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The Effect of Pre-Shear Protocol for a Thixotropic Fluid

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ABSTRACT

Recent studies have proposed pre-shear protocols that aim to negate directional bias and improve repeatability using a reset step: a short duration rotation in the opposite direction of the final step in the pre-shear. This should leave the sample in a directionally unbiased state, with little or no residual stress. Using a highly thixotropic fluid, we have tested four different pre-shear protocols: one-directional rotation, rotation with reset as suggested by Choi and Rogers (2020)[1], large-amplitude oscillations with reset proposed by Donley et al. (2026)[2] and a synthesis of the two latter. For the present material, a low-concentration aqueous solution of Laponite®-RD, our results do not indicate that either one of these protocols is better suited than the others, nor, in fact, that they perform better than using no pre-shear protocol at all.

INTRODUCTION

In rheology, a wide variety of pre-shear protocols are employed with the purpose of erasing the shear history of the sample and ensure repeatability of the measurements. Traditionally, one-directional rotational shear has been used, but several studies have raised concerns that this may leave the material in a directionally biased state due to residual stress[3–5]. Some studies have replaced rotation with large-amplitude oscillatory shear (LAOS) in an effort to reduce structural anisotropy[6–9], though, in their recent study[1], Choi and Rogers point out that even this approach does not guarantee the removal of recoverable strain. Instead, they suggested a new rotational pre-shear protocol with an additional step: a short duration rotation in the opposite direction of the final step in the pre-shear. The strain imposed by this step should be equal to the recoverable strain in order to erase the shear history imposed by the pre-shear itself. A very recent study has proposed a variation on this protocol using LAOS instead of rotational pre-shear[2].

In the present study we investigate the effect these new pre-shear protocols, called 'reset' protocols henceforth, have on rheological measurements of a thixotropic yield-stress material, and compare the results with conventional rotational pre-shear. Our aim is practical, and we focus on the effect of pre-shear on typical measurements, namely flow curves and steady state shear tests.

EXPERIMENTAL METHODS

Fluid preparation

The model fluid was an aqueous solution of Laponite®-RD (LAP-RD) of concentration 1.5 wt%, in tap water. LAP-RD is a synthetic magnesium silicate clay, made of disk-shaped particles with an approximate length of ∼ 30 nm, and a height of ∼ 1 nm. For ionic strengths above 10^{-3} M, and concentrations below ∼ 4 wt%, aqueous solutions of LAP-RD form a gel structure when left idle[10].

LAP-RD powder provided by BYK was used in this study. The solution was mixed for 20 minutes using a three-bladed ducted propeller. A 1 wt% solution of NaCl was added subsequently, to a concentration of 0.035M. A batch of 1000 g was made and stored in separate containers of size 50 ml. Samples used in the present study were left idle at room temperature for 5 - 8 weeks before measurements.

Measurement methodology

The tests were carried out using an Anton Paar MCR-702e rheometer, with a parallel plate configuration. The plate diameter was 50 mm, with a gap of 1 mm. The top plate was serrated, in order to avoid wall slip. All tests were carried out at a temperature of 20 °C.

The tested pre-shear protocols are outlined in the following:

i) Conventional: Rotational shear followed by structural recovery

ii) Rotation - reset: Rotational shear directly followed by a reset step, and structural recovery, as proposed by Choi and Rogers[1]

