Supplementary material of Shear-Banding in Entangled Xanthan Solutions: tunable transition from sharp to broad shear-band interfaces

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1 Determination of the overlap concentration $c^*$ of xanthan

To determine the overlap concentration of the xanthan used in this paper, we measured the shear rate dependence of the viscosity for a concentration series of xanthan in water (Fig. S1a). The zero viscosity for each concentration is obtained and plotted against concentration (Fig. S1b). Two regimes can be observed, namely $c \sim \eta^{1.6}$ at low concentration and $c \sim \eta^{3.1}$ at high concentration. The power law exponents are consistent with what reported for polysaccharide as in Ref. [1]. The $c^*$ is found to be around 0.08 wt%. Hence, we performed most of our experiments at approximately 10 $c^*$. 

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Fig. S 1: The viscosity vs. shear rate (a) and zero shear viscosity vs. concentration (b) for xanthan in water at 20°C. The numbers in (b) show the slopes of zero viscosity dependence on concentration in different concentration regimes.

Fig. S 2: The stress development in startup shear flow for 0M (a), 5mM (b), 10mM (c) and 1M (d) added salt concentration for 0.7wt% xanthan
Fig. S 3: Calculated velocity profiles with varying shear thinning factor $m$ in a Couette shear cell at a fixed shear rate of $50 \text{s}^{-1}$.

2 Step-rate tests

We determine the viscosity of each point in the flow curve (see main text) by performing step rate tests. Fig. S2 displays these tests for all used ionic strengths and selected shear rates. The viscosity is always determined from the plateau after the overshoot. Moreover, the hyterodyne measurements were always carried out after the system get steady state as indicated here.

3 Criterion for sharp interface selection for the velocity profiles

In this study we find that the velocity profiles deviate from classic shear banding where a sharp interface is expected, either by changing the shear rate, by lowering the xanthan concentration, or by increasing the salt concentration. The interface widens and cannot be fitted well with two straight lines, as is done in the piecewise linear function (PWL fit). Instead, the curved profiles can be well fitted with the shear thinning function (STF fit):

\begin{equation}
V(x) = \omega_0 R_1[(R_2 - x)^{1-2/m} - R_2^{1-2/m}] / [R_1^{1-2/m} - R_2^{1-2/m}],
\end{equation}
Fig. S4: Linear fit, shear thinning fit and piecewise linear function fit for velocity profile of 0.5s\(^{-1}\) (a), 10s\(^{-1}\) (b) and 40s\(^{-1}\) (c) and the resultant \(R^2\) (d) for the 0.7wt\% xanthan sample with no salt.

where, the shear thinning factor \(m\) is defined as \(\sigma \sim \dot{\gamma}^m\), and \(x\) is the distance from the stationary outer cylinder with rotational velocity \(\omega_0\), and \(R_1\) and \(R_2\) are the radii of the inner and outer cylinder, respectively. Varying the shear thinning factor \(m\), see Fig. S3, up to the point where the profile is linear so that a linear function (LF fit) is sufficient. With decreasing \(m\), the velocity profile become increasingly curved. However, the shear thinning function always gives a round interface even with \(m = 0.01\). Furthermore, the \(m\) in equation 1 is related to the shear thinning we can get from the rheological measurements. These are the reasons we employ the shear thinning function to fit the curved velocity profiles.

In order to classify the profiles, each velocity profile is fitted with the three fitting functions and the resultant \(R^2\) is compared. In Fig. S4a-c we show the fits of three typical profiles for 0.7wt\% with no added salt, and in Fig. S4d the comparison of \(R^2\) is plotted. At extremely low and high shear rates, where the velocity profile is quite linear, all three functions fit the velocity profile very well. These profiles are thus classified as linear. For 0.7wt\% zero added salt sample the ST fit gives in most cases the best fit. The PWLF stands out only at intermediate shear rates from 15 – 50s\(^{-1}\). These profiles form the core of this paper since it
Fig. S 5: Reproducibility of velocity profiles: (a) 3 data points are taken at each position with an interval of 3 seconds per point. The insert shows the magnification of the 3 data points. (b) a comparison between two repeated measurements taken at an interval of 30 minutes. Velocity profile were taken at 30$s^{-1}$ for 0.7wt% xanthan with no added salt.

confirms that classic shear banding does exist in aqueous xanthan solution. For higher salt concentrations, the ST fit is always better for the velocity profiles than the FWLF fit due to the broadening of the interface. However, since at 5mM added salt the transition is not very stringent for $30 - 40s^{-1}$ (the $R^2$ of PWLF fit is comparable to the ST fit), we also treat these velocity profiles as classic banded shear flow as discussed in the main text.

4 Confirmation of steady state shear flow in the velocity profile measurements by heterodyne light scattering

The time-resolution of heterodyne light scattering as a technique is insufficient to directly measure fluctuations in the velocity profile, which could affect the interpretation of the results. Therefore we critically review the observed correlation functions in order to demonstrate that the shear flow is steady in all occasions. First, note that all our velocity profiles were taken when the steady state has been reached as was done with the viscosity, see Fig. S2.

The stability of the velocity profiles was tested at three different time scales. First, we measured velocity profiles at a time interval of half an hour and find that the results stays the same and within the error bar, see Fig. S5b. Hence, we can confirm that the velocity profiles describes the steady state of the system. At a time scale of a few seconds we test stability by measuring at a fixed position three times in a row. Each measurement takes about three seconds. As one can
Fig. S 6: (a) Typical velocity profiles for the 0.7 wt% xanthan with no added salt. The numbers indicate the applied shear rate in s$^{-1}$. The vertical dash lines indicated the position where the correlation functions are shown. (b) Correlation functions at varying positions from the stationary outer cylinder shown on the bottom for different shear rates which are indicated on the left.
Fig. S 7: (a) Typical velocity profiles at $50s^{-1}$ for varying added salt concentration for 0.7 wt% xanthan. The vertical dash lines indicated the position where the correlation functions are shown. (b) Correlation functions at varying positions from the stationary outer cylinder shown on the bottom for different salt concentrations which are indicated on the left.
see in Fig. S5a, the three data points overlap nicely and we find that the error bar of the velocity is within 5%. The resultant averaged velocities are used in all the profiles presented in the paper. Finally, we check the stability at the shortest time scale of less than three seconds by comparing the correlation functions at different shear rates (Fig. S6) and salt concentration (Fig. S7) at three different positions in the gap. The general trend that can be observed is that for 0 mM salt the minima in the correlation functions display an upturn exactly in the region where the interface width is sharpest. The minima in the oscillations of the correlation functions become level when moving away from this region. This suggests that in the latter case single frequencies are measured, so that therefore a single velocity is probed over a time of three seconds. In the presence of sharp shear bands there is mixing of other frequencies, resulting in the upturn of the minima. This means that the widening of the interface is not due to fluctuations in the velocity, as these are mostly present exactly when there are sharp shear bands. The upturn of the minima is more pronounced closer to the walls, which suggests that the fluctuations might be related to a competition between wall slip and shear banding, see for example Ref. [2, 3].

References

