Rheologica Acta (2020) 59:921–934
https://doi.org/10.1007/s00397-020-01250-4

ORIGINAL CONTRIBUTION

Optimal conditions for pre-shearing thixotropic or aging soft materials

Jiho Choi[1] · Simon A. Rogers[1]

Received: 9 March 2020 / Revised: 9 August 2020 / Accepted: 12 October 2020 / Published online: 20 October 2020

Abstract
Pre-shearing is widely recognized as a necessary step to guarantee repeatability in rheological studies of thixotropic or aging soft materials. When one-directional pre-shear protocols are used, unrecovered elastic strain which leads to biased material states that are not always relaxed because of the build-up of structure during the relaxation process. We propose a way of guaranteeing unbiased material states by incorporating recovery steps, consisting of steps of strain opposing the initial direction of shearing, into any pre-shear protocol. Using such a multi-step pre-shear protocol, we show that it is possible to produce identical results from shearing in the positive and negative directions for the same magnitude of rate after pre-shearing. We further show how this idea of unbiased material states can be used to obtain unbiased results for other fundamental rheological experiments such as flow curves and frequency sweeps. By performing the new pre-shear protocol for every single measurement point of a flow curve or frequency sweep, it is possible to obtain data which is not affected by previous data collection, which leads to material responses with simple and clear shear histories.

Keywords Pre-shear · Thixotropy · Hysteresis · Recoverable strain · Aging

Background and criteria of optimal pre-shear

The rheology of many materials exhibits long time transience that is typically classified as being the result of thixotropy or aging. The slowly changing rheology is a reflection of structural evolution that takes place across a range of length and time scales. Prevalent structure-kinetics models, for instance, describe the degree of structure based on scalar structure parameter (λ) that evolves according to rules dictated by the shear history and Brownian motion. Aging glassy systems are described by energy landscape in a phenomenological model (Bouchaud 1992) and the soft glassy rheology model (Sollich et al. 1997; Fielding et al. 2000; Radhakrishnan and Fielding 2018). Thixotropic and aging materials are differentiated from other systems by the ability to undo or reverse such changes. In this paper, the aging we discuss indicates only "physical aging" (Cipelletti and Ramos 2005; Mewis and Wagner 2012). To accurately study these behaviors, researchers require an accurate way of "resetting" the time, which is typically achieved by either shear or thermal protocols that typically fluidize the material to erase the shear history. Thermal protocols have been termed "quenches" and have been used to erase the shear history imparted at the microscopic structural scale by providing sufficient thermal motion to fluidize a material before rheological experiments proceed (Bandyopadhyay et al. 2004; Lescanne et al. 2004). Mechanical "pre-shearing" protocols involve the application of large stresses or high rates that mechanically break structure down, leading to a fluidized state. Thixotropy and aging refer to different classes of out-of-equilibrium materials. Aging is generally found in concentrated suspensions with repulsive interactions and characterized by specific time evolution that expresses the lack of characteristic times except the "age" of the system itself. Thixotropy concerns materials with attractive interactions that drive the formation of mesoscale structure in the course of time, leading to a phenomenology that is different from that of aging. In this paper, we loosely associate the two concepts because typical experimental investigations of either class require or seek ways that the system internal clock can be reset by pre-shearing. Both approaches succeed in erasing or reversing the long-time dynamics because of the addition of energy, which places the material in some excited

✉ Simon A. Rogers
sarogers@illinois.edu

[1] Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

state, from which it returns to a macroscopically reproducible initial state. The long-time ensemble-average dynamics of thixotropy or aging can then be reproducibly studied, as the material state evolves. The timescales associated with the dynamics of thixotropy or aging in structured materials are typically longer than any viscoelastic timescale, elevating the importance of the shear history in any thixotropic or aging study.

Most pre-shear protocols for soft materials are shear based and can be classified into one of two classes based on the manner by which mechanical energy is added: one-directional shear (Bot et al. 1996; Kitade et al. 1997; Petekidis et al. 2004; Møller et al. 2006; Ewoldt et al. 2007; Baudez 2008; Osuji et al. 2008; Erwin et al. 2010; Negi and Osuji 2010; Sun et al. 2012; Fernandes et al. 2017) or oscillatory shear (Rogers et al. 2008, 2010, 2011; Goncalves et al. 2015; Moghimi et al. 2017a, b). Intervals at zero shear rate are often incorporated into the pre-shear protocol to allow the material to restructure (using the language of thixotropy) or age under quiescent conditions prior to rheological interrogation.

Traditionally used pre-shear protocols are employed to provide a rational mechanism for ensuring the repeatability of experiments. When designing or deciding on a particular pre-shear protocol, material responses in both directions in rotational rheometry have not been reported. The pre-shear procedures that are therefore intended to erase the shear history may instead be enforcing a particular history that leaves structures biased in one direction. They therefore leave the system in a reproducible initial configuration, but the bias is not taken into account when forming theoretical descriptions. We have yet to find any studies that have tested whether the results are independent of shear direction, as is assumed. Residual stresses after pre-shearing can occur as a result of both steady and oscillatory shearing. Residual stresses, which can be small, can be a manifestation of unrecovered elastic strain or structure that is biased in one direction. Many amorphous materials store residual stresses that relax very slowly, when they are sheared. The microscopic origin of the residual stress has been studied by molecular dynamics simulation and mode coupling theory for hard sphere glasses (Ballauff et al. 2013; Fritschi et al. 2014), particle-scale simulations for jammed suspensions (Mohan et al. 2013, 2015), and Brownian dynamics simulations for colloidal gels (Moghimi et al. 2017a, b). If structural anisotropy exists in the system, the rheology will be affected, and the interpretation of any subsequent experimental results must be modified to reflect the complex material state. The effect of residual stress left in the material has been recognized by Cloitre et al. (2000), Rogers et al. (2010), and Fernandes et al. (2017), where a solution to the structural anisotropy problem was sought by adding subsequent zero shear after one-directional pre-shear or, by controlling the duration and strength of the one-directional pre-shear. For the case of subsequent zero shear, Cloitre et al. (2000) tried different durations of zero-shear conditions but was not able to reach zero residual stress even after the longest time of zero shear.

To facilitate the formation of new pre-shear protocols, and to provide a way of judging the efficacy of existing protocols, we suggest here a set of criteria that an optimal pre-shear should exhibit. An optimal pre-shear should:

(i) erase the shear history of the material;
(ii) lead to a state of zero residual global (macroscopic) stress and zero recoverable strain;
(iii) lead to a material state that has rheological responses that are independent of the choice of shearing direction; and
(iv) not induce an irreversible (chemical or physical) change in the material.

When a pre-shear protocol satisfies all these criteria, we can probe the long-time dynamics of the thixotropic or aging material of interest in an unbiased state. Criteria (ii) and (iii) are really subsumed by criterion (i) but are important enough to warrant individual statements of their own. Criterion (iii) is an experimental way of verifying criterion (ii).

