Linear and Non-Linear Rheology of a Model Wormlike Micellar Solution

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ABSTRACT

Aqueous solutions of cetylpyridinium chloride and sodium salicylate (CPyCl/NaSal) self-assemble to form wormlike micellar structures. These systems behave like a Maxwell fluid under linear deformations; however, in the non-linear region the response is much harder to understand. In steady shear, ‘shear-banding’ occurs beyond a critical stress and parallel regions form within the sample leading to the coexistence of domains that exhibit markedly different microstructures and shear rates in each region[1,2]. After the critical stress has been exceeded a constant shear stress plateau develops in the flow curve; however the precise shape of the flow curve is a sensitive function of the kinematics and deformation history[3]. In contrast to this plateau in the shear stress, the first normal stress difference and second normal stress difference continue to increase monotonically with shear rate. The transient development of the shear banded structure can be interpreted in terms of the ‘nucleation and growth’ dynamics of a shear-induced phase transition[4].

MATERIALS AND METHODS

The solution studied in the present work is a 100 mM solution of Cetylpyridinium Chloride (CPyCl) + Sodium Salicylate (NaSal) [2:1 ratio] in brine (0.1 M NaCl). The solution has been extensively characterized both in the linear region using frequency and temperature sweeps and in the non- linear region using both controlled strain and controlled stress techniques. The measurements were carried out at temperatures between 20°C and 70°C which is above the precipitation point. All measurements were carried out using a cone and plate fixture. The controlled stress and controlled strain measurements were carried out on an AR1000 and ARES rheometer respectively. To probe the ‘metastable’ region close to the critical stress for the phase transition, additional controlled stress measurements were performed using a superposed oscillation about a constant stress, where the constant stress was set to either 10, 14 or 18 Pa with oscillation amplitudes of either 1 Pa or 7 Pa at 0.01 Hz.

RESULTS AND DISCUSSION

Stress-growth experiments combined with shear rate sweeps show pronounced overshoots above the steady-state shear stress and normal stress difference as shown in Figures 1 and 2.

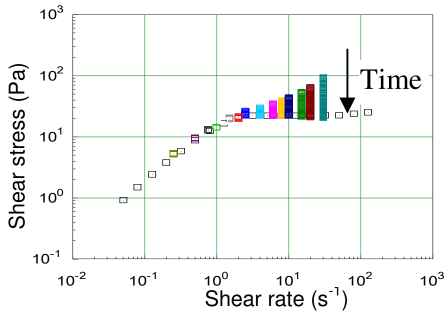

Figure 1. Transient response in the shear stress during start up of shear flow at different rates (filled symbols) with steady flow curve (hollow symbols) also shown.

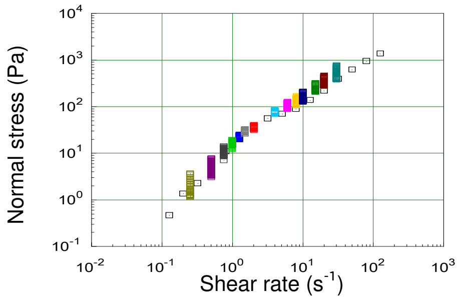

Figure 2. Transient response in the first normal stress difference during start up of shear flow at different rates (filled symbols) with steady flow curve (hollow symbols) also shown.

Frequency sweeps show that the linear viscoelastic properties can be fitted to a Maxwell model. Frequency sweeps at temperatures ranging between 20-70°C were shifted to form a master curve using Time-Temperature Superposition (TTS) as shown in Fig. 3. The shift factors at higher temperatures 60 and 70°C do not superpose perfectly, as a result of evaporation.

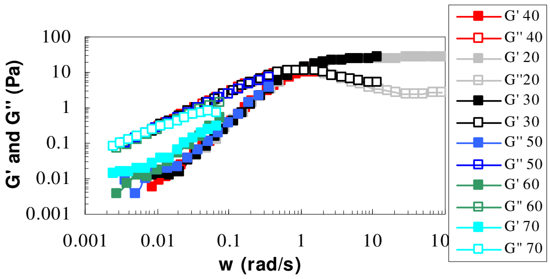

Figure 3. TTS between 20-70°C.

Parallel superposition with a steady flow stress and an additional oscillatory stress perturbation are presented in Fig.4. At very low amplitudes and frequencies, the measurements recover the expected plateau in the flow curve; however, as the oscillation amplitude is increased, there is an increasingly hysteretic response, corresponding to a periodic limit cycle about the steady shear plateau. Such measurements provide a mechanism for probing the dynamics associated with the nucleation and growth of the shear bands in the metastable regime.

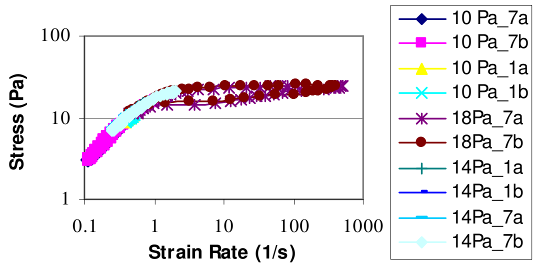

Figure 4. Controlled stress measurements; the legend notation *x*Pa_*y* corresponds to a fixed stress amplitude of *x* Pa with a superposed oscillation of *y* Pa.

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