

# 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 <sup>®</sup> Thicken Up Clear (produced by Nestlé 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  $\gamma = \dot{\gamma}t \gtrsim 5$  and/or a stricter convergence criterion of 10 consecutive readings within a tolerance of 1%.

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# 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 behaviours 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 occurred as a result of the exposure of additional hydrophobic binding sites along the backbone of the chains as they unraveled and extended 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 behaviour (which they term ‘peculiar’) in polyethylene oxide (PEO) solutions for a wide range of solution concentrations. While they propose that this behaviour 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. also observed shear thickening in Xanthan gum solutions for  $\dot{\gamma} \lesssim 0.1\text{s}^{-1}$  [6, 7] when the experiment was performed from low to high shear rate, but did not observe it when the experiment was repeated from high to low rate of shear. They attributed this curious feature to possible microstructural associations during storage of the biopolymer [7], although this does not explain the observation that hysteresis depends on the direction of the shear rate ramp. Finally, in our own studies of biopolymer solutions, we observe apparent shear thickening in a similar range of low shear rates ( $\dot{\gamma} \lesssim 0.1\text{s}^{-1}$ ) for solutions of flax seed extracts (prepared by stirring flax seeds at 300rpm in deionized water at 80°C at the ratios specified in [8]) as well as in a

commercially available food thickening agent for the treatment of dysphagia which is composed primarily of Xanthan gum, Resource <sup>®</sup> Thicken Up Clear. (It is worth noting that the shear viscosity of liquid products created for patients with dysphagia is commonly evaluated and standardized at a shear rate of  $\dot{\gamma} = 50\text{s}^{-1}$  where the artifacts discussed in our article are not thought to be significant [9]). The rheological data summarizing these observations is shown in Figure 1.

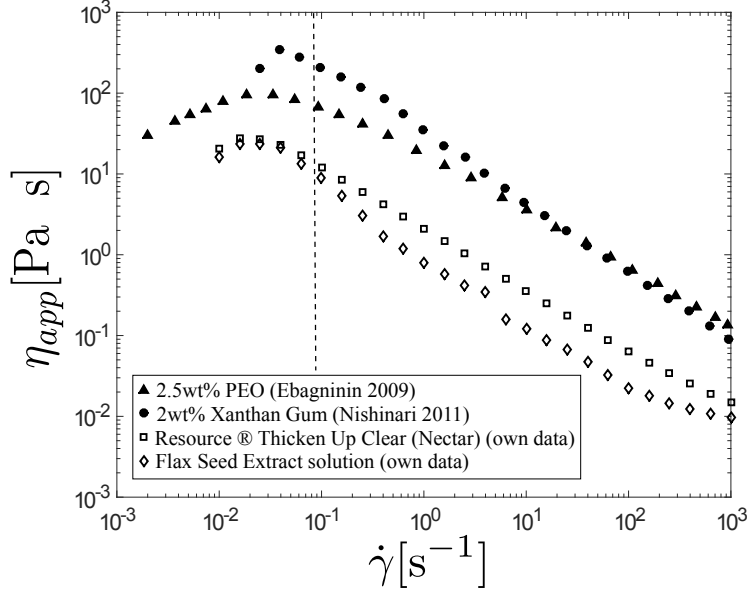


Figure 1: Shear viscosity  $\eta(\dot{\gamma})$  versus shear rate for literature measurements of 2.5wt% PEO (solid triangles) [4], 2wt% Xanthan gum (solid circles) [7], and our own measurements of the ‘nectar’ (1.2wt%) preparation of Resource <sup>®</sup> Thicken Up Clear (hollow squares) and a solution of flax seed extract (hollow diamonds). A local maximum in the viscosity occurs for all solutions in the range  $\dot{\gamma} \lesssim 0.1\text{s}^{-1}$ . The dashed line denotes the lowest value of  $\dot{\gamma}$  for which a total strain of  $\gamma \geq 5$  is accumulated in the samples, assuming a default one minute maximum sampling time per data point.