One-directional shearing at high rates has been shown to not only effectively “reset’ materials” internal clocks but may also leave the material in a biased configuration. Oscillatory shearing at large strain amplitudes has been suggested as a way to negate the biasing effects of one-directional shearing, but a picture is starting to emerge from recent studies of large-amplitude oscillatory shearing (LAOS) of soft materials that indicates the oscillatory protocols may be less reliable in meeting the second and third criteria outlined above (Lee et al. 2019a, b). That is, with an ever-evolving recoverable strain in oscillatory testing, the duration of the pre-shear protocol must be precisely controlled to ensure the same repeatable amount of recoverable strains at the end of each pre-shear. It has also been shown that LAOS can elicit linear viscoelastic responses typical of small amplitude shearing, followed sequentially by nonlinear viscometric flow typical of steady-shearing protocols. If a pre-shear protocol that relies on LAOS to erase the shear history of a material is stopped at the condition of zero total strain, the system may have exactly the same amount of recoverable strain as if steady shearing at the same rate (amplitude) had been applied. Pre-shearing with oscillatory protocols is therefore not guaranteed to be better than steady-shear protocols just because of the oscillatory nature of the shearing.

Here, we show how the addition of a step that removes recoverable strain at the end of an interval of shearing at a high rate accounts for two of our four criteria proposed above, making it an essential ingredient in any successful pre-shear protocol.

This work consists of two major sections. The first (Sec. III A) details experimental results showing the difference between positive shearing and negative shearing according to a traditional protocol and one in which a strain recovery step is inserted. The effect of altering the rebuilding or aging time is discussed in Sec. III A. This first section ("Determination of recovery step") is followed by experimental results showing the effects of employing strain recovery steps in pre-shear protocols for collecting important rheological information such as that contained in flow curves and frequency sweeps in "Comparison between pre-shears with and without strain recovery" and "Determination of recovery step."

Materials and method

We study the effects of different pre-shear protocols on a canonical thixotropic dispersion, a fumed silica colloidal suspension, first studied by Dullaert and Mewis (2005) and more recently by Armstrong et al. (2016) and Wei et al. (2016). It consists of fumed silica suspended in paraffin oil, with large molecular weight polyisobutylene added to the suspension. The polyisobutylene from BASF used in the work of Dullaert and Mewis (2005) is not available, so alternatives from TPC Group or INEOS Oligomers have been used in Armstrong et al. (2016) and Wei et al. (2016), respectively. We follow the specific recipe of this suspension in Wei et al. (2016). The fumed silica (R972, Evonik) is dispersed in paraffin oil (18512, Sigma-Aldrich) and polyisobutylene (H25, Indopol). The fumed silica has 2.9 vol%, and the ratio between paraffin oil and polyisobutylene is 0.61:0.39. When we measure rheological parameters for this fumed silica suspension, the suspension has loading and batch variations. All rheological experiments in the paper are performed with the same batch of this suspension.

All rheological measurements except for creep and recovery test were performed on an ARES-G2 strain-controlled rheometer (TA Instruments) at 20 °C by using a cone and plate geometry (stainless steel) with a diameter of 40 mm and a cone angle of 2° (part number 402760.901). Creep and recovery test were performed on a DHR-3 stress-controlled rheometer (TA Instruments) at 20 °C by using a cone and plate geometry (stainless steel) with a diameter of 40 mm and a cone angle of 4° (part number 511407.905). All rheological properties were collected via the TRIOS software (TA Instruments).

Results and discussion

Determination of recovery step

To solve the problem of a biased structure that is observed by direction-dependent rheology, and to meet our third criterion, we propose to add a strain recovery step at the end of the high-rate shearing portion of the pre-shear protocol. When soft materials are sheared, it is known that some of the strain is acquired in a recoverable manner (Weissenberg 1947; Philippoff et al. 1957; Lodge 1958; Reiner 1958; Smith and Tschoegl 1970; Leonov 1976; Laun 1986). In his lectures on viscoelasticity theory, Pipkin (1986) refers to the recoverable strain as "the deformation that the fluid can remember." To truly erase the shear history, so that the materials remember no deformation, and to satisfy the criteria we propose for a good pre-shear, it is necessary to remove all recoverable elastic strain after the one-directional pre-shear.

Traditionally, subsequent zero shear rate has been considered a way of removing recoverable strain generated by high rates in pre-shear. However, many thixotropic or aging materials have very long relaxation times. The rate at which structure rebuilds can be significantly faster than any relaxation mechanism, meaning that the zero-rate steps may simply be ensuring that structure rebuilds in a biased manner. We therefore need a more efficient and accurate way of removing recoverable strain after one-directional pre-shear. We choose to remove recoverable strain via the addition of a strain recovery step, applied in the direction opposite to the pre-shear. Here, we suggest an iterative method for finding the amount of recoverable strain generated by the break-down step.

The simplest way of determining how much strain can be recovered by any system is via the removal of shear stress, in a so-called recovery experiment. We begin our iterative process with a creep and recovery test in a stress-controlled rheometer. (For clarification, expression of "recovery step' discussed in the paper means recovery step in our proposed pre-shear protocol, not recovery part in creep-recovery tests.) A constant stress is applied, equal to that reached at steady state of the initial one-directional shear. After the flow reaches a steady state, the stress is removed and the recovered strain is measured. For the fumed silica suspension, 300 s^{-1} has been used as the pre-shear to ensure that all structure is broken down and all shear history is removed. Structure kinetics models typically refer to this as the unstructured state corresponding to $\lambda = 0$ (Dullaert 2005, see Fig. 7.9 in Mewis and Wagner 2011). When we apply 300 s^{-1} to the material, the stress reaches 520 Pa at steady state. So the creep and recovery test are therefore performed with 520 Pa in a stress-controlled rheometer. While the amount of recoverable strain is measured to be 70%, this is only the start point of our iterative process. The need to iterate arises because of the time taken to reach full strain recovery. Any non-zero recovery time will be convolved with structural rebuilding, which may affect the final amount of recovered strain. Because we want to erase the shear history completely without allowing the rebuilding to occur on a biased state, it is advantageous to apply the recovery step as quickly as possible. The amount or recovered strain measured in a creep and recovery test is therefore the starting value. Our mechanism for checking if the strain value from the recovery step is suitable or not is based on our third criterion for optimal pre-shear.