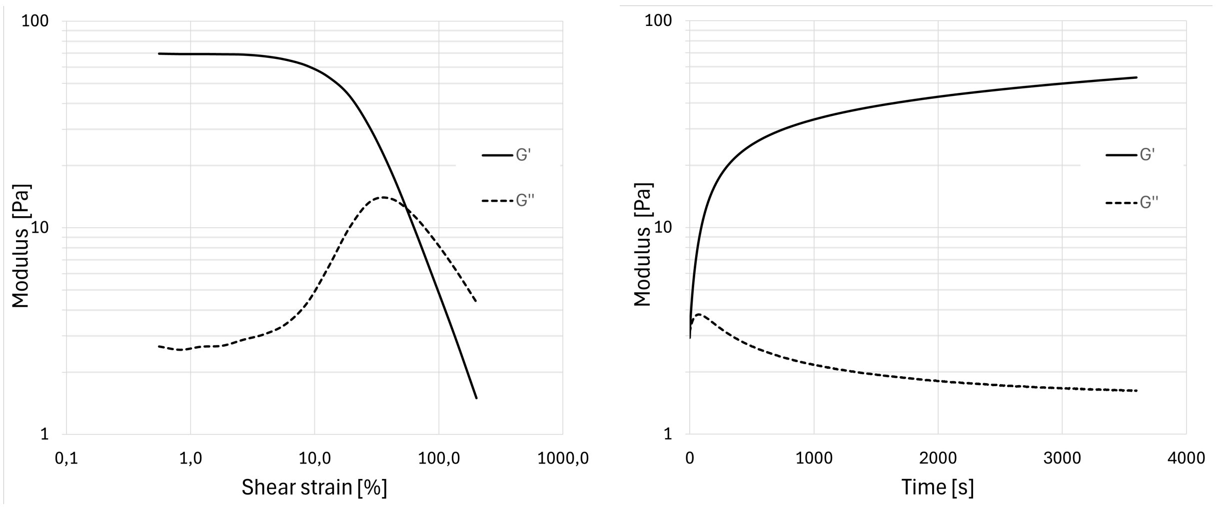
iii) LAOS - relax - reset: LAOS followed by a relaxation interval, a subsequent reset step, and a final relaxation interval, as proposed by Donely et. al.[2],

iv) LAOS-reset: LAOS directly followed by a reset step and structural recovery

The last protocol is suggested by the present authors, to bridge the gap between protocols ii) and iii). The relaxation interval between pre-shear and the reset step was an addition suggested by Donley et al.[2]. Choi and Rogers[1], however, stress the importance of running the reset step directly after pre-shear, in order to avoid structural recovery in a biased state. For this reason, we run tests for both cases: LAOS with direct reset and LAOS with a relaxation interval before the reset step. In the LAOS-relax-reset protocol, the final relaxation occurs under small-amplitude oscillations (SAOS), whereas for the remaining protocols structural recovery occurs at $\tau = 0$.

Prior to starting the measurement campaign, pretests were carried out in order to determine the linear viscoelastic range, and structural recovery time scales. Amplitude sweep and SAOS recovery results are shown in figure 1. From figure 1a, we see that $\gamma = 1$ % is within the linear viscoelastic range, whereas $\gamma = 10$ % is clearly in the non-linear region, though far away from the flow point (.i.e. the cross-over between the storage modulus G' and the loss modulus G''). Thus, these values are suitable for SAOS and LAOS, respectively.

The recovery test was carried out at s strain amplitude of $\gamma = 1$ % and a frequency of $\omega = 10$ rad/s. LAP-RD is highly shear-thinning at low concentrations, and exhibits long structural recovery times after shear, seen in figure 1b. Initially, recovery occurs over a short time scale, then the growth rate of G' decreases. From practical considerations, the duration of the recovery interval was set to 30 minutes, i.e. 1800 s. This is long enough to be well outside the short recovery time scale, although a slow increase of G' continues beyond this point.



(a) Amplitude sweep.

(b) Structural recovery.

FIGURE 1: Pretests to determine linear viscoelastic range and structural recovery time scale.

The recoverable strain, γ_{rec}, for the rotation-reset protocol was determined by creep tests. This entails that a constant shear stress is applied for a given duration, then the stress is set to zero, while the subsequent development of the strain is monitored. The steady-state value of the strain is taken as γ_{rec}. The rotational part of the rotation-reset protocol applies a shear rate of $\dot{\gamma} = 200\ \text{s}^{-1}$ for 200 s, equal to the conventional protocol, which gives a steady-state stress of $\tau \approx 6.2$ Pa. This value was used as the applied stress in the creep test, and the duration of the applied stress interval was the same as the rotational part of the protocol.