Following the repeated observation of this low shear rate thickening in the literature for polymer solutions and the lack of a clear mechanistic explanation for its occurrence, we felt that it was beneficial to investigate this phenomenon further. Specifically, we aimed to determine if this behaviour was a true rheological feature or an experimental artifact. As a result of its shelf-stability, well controlled and constant composition, and reproducible rheological properties, we use the Resource <sup>®</sup> Thicken Up Clear product as a canonical demonstration fluid, and show in this short note that many observations of apparent shear thickening at low rates can be completely attributed to non-equilibrium measurements of the viscosity. We show that upon imposition of a stricter convergence criterion or a significant increase in the allowed point sampling time for a given measurement in the shear rate range of  $\dot{\gamma} \leq 0.1\text{s}^{-1}$ , no

shear thickening is observed. Ultimately, the aim of this article is to propose a cut-off or minimum total accumulated strain value below which the steady shear viscosity should not be assumed to have equilibrated, as well as suggested rheometer settings to achieve this equilibration.

## 2 Methods

Shear rheological measurements were performed using a TA Instruments (New Castle, DE, USA) stress controlled AR-G2 rheometer with a 60mm, 2° cone-and-plate fixture.

Resource<sup>®</sup> Thicken Up Clear solutions were prepared at 1.2wt%, which is often referred to as a ‘nectar’ consistency [10]. Specifically, powder was added to deionized water and stirred vigorously at approximately 600 rpm using a magnetic stirrer for 5 minutes. Subsequently, the solution was placed on a roller mixer and gently stirred for at least 2 hours to ensure complete hydration. Based on previous measurements, the fluid microstructure is consistent with a semi-dilute polymer solution at this concentration, but the polymer chains are not yet entangled.

## 3 Results and Discussion

It is clear from the shapes of the curves shown in Figure 1 that to explore the local maximum in the apparent viscosity for this high molecular weight biopolymer solution it is necessary to obtain steady shear viscosity data at shear rates of  $\dot{\gamma} = 0.01\text{s}^{-1}$  and below. We first performed 2 minute continuous ramps in the ‘up’ (increasing shear rate) and ‘down’ (decreasing shear rate) directions for  $0.01\text{s}^{-1} \leq \dot{\gamma} \leq 500\text{s}^{-1}$  at 5 points per decade. In these experiments, the measurement time for each data point is simply the quotient of the total ramp time and the number of data points —there is no verification of equilibration by the software before continuation to the next shear rate of interest.