Before going into detail about our suggestion of checking if the strain recovery is sufficient to erase the material memory, it is beneficial to classify four different experimental protocols without the recovery step as shown in Fig. 1a. The break-down step consists of a high rate with constant value, and the main experiments can be an experiment with directionality such as shear start-up tests. The four experiments are differentiated by the directions of the break down and main experiments. Cases A and B have the high shear rate structural break down step performed in the positive direction, with the main experiment in the positive and negative directions, respectively. Cases C and D have a pre-shear in the negative direction, with positive and negative main experiments, respectively. Cases A and D therefore correspond to pre-shears and experiments carried out in the same direction, while cases B and C correspond to pre-shears acting in the opposite direction to the main experiment. Positive pre-shear generates structural anisotropy in the system in the positive direction, and so there exists a difference between the stress responses from the positive (case A) and negative

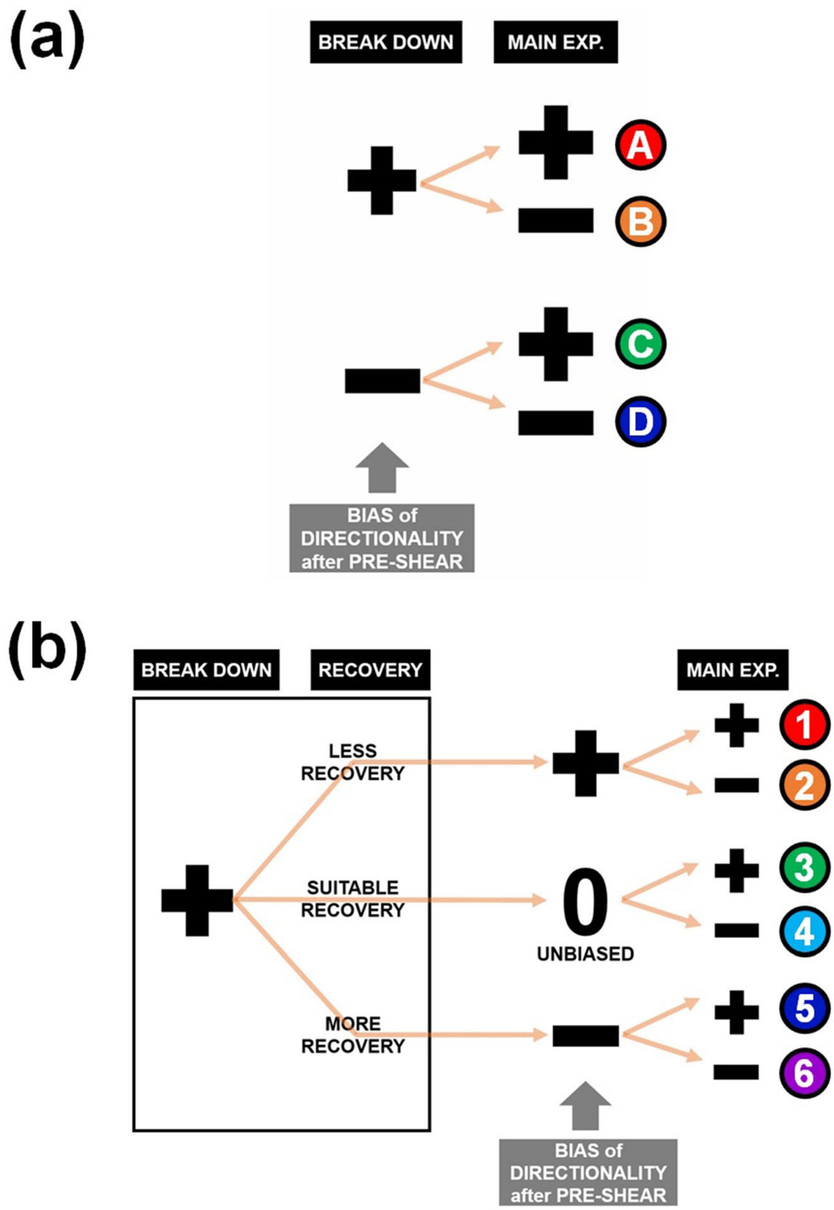

Fig 1 Diagram for equivalent experimental protocols. Identical experiments are connected with light orange lines. **a** Four cases without recovery step in pre-shear protocol; **b** 6 cases with recovery step in pre-shear protocol

(case B) shear start-up. We confirm these equalities with the fumed silica suspension with 300 s^{-1} of pre-shear and 10 s^{-1} of shear start-up in the main experiment. In Fig. 2a, we can check cases A and D have identical stress responses and cases B and C have equivalent stress responses. We can extend these equalities to 6 different experiments with recovery steps as shown in Fig. 1b. When we try the starting value of strain obtained from creep and recovery test in the recovery step, the applied strain can be deficient, suitable, or excessive. When the strain value in the recovery step is less than required to completely recover the strain, the system is left in a positively biased state. On the other hand, when the strain value in the recovery step is more than required, a negatively biased structural configuration remains after the pre-shear. For these reasons, we can equate case 1 (positive break-down, less recovery, and positive main experiment) and case 6 (positive break-down, more recovery, and negative main experiment. Similarly, case 2 (positive break-down, less recovery, and negative main experiment) and case 5 (positive break-down, more recovery, and positive main experiment) are equivalent. In Fig. 2b, we experimentally investigate these equalities. When we apply a suitable amount of strain in the recovery step, which is identical to the recoverable strain generated from the high rate in the break-down step, we obtain identical stress responses, regardless of the shearing direction in the main experiments, which shows the equality between cases 3 and 4 as shown in Fig. 2c.

Thus, when we try the starting strain value in the recovery step that was determined from the creep and recovery step, it is necessary to check and compare positive and negative shear