Finding the right values for γ_{rec} was something of a challenge, because the creep tests themselves were not very repeatable, with significant spread for samples taken from the same container during the same day. A representative collection of creep tests is shown in figure 2. Ironically, perhaps, tests may have been more repeatable with a pre-shear protocol in place, but as the object of this study is to consider such protocols, it was not deemed suitable to use one. In lieu of pre-shear, samples were sheared by deploying them slowly (meaning for approximately 15 s) to the bottom plate with a syringe. This ensured an equal sample volume (3 ml) for every repetition, if not completely equal deployment shear rate. After being placed, the sample rested for 60 minutes before the creep test started.

The rheometer used in this study can be run as both stress-controlled and strain-controlled. In order to be consistent with the method of Donley et al.[2], whose rheometer was strain-controlled, an oscillating strain is used for the LAOS protocols. This entails that γ_{rec} must be estimated from the residual stress, or determined by trial and error, that is, finding a shear rate interval that gives zero, or near-zero, residual stress after pre-shear. We have attempted to estimate the γ_{rec} using

$$\gamma_{rec} = c_g \frac{\tau_{res}}{G'_l} \frac{(G'_l + G''_l)}{G'_l}, \tag{1}$$

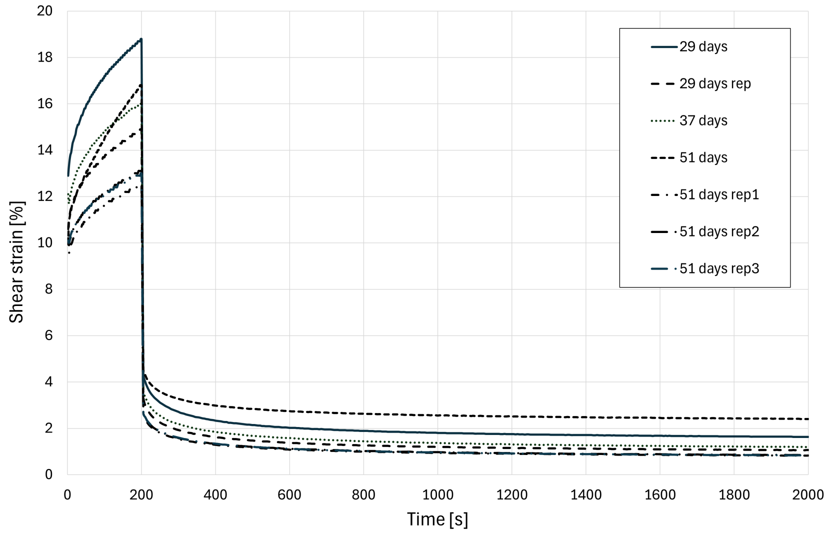


FIGURE 2: Creep tests at different sample idle times.

	$\dot{\gamma}_1$ 1/s	γ_1 %	ω_1 rad/s	t_1 s	t_2 s	$\dot{\gamma}_3$ 1/s	t_3 s	γ_4 %	ω_4 rad/s	t_4 s
Conventional	200			200					1800	
Rotation-reset	200			200		-12	0.1			1800
LAOS-relax-reset		10	1	64	60	-0.0075	0.01	-7.5×10^{-5}	10	60
LAOS-reset		10	1	64		-0.4	0.1			1800

Table 1: Pre-shear protocol variables

where τ_{res} is the residual stress, c_g is a geometry dependent correction factor, and G'_l and G''_l are the storage and loss moduli within the linear viscoelastic range[2]. For parallel plates, $c_g = \pi/\sqrt{2} \approx 2.22$.

In practice, the residual stresses in the material are very low, and there is a slight variation for each realization. This makes it difficult to find an accurate value of γ_{rec} either by estimation or trial and error. If τ_{res} is taken as the value directly after the LAOS interval, this typically gives $\gamma_{rec} \approx 0.04$, whereas the value when a 60 s relaxation interval is allowed, is $\gamma_{rec} \approx 7.5 \times 10^{-5}$.