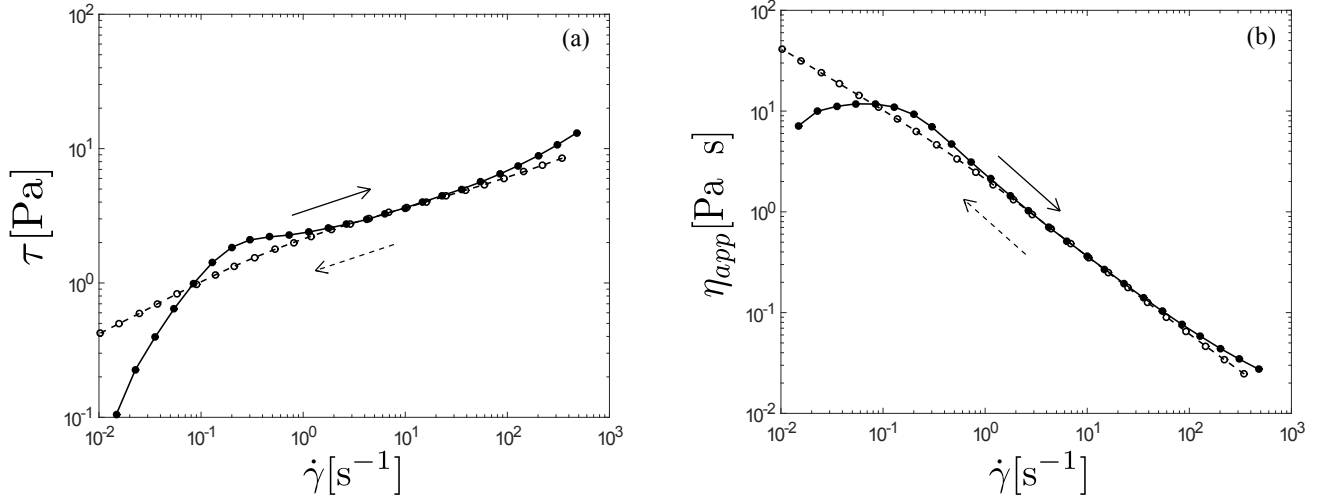


Figure 2: 2 minute continuous ramp data for the shear stress  $\tau$  (a) and the apparent shear viscosity  $\eta$  (b) for the ‘nectar’ preparation (1.2wt%) of Resource<sup>®</sup> Thicken Up Clear. Data is shown for both an ‘up’ ramp (increasing  $\dot{\gamma}$ , filled circles and a solid line) and a ‘down’ ramp (decreasing  $\dot{\gamma}$ , unfilled circles and a dashed line). A local maximum in  $\eta$  is observed during the up ramp only.

Figures 2 a and b report the measured shear stress  $\tau$  and, equivalently, the apparent shear viscosity  $\eta_{app} = \tau/\dot{\gamma}$ , respectively, as a function of the imposed shear rate  $\dot{\gamma}$  for the up (solid line and filled circles) and down (dashed line and hollow circles) portions of the continuous ramp. The continuous ramp ‘up’ data suggests that the viscosity passes through a local maximum at  $\dot{\gamma} \approx 0.1\text{s}^{-1}$  prior to the onset of strong shear thinning at all higher rates. This is consistent with the ‘steady state’ flow data reported in Figure 1 which were obtained using the default steady state flow equilibration setting for the rheometer software, which permits a maximum point time of 1 minute and requires 3 consecutive points within a 5% tolerance in order to achieve equilibrium at a given shear rate. This local maximum is not observed during the ‘down’ ramp, with  $\eta$  increasing monotonically with decreasing  $\dot{\gamma}$  for this experiment.

In order to further probe the rate of equilibration of this material, [stress growth upon inception of steady shear flow](#) experiments were performed, in which the shear rate is fixed at a specified value  $\dot{\gamma}_0$  and the resulting evolution in the shear stress  $\tau^+(t; \dot{\gamma}_0)$  is measured as a function of time. Although more time-consuming to obtain, transient stress growth curves are an elegant protocol with which to construct steady state flow curves and simultaneously ensure measurement equilibration at each imposed rate of shear. In order to tease out the behaviour at low shear rates, values of  $\dot{\gamma}_0 = 0.003\text{s}^{-1}$ ,  $0.01\text{s}^{-1}$ ,  $0.03\text{s}^{-1}$ ,  $0.01\text{s}^{-1}$ , and  $1\text{s}^{-1}$  were selected. The results of these experiments are shown in Figure 3.