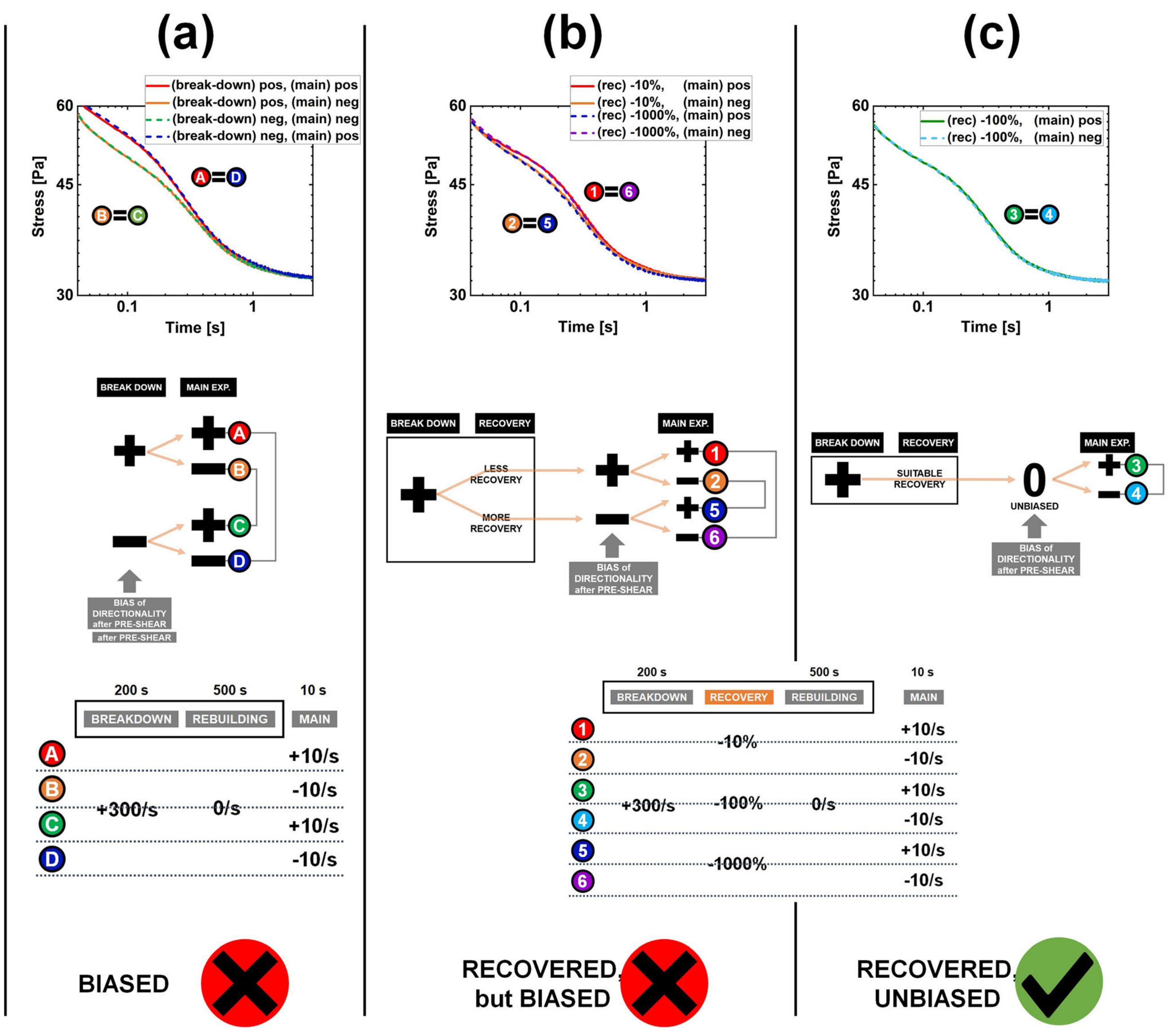

Fig. 2 Stress responses to shear startup (10 s^{-1} and − 10 s^{-1}) with different pre-shear protocols suggested in Fig. 1. Stress responses for **a** cases A, B, C, and D, **b** cases 1, 2, 5, and 6, and **c** cases 3 and 4

start-up test after the pre-shear. When the stress response from a positive shear start-up is larger than that from a negative shear start-up, we need to increase the magnitude of the negative strain in the recovery step. For the reverse case, we can use a smaller strain value in the recovery step.

It is important that the strain recovery step be made as quickly as possible (Holroyd et al. 2017) to avoid imparting a new strain history. Thus, it is better to use the step strain functionality available is commercial rheometers instead of a specific rate input for a fixed short duration in the recovery step.

Pre-shear guaranteeing repeatability and unbiased experimental results

In this section, we show how pre-shearing with a strain recovery step meets our success criteria for an optimal pre-shear, while a pre-shear without strain recovery produces biased experimental results.

Comparison between pre-shears with and without strain recovery

In this section, we experimentally investigate whether shearing in the positive or negative direction after the pre-shear with and without strain recovery leads to the same results. An often-used protocol for pre-shearing is visualized in Fig. 3a. We follow (Armstrong et al. 2016) and apply one-directional shearing at 300 s^{-1} for 200 s. Following the high-rate shearing is a structure-rebuilding step at 0 s^{-1} for 500 s. After applying this type of pre-shear protocol, we apply both positive and negative (step) shear rates to the material with different magnitudes: 0.5 s^{-1}, 1 s^{-1}, 2 s^{-1}, 4 s^{-1}, 50 s^{-1}, and 100 s^{-1}. The results are shown in Fig. 3b.

The solid lines in Fig. 3b indicate the stress response to constant shearing in the (arbitrarily chosen) positive direction, and the dashed lines show the stress response to constant shearing in the negative direction. We can clearly observe significant differences, in both the magnitude and the transience, between the results obtained from the two directions after applying traditional pre-shear protocol without strain recovery. Though the magnitude and timing of the various features in the initial response to each shear rate is different, the responses to the different directional shearing eventually converge to the same stress value at long times. The differences show that a directionally dependent structure is achieved by applying a traditional pre-shear protocol. The traditional one-directional pre-shear therefore violates our third criterion and would not be considered a "good" pre-shear protocol.

Having followed the procedure in "Determination of recovery step," we end up with the pre-shear protocol shown in Fig. 4a. A strain of 100% in the direction opposing the high shear rate step is inserted between one-directional shear and rebuilding step in Fig. 3a. After applying this new pre-shear protocol, we perform step shear rate tests as before, testing whether the new protocol with strain recovery results in identical transient results in the positive and negative directions across the same range of shear rates. The results of these tests are displayed in Fig. 4b. The results of the positive shearing, indicated by the solid lines, are indiscernible from the negative shearing, as indicated by the dashed lines The quality of the overlap shown in Fig. 4b indicates that adding recovery step eliminates any directional bias produced from the one-directional pre-shear, meeting the criteria we have established for a good pre-shear.

The addition of a recovery step in pre-shear protocols does not affect the steady-state responses, but we can obviously recognize the change caused by the inclusion of the recovery step in the transient responses as shown in Fig. 3b and Fig. 4b. Thixotropy or aging are inherently time-dependent phenomena, so it is essential to have unbiased results in the transient regime. Existing thixotropic models often have their parameters determined by comparison with shear rate reduction tests, which are standard thixotropic probes. Shear rate reduction and increase consists of two different constant rates and model-fitting is usually performed in the transient regime that exists between the two different steady states at short and long times. The shear start-up tests shown in Fig. 3b and Fig. 4b can also be considered a special case of shear rate

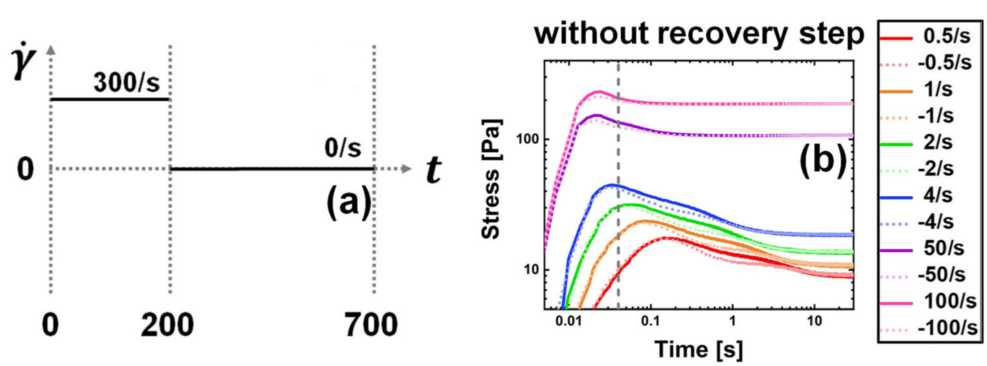

Fig. 3 **a** Pre-shear protocol: positive directional shear followed by zero shear for structure rebuilding and **b** stress responses from positive shear and negative shear after pre-shear of (**a**). Grey dashed line in (**b**) represents instrumental delay to apply constant shear rate

