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## Transient Overshoot Extensional Rheology: Experimental and Numerical Comparisons

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amplitude to study the transition from the linear to the nonlinear regime in the frequency range from 0.1 to 10 rad/s. The results will be discussed based on recently proposed nonlinear parameters.

A 0.5mM solution of SPAN65 in dodecane has been used in this study to measure the interfacial shear properties at the water-dodecane interface. The rheological signature of the test results is similar to those obtained for bulk properties of viscoelastic materials. At the onset on the nonlinear response,  $G'$  decreases as a function of strain whereas  $G''$  goes through a shallow maximum first. This additional dissipation at the onset is probably due to slight rearrangements of the surfactant molecules at the interface. The maximum in  $G''$  is typically found in bulk properties of gels. At the transition from the linear to the nonlinear regime, the 3<sup>rd</sup> harmonic intensity (stress magnitude of the fundamental/3<sup>rd</sup> harmonic) emerges from the noise with a slope of two and approaches a plateau value of 0.2 at 10% strain.

The results are presented as a function of strain and frequency and in order to obtain a better understanding of the mechanisms occurring at the interface when large deformations are applied, evaluated in terms of the nonlinear parameters S (stiffening/softening) and T (thickening/thinning) coefficients.

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## TRANSIENT OVERSHOOT EXTENSIONAL RHEOLOGY: EXPERIMENTAL AND NUMERICAL COMPARISONS

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### ABSTRACT

The true steady state value for the extensional stress growth is still an open topic in the field of polymer melts. Shear and extensional flows are often used to fit the various parameters in constitutive models. Extensional flow is much more effective than shear flow at orientating and stretching polymer chains, and not having steady state values for the extensional viscosity makes understanding and modelling molecular rheology in extensional flow challenging. Here we present a comparison between three extensional rheometers: the Sentmanat extensional rheometer (SER), the filament stretching rheometer (FSR) and the cross-slot extensional rheometer (CSER). The first two are uni-axial stretching rheometers and the third is a planar extensional rheometer. The FSR and CSER are capable of achieving steady state flows, although in different strain-rate regimes.

The SER has been a widely adopted tool as it conveniently adapts to a standard shear rheometer. However, the SER is only capable of reaching Hencky strains up to 4. We compare this to the transient measurements of the FSR which uses an active feedback system to control sample necking and is capable of Hencky strains of around 7.

We then compare the steady state measurements from the FSR to the predictions of the CSER, which measures the viscosity using optical flow induced birefringence techniques. The FSR is capable of measuring a steady state for strain rates less than 0.5/s and the CSER for strain rates typically in the range of 0.1/s to 10/s. Although we are comparing uni-axial to planar flow, these flows produce the same polymer deformation and hence stress in the strain hardening regime. The techniques show a good quantitative agreement where the two experimental windows overlap.

In comparing the FSR to the CSER we are able to explain an observed feature of the optical birefringence stress patterns, known as W-cusping. It has been shown that the Pompon model, a constitutive model for branched polymers, does not capture this feature. Here we show the cause of the observed W-cusps is due to the presence of a transient overshoot in the extensional viscosity. We present a modified Pompon model capable of capturing these overshoots and show finite element simulations of the cross-slot flow using this model. In doing this we show how the overshoot causes the W-cusp and how the shape of the cusps is dependent upon the difference between the maximum extensional viscosity and the steady state value.