Apparent Shear Thickening at Low Shear Rates in Polymer Solutions Can Be an Artifact of Non-equilibration

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Abstract:

While shear thickening is a well-known feature of some polymer solutions, its observation in the absence of a clear specific chemical or structural mechanism and at very low rates of shear ($\dot{\gamma} \lesssim 0.1\ \text{s}^{-1}$) in our own data, as well as in several polymer systems in the literature, has prompted further investigation. Using the rheologically-reproducible and commercially available dysphagia product Resource® Thicken Up Clear (produced by Nestle Health Science) as a canonical demonstration fluid, we show that the observation of a local maximum in the steady shear viscosity at very low shear rates can be completely attributed to the sample not having reached steady state conditions, and correspondingly, to the measurement not having been performed in steady simple shear flow. We propose two criteria to ensure equilibration during steady state flow rheological measurements: a substantial increase in the measurement time allotted for each point such that the total material strain accumulated in the sample is allowed to reach $\gamma = \dot{\gamma}t \lesssim 5$ and/or a stricter convergence criterion of 10 consecutive readings within a tolerance of 1%.

1 INTRODUCTION

When polymer solutions are subjected to shearing flows, the ability of the constituent chains to flow-align, disentangle, and unravel in the flow direction often leads to the phenomenon of shear thinning in which the viscosity of the solution is observed to decrease with increasing applied rate of shear due to the increasing flow alignment of the chains [1, 2]. In a smaller number of cases, the opposite effect of shear thickening is observed, characterized by an increase in the viscosity of the solution with applied rate of shear over a specific range [1]. The mechanisms behind these behaviors depend on the chemistry of the dissolved macromolecules. By way of one specific example, Jaishankar et al. observed shear thickening in their study of solutions of Mamaku gum, a polysaccharide extracted from the black fern tree in New Zealand [3]. In this system, shear thickening occurs as a result of the exposure of additional hydrophobic binding sites along the backbone of the chains as they unravel and extend during shearing, resulting in the formation of physical cross-links and an effective increase in the hydrodynamic size of the polymer chains [3].

While shear thickening in Mamaku gum solutions occurs at relatively high rates of shear ($\dot{\gamma} \gtrsim 1\ \text{s}^{-1}$ even at significant polymer concentrations [3]), there are also reports of shear thickening in polymer solutions at very low shear rates ($\dot{\gamma} \lesssim 0.1\ \text{s}^{-1}$) before the observation of a zero-shear rate plateau viscosity or the onset of shear thinning. Ebagninin et al. [4] report this behavior (which they term 'peculiar') in polyethylene oxide (PEO) solutions for a wide range of solution concentrations. Despite proposing that this behavior could be due to intermolecular interactions, they conclude that the mechanism is unclear [4]. Indeed, uncharged, flexible, and hydrophilic linear PEO chains do not seem like a likely candidate for significant intermolecular association in the bulk although there is some evidence of dimerization [5] and also moderate interfacial activity. In their studies of food thickening agents, Nishinari et al. [6, 7] also observed shear thickening in xanthan gum solutions for $\dot{\gamma} \lesssim 0.1\ \text{s}^{-1}$ when the experiment was performed from low to high shear rate, but did not observe it when the ex-
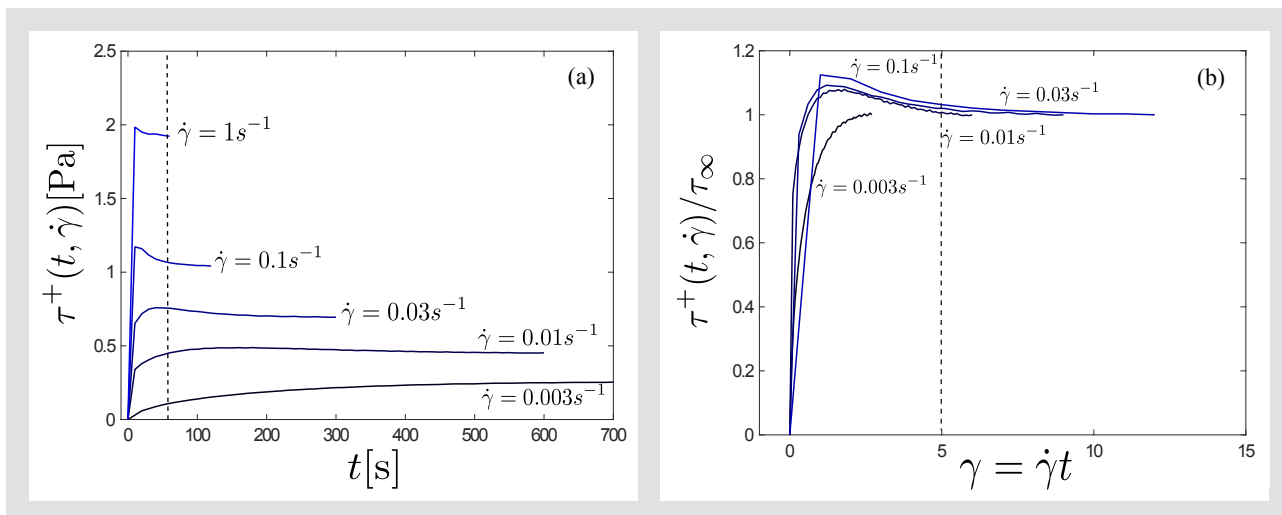
Figure 3: Stress growth upon inception of steady shear flow data for the 'nectar' preparation (1.2wt %) of Resource® Thicken Up Clear at shear rates of $\dot{\gamma}_0$ = 0.003, 0.01, 0.03, 0.01, and 1 s⁻¹. In (a), the shear stress τ^+ is shown as a function of time t, with the dashed line denoting the default maximum point time of 1 minute for steady state flow measurements. In (b), the shear stress τ^+ normalized by steady-state shear stress value τ_∞ at each $\dot{\gamma}_0$ is reported as a function of the total accumulated strain. The dashed line denotes a shear strain of γ = 5.
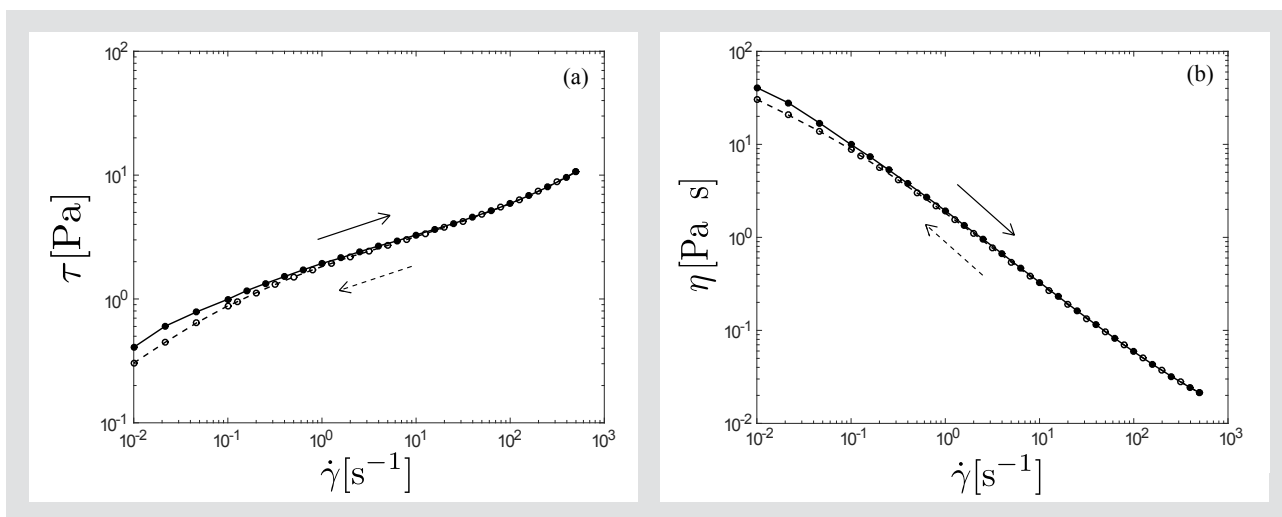