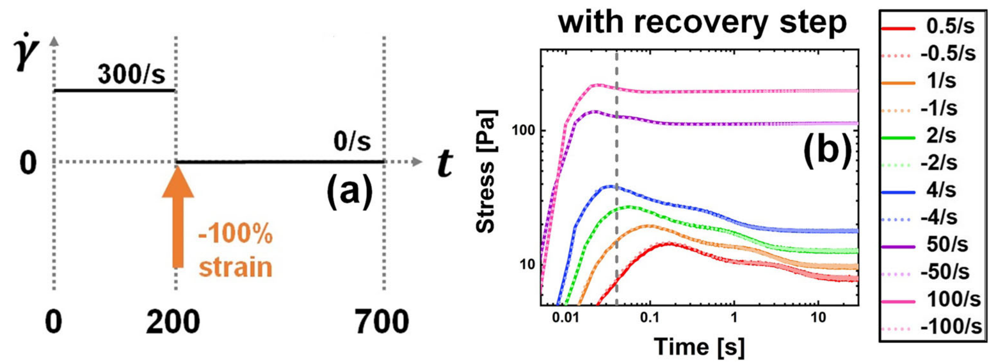

Fig. 4 **a** Pre-shear protocol: positive directional shear and subsequent recovery step with negative directional shear followed by zero shear for structure rebuilding and **b** stress responses from positive shear and negative shear after pre-shear of (**a**). Grey dashed line in (**b**) represents instrumental delay to apply constant shear rate

increase tests, with zero rate as the initial shear rate. Thus, the results in Fig. 3b and Fig. 4b provide caution for researchers wishing to validate models with experimental data. The data in Fig. 3b and Fig. 4b clearly show the effects of starting experiments in biased states, while model responses may assume unbiased initial configurations.

Determination of duration for rebuilding step

It is traditionally assumed that the restructuring step will allow the material to rebuild in an isotropic manner, thereby erasing any biasing effects of the pre-shear (Cloitre et al. 2000; Rogers et al. 2010). We test this hypothesis by using pre-shear protocols with and without a strain recovery step with extended restructuring or aging times between the end of the pre-shear and the start of the rheological test. The results of these tests are displayed in Fig. 5 for the start-up response to 10 s^{-1}. As before, we probe the positive and negative directions as an indicator of directional bias. As in Fig. 3b and Fig. 4b, Figure 5a shows the results with a traditional pre-shear without strain recovery, and Fig. 5b shows the results when a strain recovery step is included in the pre-shear. We find that without the strain recovery step, the directional bias remains even after restructuring times as long as 1000 s. This observation indicates that it is necessary to remove the recoverable strain immediately after the high rate step of the pre-shear protocol, or it will affect future results.

For experiments preceded by pre-shear with and without a strain recovery step, the longer the rebuilding or aging step is, the higher is the stress. That is, when the material is more structured or older, there exists more resistance in the system which means more stress, as expected. It is clear from the data displayed in Fig. 5 that a directional bias still exists at even the longest restructuring or aging times. Allowing the material to rebuild under zero shear rate conditions therefore does not provide an isotropic structure: the directional memory imprinted by the pre-shear is remembered at later times until steady state is reached. We can connect this result to how we define the structure parameter in structure-kinetics models which have been used for modeling of thixotropic materials. In many models, the structure parameter (λ) is zero at very high shear rate which means no structure exists in the system (Mewis and Wagner 2012). However, the result in Fig. 5 suggests that thixotropic materials can have structural

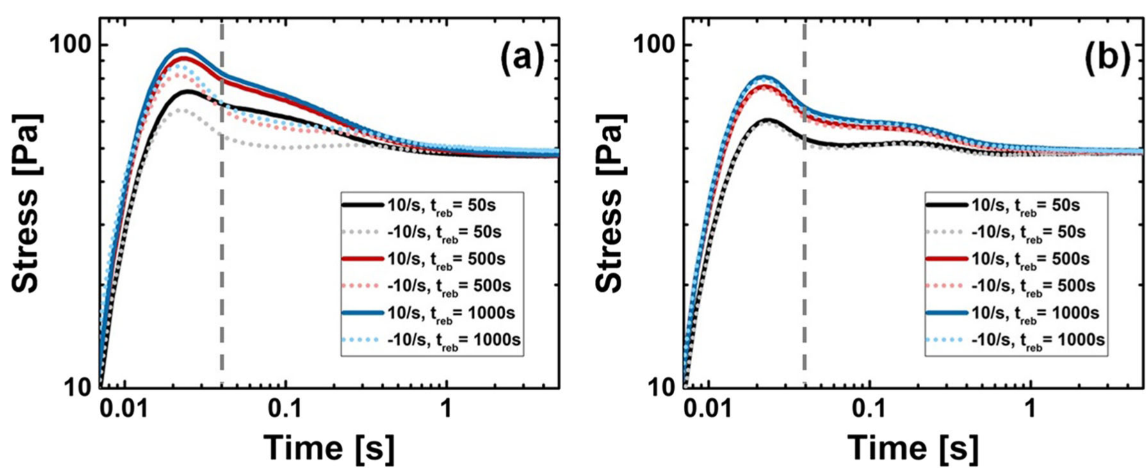

Fig. 5 Stress responses from different duration of rebuilding step, 50 s, 500 s, and 1000 s. **a** After pre-shear of Fig. 3a; **b** after pre-shear of Fig. 4a. Grey dashed lines represent instrumental delay to apply constant shear rate

anisotropy even after the application of very high rate, where such models predict no structure. This result shows the limitation of the current structure parameter description in structure-kinetics models, in that the parameter is a non-specific scalar measure.

As with the results shown in Fig. 3b and Fig. 4b, when the strain recovery step is included, the results show no directional bias. Additionally, when the strain recovery step is included, as shown in Fig. 5b, the stress values are lower during the transient phase for both directions than for either direction in the tests without strain recovery for all restructuring times. At long times after shearing has begun, the responses with and without a strain recovery step reach the same final stress, as expected.

We also investigate how stress response varies with respect to rebuilding time for different shear rates in the range 1 to 100 s^{-1}, when the pre-shear has a strain recovery step included. Stress responses from 1 s^{-1}, 10 s^{-1}, and 100 s^{-1} are shown in Fig. 6a–c, respectively. The effects of rebuilding times ranging from no rebuilding time, up to 500 s are shown in Fig. 6, as indicated.

We observe that the stress responses from different duration of rebuilding step converge to stress response with 500 s of rebuilding step. For this reason, we determine 500 s as minimum duration of rebuilding step for guaranteeing fully structured initial state.