The pre-shear variables as summarized in Table 1. Here, subscript 1, 2 and 3 refer to the initial shear interval, the relaxation interval, and the reset step, respectively. 4 refers to the structural recover or final relaxation interval. t denotes interval duration.

Because LAP-RD undergoes physical aging due to dissociation of sodium ions[11], timing of the test schedule is important. For results to be comparable, the tests cannot be very far apart in time, otherwise the storage modulus of the material will have increased beyond repeatability. Therefore, all steady shear rate tests were carried out within 24 hours for each rotational protocol. Likewise, three repetitions of the flow curve were carried out within 24 hours, per pre-shear type. Despite our sincere efforts, tests cannot be carried out simultaneously. This means a certain degree of physical aging will have occurred between testing one pre-shear protocol and the next. Therefore, the results are not compared directly. Rather, the degree of directional bias and repeatability obtained with each protocol is evaluated. The rotational protocol measurements were carried out first, after an idle time of approximately 5 weeks, while the LAOS-reset and LAOS-relax-reset were carried out after 7 and 8 weeks of idle time, respectively.

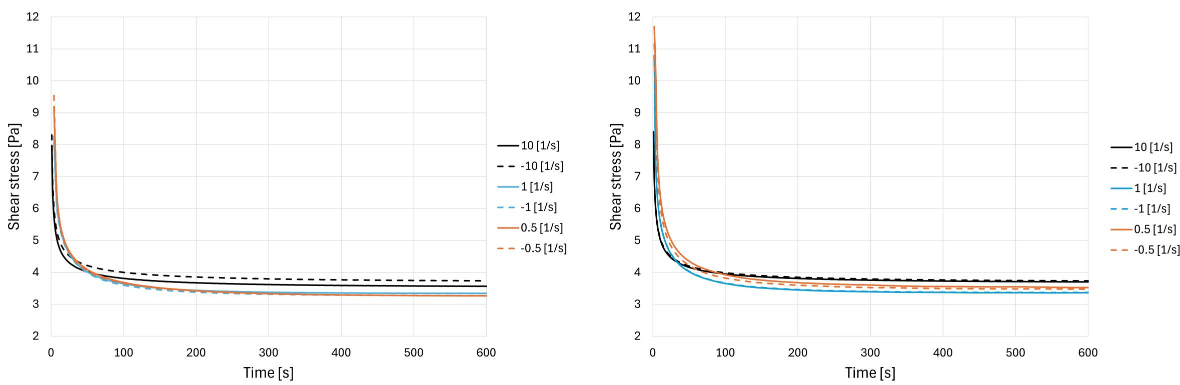
Each test series was carried out with material from the same container, in case small differences in structure arise during idle time. However, the pretests will in some instances have been carried out with material from a different container than the final measurements, which gives rise to some uncertainty.

Finally, each test was carried out with a new sample, in order to avoid drying effects, given the long duration of the structural recovery interval.

RESULTS AND DISCUSSION

Constant shear rate tests

A set of constant shear rate tests were carried out for the rotational pre-shear protocols, in order to check for signs of directional bias in the steady-state values. Three shear rates were tested for both directions, and the results are shown in Figure 3. Agreement between positive and negative directions is generally quite good. For the two lowest shear rates, agreement is best for the conventional protocol, whereas a larger discrepancy is seen for this protocol at a higher shear rate. As such, it is difficult to conclude whether or not these differences are caused by directional bias. In the study of Choir and Rogers[1], directional bias tended to be smoothed out for steady-state conditions, and was primarily visible in the initial transient phase of the measurement.



(a) Conventional

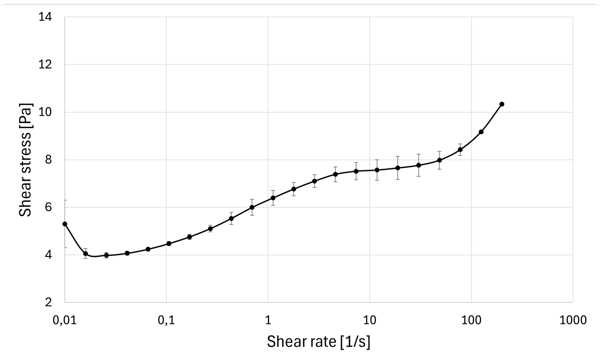
(b) Rotation-reset

FIGURE 3: Constant shear rate tests for the rotational protocols. Dashed lines represent negative rotational direction during measurement.

