements. The rheometer was programmed to apply a steady angular speed to the plate confining the polymer. This angular speed is converted to a mean shear rate felt by the liquid. The shear rate was linearly increased from 0 s^{-1} to 300 s^{-1} over a 2h 30 min period, and then decreased back to zero over another 2h 30 min. This experiment was repeated multiple times with different parameters, but in the end all results point to the same conclusion.

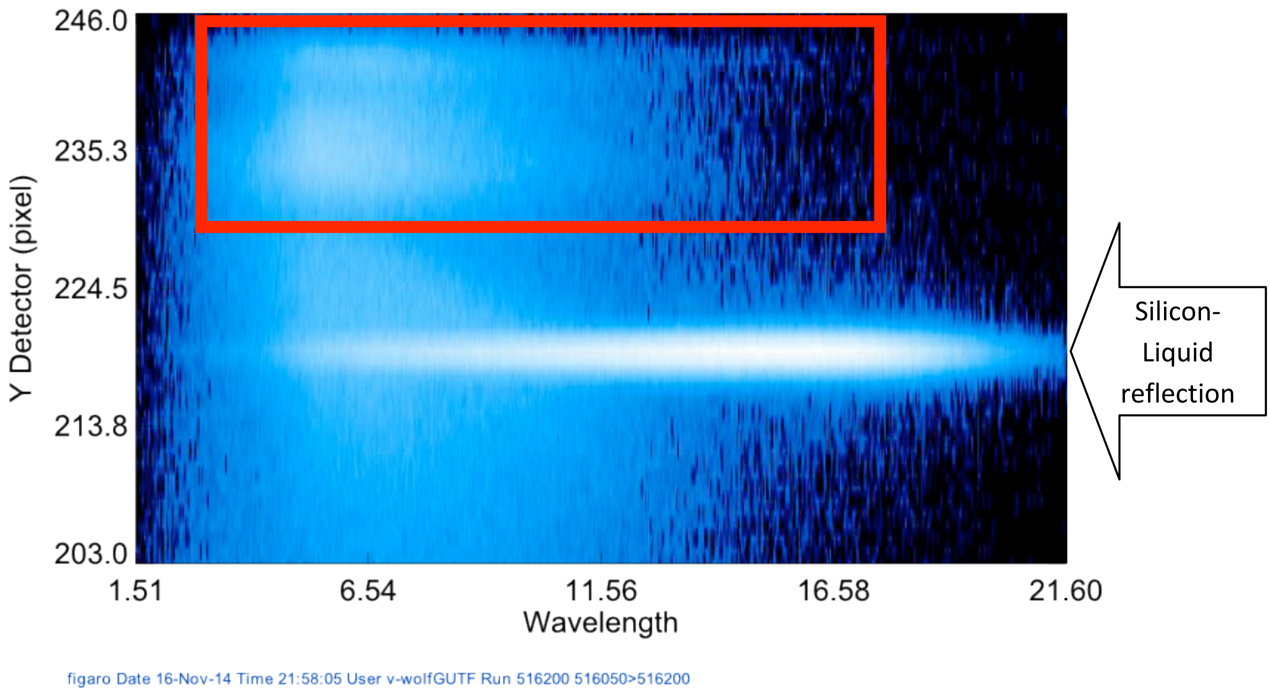
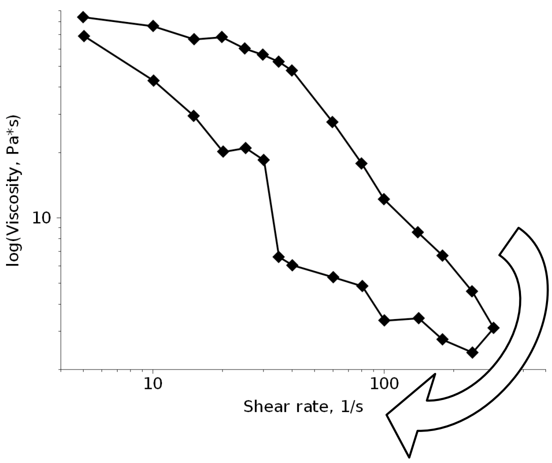


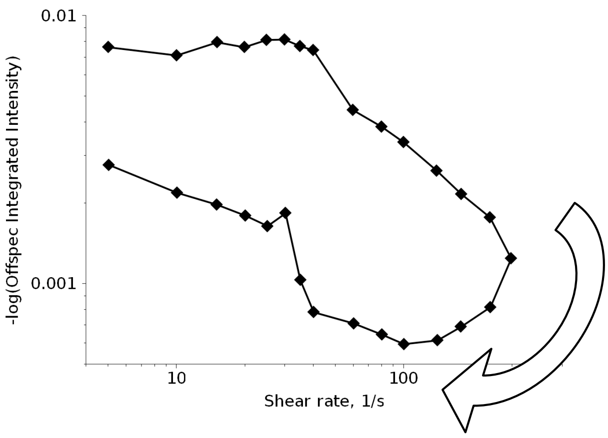
Figure 1 The detector image under shear and the integration region (red square)

Discussion. There exists a critical shear rate above which we observe a sharp increase in the off-specular signal. For the 33% solution this shear rate is about 40 s^{-1}. A 25% solution went critical at about 100 s^{-1}. To quantify the off-specular signal, we simply integrate the intensity on the detector in the region of interest, marked by the red square in Fig. 1.

If we now plot the integrated off-specular intensity as a function of the applied shear rate, a hysteresis loop emerges. The off-specular signal retains a strong intensity even after the shear has been completely stopped. The initial equilibrium level is only reached 8 hours after staying at zero shear.

At this preliminary stage, we do not have a definite answer as to what causes the off-specular scattering. Our best guess its origin is small angle scattering from disentangled polymer in the bulk.





In addition, we have plotted the measured viscosity as a function of the applied shear rate. Curiously, the viscosity shows a very similar hysteresis loop as the off-specular signal.

Conclusion. We have established that in 33% wt dPS solutions, a strong off-specular contribution appears for shear rates exceeding 40 s^{-1}. This signal is clearly correlated with bulk rheological properties. Further investigation is required to establish the exact cause of the off-specular signal.