All of the stress responses in Fig. 6 have two peaks in the stress trajectories. We associate the first peak with the instrumental input. Specifically, it takes 0.04 s for the rheometer to reach the input shear rate, so there is always a peak in the stress trajectories around that time. While the first peak is instrumental, the second peak is solely due to the material response. We can describe this second peak in two related ways. Firstly, to change from more structured state to less structured state, yielding happens in the thixotropic material. This yielding leads to the second peak observed in the stress trajectories. Secondly, we can consider the shear start-up test generically as a shear rate increase test that is typical of thixotropic studies, but with zero rate as the initial shear rate. For thixotropic materials, the stress response to the shear rate increase always has an overshoot as a result of structure breakdown. Thus, it is possible to interpret the second peak as either a thixotropic or yielding effect. In this regard, yielding and thixotropy are synonymous.

Application of pre-shear with strain recovery to traditional experiments

Traditionally, rheological experiments such as the collection of flow curve and frequency sweep information are performed in a *consecutive* manner, which imparts a complex shear history. In systems that do not have long-time dynamics such as thixotropy or aging, these can be performed in multiple ways that all lead to the same response. That is not the case with thixotropic or aging systems, where the memory of the shear history lasts much longer than viscoelastic timescales. By consecutive, we mean that we measure stress values in a consecutive series of measurements for different shear rates or frequencies without placing the material into the same reproducible initial configuration via pre-shearing. To obtain an unbiased flow curve or set of frequency sweep data, it is necessary to *separate* every single point in flow curve or frequency sweep by inserting a pre-shear protocol with strain recovery between each datum. This practice has a major benefit in the study of long time-varying dynamic systems: the transient rheograms that are ultimately obtained from the data can be interpreted cleanly as the response of the material at any specified time after rejuvenation with the same simple shear history. The distinction between consecutive and separated measurements is nicely summarized by the mutation number of Mours and Winter (1994). If we consider the flow curve or a frequency sweep as a single measurement that takes some time to measure, the mutation number tells us that the materials response cannot be changing significantly during this interval for our measurement to carry the intended interpretation. For aging or thixotropic materials, the rheology changes most rapidly immediately after pre-shear or after changing conditions have been imposed. To avoid large mutation numbers, most researchers will therefore wait until the material has fully

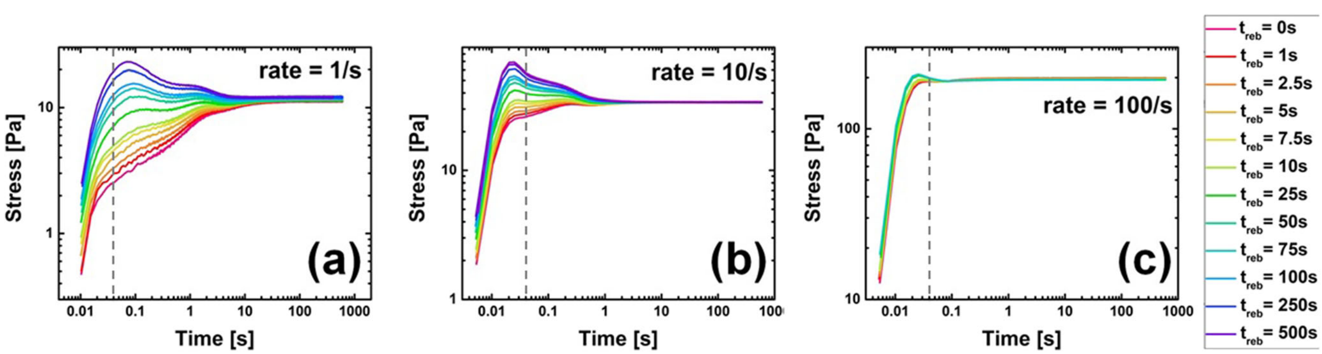

Fig. 6 Stress responses from different rebuilding time of 0 s, 1 s, 2.5 s, 5 s, 7.5 s, 10 s, 25 s, 50 s, 75 s, 100 s, 250 s, and 500 s. When input shear rate is at **a** 1 s^{-1}, **b** 10 s^{-1}, and **c** 100 s^{-1}. Grey dashed lines represent instrumental delay to apply constant shear rate

restructured (for thixotropic systems) or until the materials has aged enough that its continued aging does not lead to significant changes over the duration of the measurement. This process does not only avoid generating large mutation numbers but also avoids the transience that is at the heart of thixotropy and aging. To investigate the transience without generating large mutation numbers, it is therefore best to measure the flow curve or frequency sweep in a separated manner making the evolution of the stress or dynamic moduli at each shear rate or frequency clearly related to the evolution of the material response, rather than a convolution of the material response and measurement protocol. In the case of measuring the dynamic moduli, it is imperative that the mutation number issues associated with individual measurements of the dynamic moduli discussed in by Mours and Winter are kept in mind.

Comparison between consecutive and separated frequency sweep

If the shape of the frequency sweep for a particular material depends on how the frequencies are swept (high to low, or low to high) then the material response is convolved with additional experimental effects. The rheogram obtained is therefore not easily interpreted as *the* linear response of the material at a particular time, because the complex shear history is convoluted into the data. That is, if we measure the dynamic moduli with respect to angular frequency in the traditional sequential way, every single point is affected by all previous points. Only the first point measured is therefore unaffected by the complex

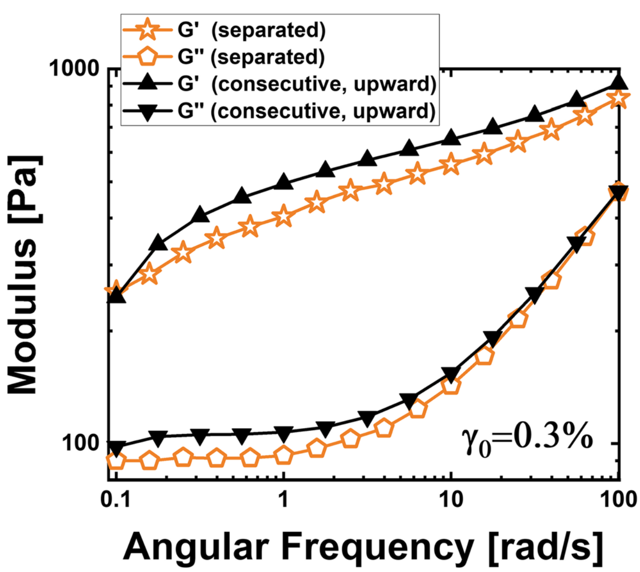

Fig. 7 Dynamic moduli (G', G'') with respect to angular frequency of fumed silica suspension measured in consecutive (upward) and separated manner. Consecutive and separated measurements are colored with black and orange, respectively. Storage and loss moduli in consecutive measurement are indicated with upper and lower triangles, respectively. Storage and loss moduli in separated measurement are indicated with star and pentagon, respectively

shear history. Because it is possible to choose the number of points per decade, the range of the angular frequencies swept, and the direction of the sweep, we, the experimenters, can have significant unintended influence on our results that may not always be acknowledged. However, if we separate every single point in the frequency sweep with a pre-shear that includes strain recovery, the final rheogram retains the intended interpretation. The comparison between consecutive and separated ways of collecting frequency sweep data is visualized in Fig. 7.