Figure 4: Steady state flow experimental data for the shear stress (a) and the shear viscosity (b) for the 'nectar' preparation (1.2 wt %) of Resource® Thicken Up Clear. Data is shown for both an 'up' ramp (increasing $\dot{\gamma}$, filled circles and a solid line) and a 'down' ramp (decreasing $\dot{\gamma}$, unfilled circles and a dashed line). Allowing the solution to equilibrate at low shear rates eliminates the previously observed local maximum regardless of ramp trajectory.

In Figure 4 we report the true steady shear stress τ and the shear viscosity η, respectively, as a function of the shear rate $\dot{\gamma}$ for up (solid line and filled circles) and down (dashed line and hollow circles) trajectories of a steady state flow experiment using our proposed total strain criterion ($\gamma \geq 5$) for $\dot{\gamma} \leq 0.1$ s⁻¹. As can be seen, by allowing the fluid to come to equilibrium at each point within this low shear rate range, no shear thickening is observed. Stress growth measurements performed during the steady state flow experiment at low shear rates indicate that the small amount of hysteresis between the up and down trajectories is in fact a true feature of the solutions (data not shown) and an indication of a small amount of shear induced degradation in the sample.

4 CONCLUSION

In this short note, we have demonstrated that although shear thickening is a genuine feature of some biopolymer solutions, the appearance of a local maximum in the shear viscosity at very low rates of shear ($\dot{\gamma} \lesssim 0.1$ s⁻¹) may often be an artifact attributable to non-equilibration of the sample. Specifically, if the allotted time for the measurement of the transient response during steady state flow (which is related to rearrangements of the fluid on the microstructural scale) is insufficient, the viscosity will generally be under-predicted at the shear rate in question. Using the 'nectar' preparation (1.2 wt %) of Resource® Thicken Up Clear as a canonical test fluid, we show that the local maximum in the ap-

parent shear viscosity observed during the 'up' ramp of a 2 minute continuous ramp is completely eliminated when measurements taken at lower shear rates are allowed to properly reach their steady state values. We therefore propose two simple guidelines for ensuring sample equilibration during steady shear rheological measurements. In doing so, we more rigorously quantify extant low shear rate equilibration recommendations such as those found in the handbook by Mezger [12]. The first guideline involves using an algorithm to ensure the data acquisition time at each point is sufficient to achieve a strain of at least $\gamma = 5$. A suggested formulation for this acquisition time can be summarized as

$$\Delta t_{point} = (60 + 5 / \dot{\gamma})s \tag{1}$$

This can be done manually or using special features often deeply buried in a specific rheometer's operating software. The value of $\gamma = 5$ is selected based on our observations of stress growth during start up of steady shear flow (see Figure 3). This can, of course, be extended to $\gamma = 10$ or higher for even more conservative experimentalists. Moreover, a more stringent point-wise convergence criterion can also help prevent slowly varying signals such as the stresses shown in Figure 3a from being confused by a software program as being at 'steady state'. For example, we found that specifying in the software 10 consecutive readings within a tolerance of 1 % resulted in sample equilibration in both the Thicken Up Clear and flax seed systems.

ACKNOWLEDGEMENTS

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