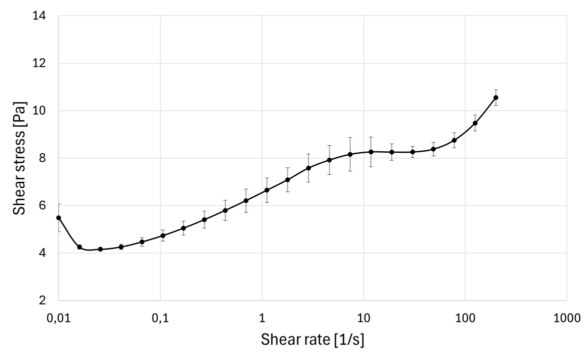
Shear rate ramps

Figure 4 shows flow curves generated from logarithmic shear rate ramps. The shear rate was increased stepwise from 0.01 s^{-1} to 200 s^{-1}, and the time per step was decreased from 200 s to 2 s. The curves shown are averaged over three consecutive measurements, and the error bars represent the standard deviation (STD) at each point. In addition to the pre-shear tests, a series with no pre-shear was taken for comparison.

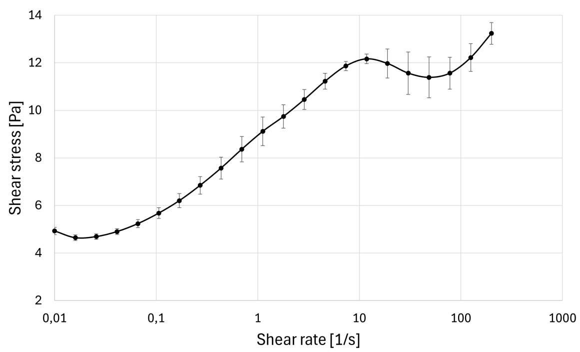
From Figure 4d, we see that for low to intermediate shear rates, LAOS-reset outperforms the other protocols, though the standard deviation increases significantly in the region beyond $\dot{\gamma} \approx 5\ s^{-1}$.