There exists a large difference in both the storage and loss moduli determined from both tests, with the consecutive approach having the much higher values. We attribute this increase in apparent elasticity to strain stiffening caused by probing a material state in which not all of the elastic strain in the system has previously been removed, as we observed in the steady-shear start-up tests shown in Fig. 5.

Transient flow curve

In addition to looking at the effects of the strain recovery step in the pre-shear of steady-shear start-up at fixed shear rate and the linear regime frequency sweep, we also investigate the difference between the consecutive and separate approaches on the flow curve. As seen by the steady-shear start-up tests at different rates, the shape of the transient flow curve depends on the duration of the measurements and rebuilding steps. (In this paper, we call stress responses from shear start-up tests with different rates visualized in stress/rate space before reaching steady state as “transient flow curve”). We show in Fig. 8 the evolution of the flow curve as determined by the consecutive and separated measurement methods. The separated approach is constructed by reading the value of the stress at each shear rate at the times indicated in Fig. 8. Flow curves measured via the consecutive approach with downward and upward sweeps are also shown in Fig. 8.

On ARES-G2, the earliest equilibration time we can access in “Flow Sweep” mode was 2.05 s. For this reason, we visualize only separated curves for equilibration time shorter than 2.05 s. And, there exists a difference between ordered and measured equilibration times on ARES-G2: ordered equilibration time for measured equilibration time of 2.05, 3.55, and 31.06 s were 1, 2.5, and 25 s. A significant difference exists in the interpretation of each of the measurement approaches. The separated approach leads to a transient flow curve that represents the response of the (unbiased) material to all shear rates at the specified time after shear initiation. The shear history is therefore simple and clear. Contrary to this clarity of interpretation, the consecutive measurement approach produces data that is convoluted with the complexity of the shear history caused by the choices made by the experimenter, including duration at each point, and whether rates are swept from low to high or vice versa. Comparison of the flow curves obtained by the two methods highlights the possibility of

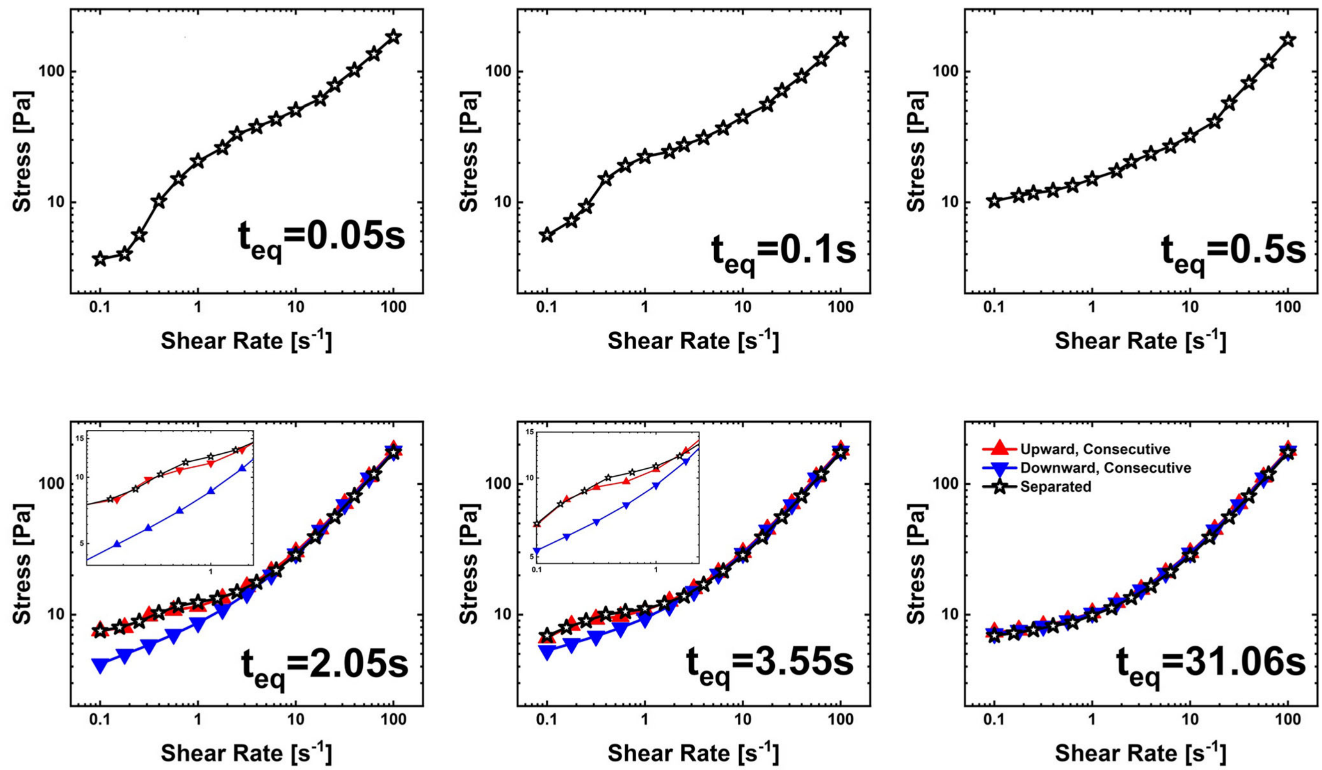

Fig. 8 Flow curves of fumed silica suspension measured in traditional (consecutive) and separated manner. Upward (low to high) consecutive flow curves are indicated with red upper triangles and lower (high to low) traditional flow curves are indicated with blue lower triangles. Black stars represent separated flow curves. t_{eq} means equilibration times for traditional flow curves and stress value after applying shear fixed rate with specific duration for separated flow curves

misinterpreting the convolution of material properties and experimental procedures with material properties. Divoux et al. (2013) discussed hysteresis loops for soft glassy materials. The approach of Divoux et al. was to use a protocol that imparted a complex shear history that is very difficult to separate from material responses, which was their intention. The method of separating the transient responses from each shear rate allows for more reliable determination of material responses, separately from the complex history.

Conclusion

One-directional shearing at high rates is often used as a pre-shear protocol for thixotropic and aging materials. We have shown that such protocols lead to biased material states that lead to directional-dependent rheology. By contrast, the addition of a shear recovery step, achieved by shearing in a direction opposite to that of the break-down step, allows us to obtain the same stress response from positive and negative shear rates of the same magnitude. The addition of the recovery step is therefore necessary for an optimal pre-shear, in which our four criteria are met. The rebuilding step that is often employed in pre-shear protocols to reduce the effects of any biasing from the high shear rate step actually leads to a biased structured state unless the recoverable strain is addressed immediately after the high shear rate step. The rebuilding step by itself is sufficient for recovery of any biased structure formed by the initial one-directional shear.