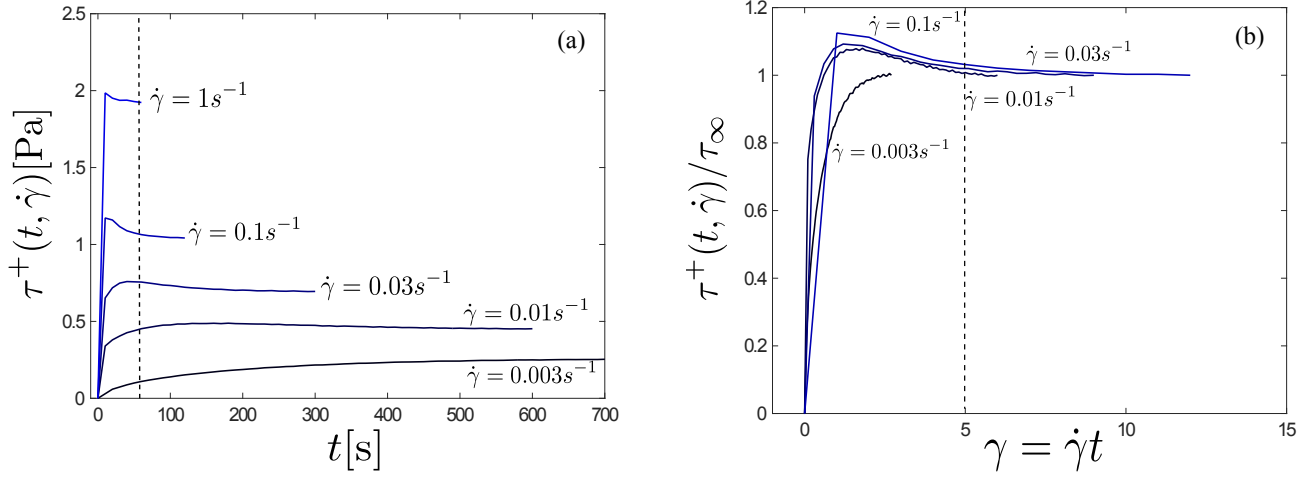


Figure 3: **Stress growth upon inception of steady shear flow** data for the ‘nectar’ preparation (1.2wt%) of Resource<sup>®</sup> Thicken Up Clear at shear rates of  $\dot{\gamma}_0 = 0.003\text{s}^{-1}$ ,  $0.01\text{s}^{-1}$ ,  $0.03\text{s}^{-1}$ ,  $0.1\text{s}^{-1}$ , and  $1\text{s}^{-1}$ . In (a), the shear stress  $\tau^+$  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  $\tau^+$  normalized by steady-state shear stress value  $\tau_\infty$  at each  $\dot{\gamma}_0$  is reported as a function of the total accumulated strain  $\gamma$ . The dashed line denotes a shear strain of  $\gamma = 5$ .

It is immediately obvious from Figure 3a that at the default maximum data acquisition time of 60s for each point of the steady state flow experiments (shown by the dashed vertical line), the values of the shear stress for all shear rates  $\dot{\gamma}_0 \lesssim 0.1\text{s}^{-1}$  have not yet reached an equilibrium value. Furthermore, the value of the stress at  $t = 60\text{s}$  may be below the equilibrium value (e.g. at  $\dot{\gamma} = 0.003\text{s}^{-1}$ ) or above the steady state value (e.g. at  $\dot{\gamma} = 0.01\text{s}^{-1}$ )!

In order to quantify this further, in Figure 3b, we plot the shear stress normalized by its steady state value  $\tau_\infty$  (as estimated by the long time asymptote shown in Figure 3a) as a function of the total accumulated shear strain  $\gamma = \dot{\gamma}_0 t$ . As is well documented for start-up of steady shear in polymer solutions, at very low shear rates ( $\dot{\gamma}_0 \lesssim 0.003\text{s}^{-1}$ ), the shear stress increases monotonically towards its equilibrium value, defining a linear viscoelastic envelope [1]. At higher shear rates ( $\dot{\gamma}_0 \gtrsim 0.01\text{s}^{-1}$ ), the transient stress deviates from this envelope, and the shear stress passes through a local maximum before reaching a steady-state value. Consistent with data for other polymer solutions in the literature, this non-linear maximum in the shear stress occurs at intermediate strains of  $1 \lesssim \gamma^* \lesssim 3$  [1].

It is clear from Figure 3b then that what is perceived to be shear thickening at intermediate rates in

Figure 2a is in fact an artifact resulting from under-reporting of the true steady-state shear stress at very low shear rates, leading to an underprediction of the viscosity that is evaluated from direct application of the formula  $\eta_{app} = \tau^+/\dot{\gamma}_0$ . Additionally, we can conclude from Figure 3b that  $\gamma = 5$  appears to be a safe estimate for the total amount of strain required for equilibration to be achieved, with the dashed line in Figure 3b designating this cut-off value. There are examples in the literature of certain polymer solutions requiring  $\gamma > 5$  to equilibrate (for instance the 3wt% guar gum solution considered in [11]), although in many cases these materials are thixotropic and this observation is made during monitoring of the transient evolution in the shear stress. Figure 1 provides additional support for this proposed limit: beyond the dashed vertical line corresponding to a total accumulated strain of  $\gamma \approx 5$  (based on the allotted 60s measurement time for each data point, or equivalently  $\dot{\gamma}_{min} = 5/60 \approx 0.083\text{s}^{-1}$ ), no shear thickening is observed. Furthermore, this requirement of an initial ‘pre-shearing’ of  $\gamma \geq 5$  for the sample to equilibrate justifies why the local maximum is not observed during the ‘down’ ramp of Figure 2b. Data reported in a down sweep from high rates has already accumulated essentially an infinite strain (e.g. at a strain rate of  $100\text{s}^{-1}$ , a test point time of 30s corresponds to  $\gamma \approx 30,000$ ).