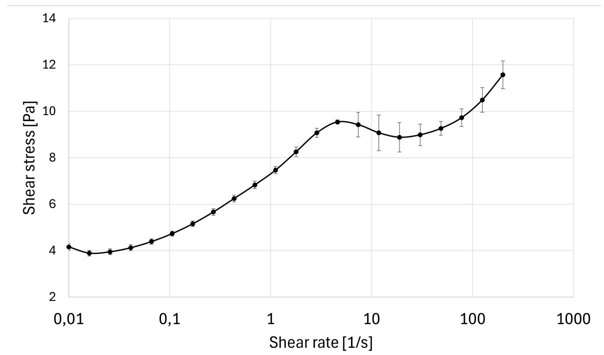
(a) Conventional



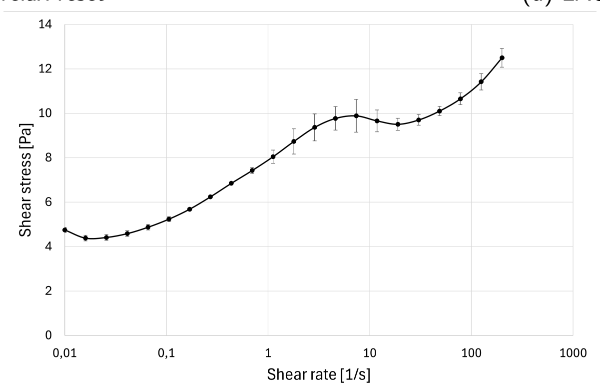
(b) Rotation-reset



(c) LAOS-relax-reset



(d) LAOS-reset



(e) No pre-shear

FIGURE 4: Shear rate ramps

The rotation-reset and LAOS-relax-reset protocols exhibit relatively high STD over a large portion of the measurement range, though not necessarily for the same values. Some of this error likely comes from the difficulty of obtaining consistent parameters for recoverable strain. It is quite conceivable that an erroneous value in the reset step may impart additional shear history instead of erasing it, which makes matters worse where repeatability is concerned. When considering the data from each run separately (not shown), we see that residual stress is normally not completely removed by the pre-shear, though the values are typically in the order of 10^{-3} Pa. This means that the material will recover with growing stresses that may influence the measurement. This observation is underlined by the fact that the tests without pre-shear have very good repeatability, in particular in the low shear rate range.

Notably, save the LAOS-relax-reset protocol, low shear rates have the best repeatability in most cases, whereas higher STD values are found for intermediate to high shear rates. This is likely related to the initial process of breaking the microstructure of the material before steady-state conditions are achieved. Several studies have reported shear banding across the measurement gap for various geometries[12–14]

Martin & Hu[14] found that increasing the shear rate may lead to a lower transient stress; the microstructure breaks down faster at higher shear rate, so that the stress overshoot decreases faster than for a low shear rate. It was also pointed out that the stress at $\dot{\gamma} = 10$ s^{-1} took "tens of seconds" to plateau. While the concentration of LAP-RD in that study was 3 wt %, double that of the present study, the results are still comparable. Increasing the solid content of the solution within the gel phase does not alter the overall material structure, though the elastic properties are strengthened.

In Figure 4, all curves display a bump in the vicinity of $\dot{\gamma} \sim 5 - 10$, though the maximum of this bump is not exactly in the same place. Considering the constant shear rate curves in Figure 3, we see that the two lowest shear rates need a longer time to reach steady state conditions. This means that if the measurement time per point is somewhat too low, the reported stress may be higher than the would-be steady state value.

The flow in the gap is a constant competition between structural breakdown and rebuilding[14], and the initial microstructure at the start of a measurement point on the flow curve is in reality a compilation of the shear history from all prior treatment of the material. Shear-banding is very sensitive to the initial microstructure, so variations in the same due to slight variations in the post pre-shear conditions may very well cause a rise in STD. There are noticeable differences between the pre-shear protocols in the shape of the flow curve as well as in the location of STD maxima and minima, which underscores this point.

It should be added here that Donely et al.[2] explicitly suggest their method may not be suitable for aging or very time-dependent materials. Their purpose was to develop a path-independent method, where a set of measurements may be taken on the same sample in any given order, always preceded by pre-shear. We are not able to test this notion, for the sheer time required to run a single measurement step with pre-shear and recovery (and the inevitable drying that would follow). That being said, it seems as though LAOS may be more suitable for this material than rotational pre-shear, albeit with a properly tailored reset step directly after the initial shear.

CONCLUDING REMARKS

In this study, we have evaluated the effect of pre-shear on rheological measurements of a distinctly thixotropic fluid, a low-concentration aqueous solution of Laponite-RD. Four pre-shear protocols were tested, where one was conventional rotational shear, while the others incorporated a so-called reset step, i.e. short-duration shear in the opposite direction, with the purpose of negating the history of the pre-shear itself. Two of the protocols hail from previous studies by Choi and Rogers[1] and Donley et al.[2], while protocol number four was our own synthesis of the two.

Our results indicate that there is little directional bias for the material we have used, and residual stresses after the initial pre-shear protocol are very low. From the flow curves, we cannot conclude with certainty that any of the pre-shear protocol is significantly better than the others, nor, in fact, that they are significantly better than simply refraining from pre-shear. However, a synthesis of the two protocols from the literature, shows promise.

Here, LAOS is used in lieu of rotation, and the reset step is added directly after pre-shear. Refining this method further may be interesting for future work.

Our efforts show that finding the correct shear rate and duration for the reset step can be challenging, and requires that the researcher devote considerable time before starting the main measurements. As such, extensive protocols like those tested herein are perhaps more suited for fundamental research rather than applications.

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