In order to ensure equilibration for reliable measurements of the steady shear viscosity in the range of  $\dot{\gamma} \leq 0.1\text{s}^{-1}$ , the steady state flow equilibration settings on the AR-G2 rheometer were modified such that the maximum allotted measurement time per point allowed a total strain of  $\gamma \geq 5$  to accumulate in the system given the imposed shear rate  $\dot{\gamma}$ .

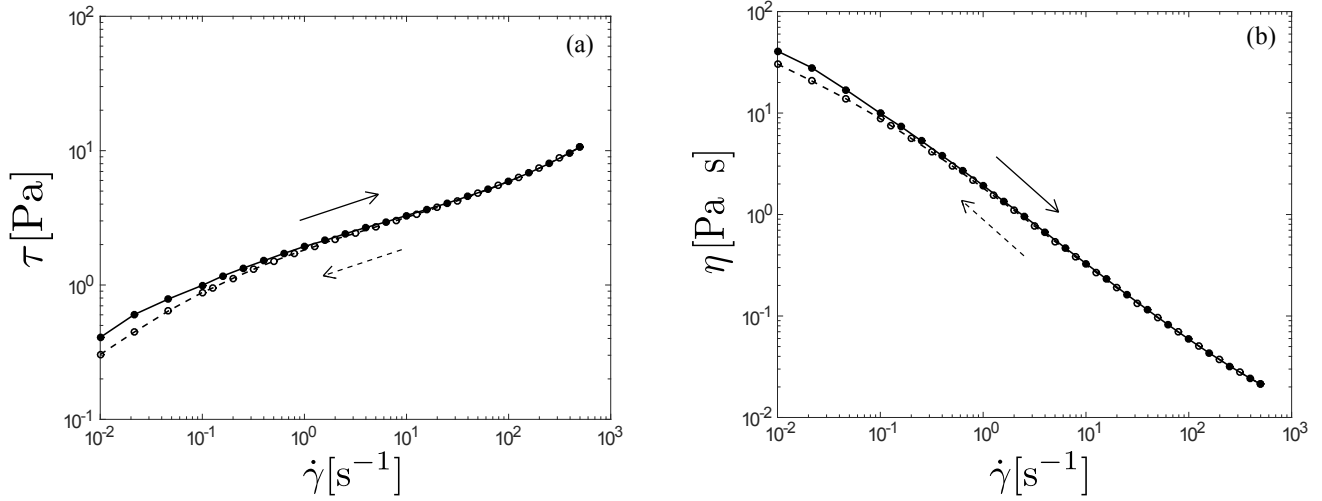


Figure 4: Steady state flow experimental data for the shear stress  $\tau$  (a) and the shear viscosity  $\eta$  (b) for the ‘nectar’ preparation (1.2wt%) of Resource<sup>®</sup> Thicken Up Clear. Data is shown for both an ‘up’ ramp (increasing  $\dot{\gamma}$ , filled circles and a solid line) and a ‘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 Figures 4 a and b we report the true steady shear stress  $\tau$  and the shear viscosity  $\eta$ , 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  $\dot{\gamma} \leq 0.1s^{-1}$ . 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  $\eta$  at very low rates of shear ( $\dot{\gamma} \lesssim 0.1s^{-1}$ ) 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 (1.2wt%) of Resource<sup>®</sup>



Thicken Up Clear as a canonical test fluid, we show that the local maximum in apparent shear viscosity observed during the ‘up’ ramp of a 2 minute continuous stress 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

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

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) and can, of course, be extended to  $\gamma = 10$  or higher for even more conservative experimentalists. Alternatively, a more stringent point-wise convergence criterion can also help prevent slowly varying signals such as the stresses shown in Figure 3a 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.

## 5 Acknowledgements

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