This way of pre-shearing thixotropic and aging materials, which includes a high shear rate structural break down step followed by a strain recovery step, allows us to measure unbiased material responses that can manifest in traditional measurements of frequency sweeps and flow curves. By measuring every single point in a frequency sweep or flow curve separately, following with the new pre-shear protocol, we obtained different results than had the tests been carried out in the traditional consecutive manners. This idea provides frequency sweep and flow curve data with simple shear histories, free of artifacts associated with choices made by the experimenter. Fitting model parameters for thixotropic and aging materials has been performed with experimental results with traditional one-directional pre-shear. Our new pre-shear protocol and modified way of obtaining frequency sweep and flow curve information will lead to more accurate model descriptions for thixotropic and aging materials with simple shear histories.

Funding This material is based upon work supported by the National Science Foundation under Grant No. 1847389.

Appendix 1. Stress response during recovery step and rebuilding step

We propose the third criterion for optimal pre-shear as a way of checking the second criterion. If there exists a residual stress or residual strain in the system, we can recognize them by comparing stress responses to positive and negative shear start-up tests. Checking the stress response during the recovery and rebuilding steps is another way of ensuring the pre-shear satisfies the second criterion. We show in Fig. 9 that the step-strain recovery protocol we propose does indeed reduce the stress to essentially noise during the step process, as well as in the rebuilding phase.

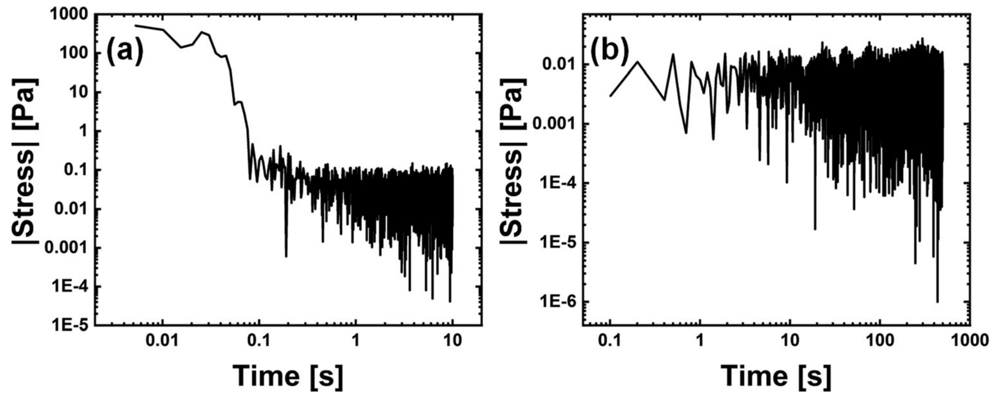

Fig. 9 Stress response (absolute values) during **a** recovery step and **b** rebuilding step

Appendix 2. Shear rate input in ARES-G2 rheometer

On ARES-G2 rheometer, when constant shear rate is applied to the rheometer, it takes 0.04 seconds to apply desired shear rate. For example, when we apply 10 s^{-1} of shear rate to the rheometer, the measured shear rate is visualized in Fig. 10. Regardless of shear rate magnitude, the rheometer has 0.04 seconds of delay.

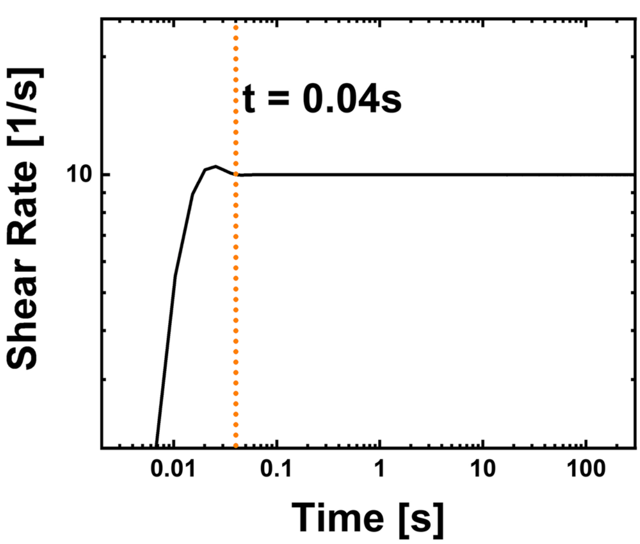

Fig. 10 Measured shear rate with respect to time on ARES-G2 rheometer, when 10 s^{-1} of constant shear rate is applied to the rheometer

Appendix 3. Determination of minimum rate amplitude for breakdown step

We can divide up the steady flow curve into three sections as shown in Fig. 11: plateau (P), high shear region (H), and transition (T). In high shear rate regime, the steady flow curve is a straight line. An intermediate section between the plateau and the high shear rate section exists, which is called the transition.

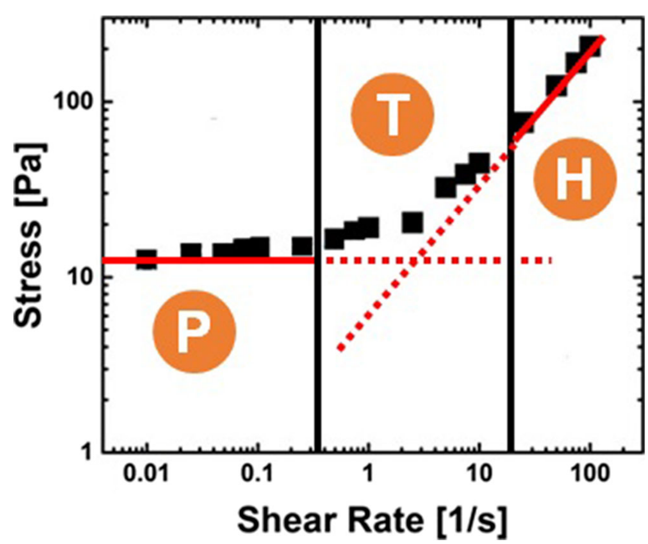

Fig. 11 Steady flow curve of fumed silica suspension. P, plateau; T, transition; H, high rate regimes, respectively

Any rate value in high rate regime can be used as shear rate value in breakdown step.

Appendix 4. Traditional frequency sweep with and without recovery step

We have focused our attention on the effects of pre-shearing with and without a strain recovery step on steady-shear start-up experiments in "Comparison between pre-shears with and without strain recovery." In this section, we expand this to frequency sweep which is traditional linear rheological experiments to show the importance in a general rheological investigation of time-varying materials. We have performed frequency sweeps with four different pre-shear protocols: a traditional one-directional pre-shear at 300 s^{-1} without a strain recovery step; a traditional one-directional pre-shear at − 300 s^{-1} without a strain recovery step; positive one-directional pre-shear at 300 s^{-1} with recovery step with negative direction; and negative one-directional pre-shear at − 300 s^{-1} with recovery step with positive direction. Moreover, frequency sweep can be measured in upward or downward manner. So, we visualized upward frequency sweep without recovery step from positive and negative traditional pre-shear in Fig. 12a, upward frequency sweep with recovery step from positive initial shear and negative initial shear in Fig. 12b, downward frequency sweep without recovery step from positive and negative traditional shear in Fig. 12c, and downward frequency sweep with recovery step from positive initial shear and negative shear in Fig. 12d

.

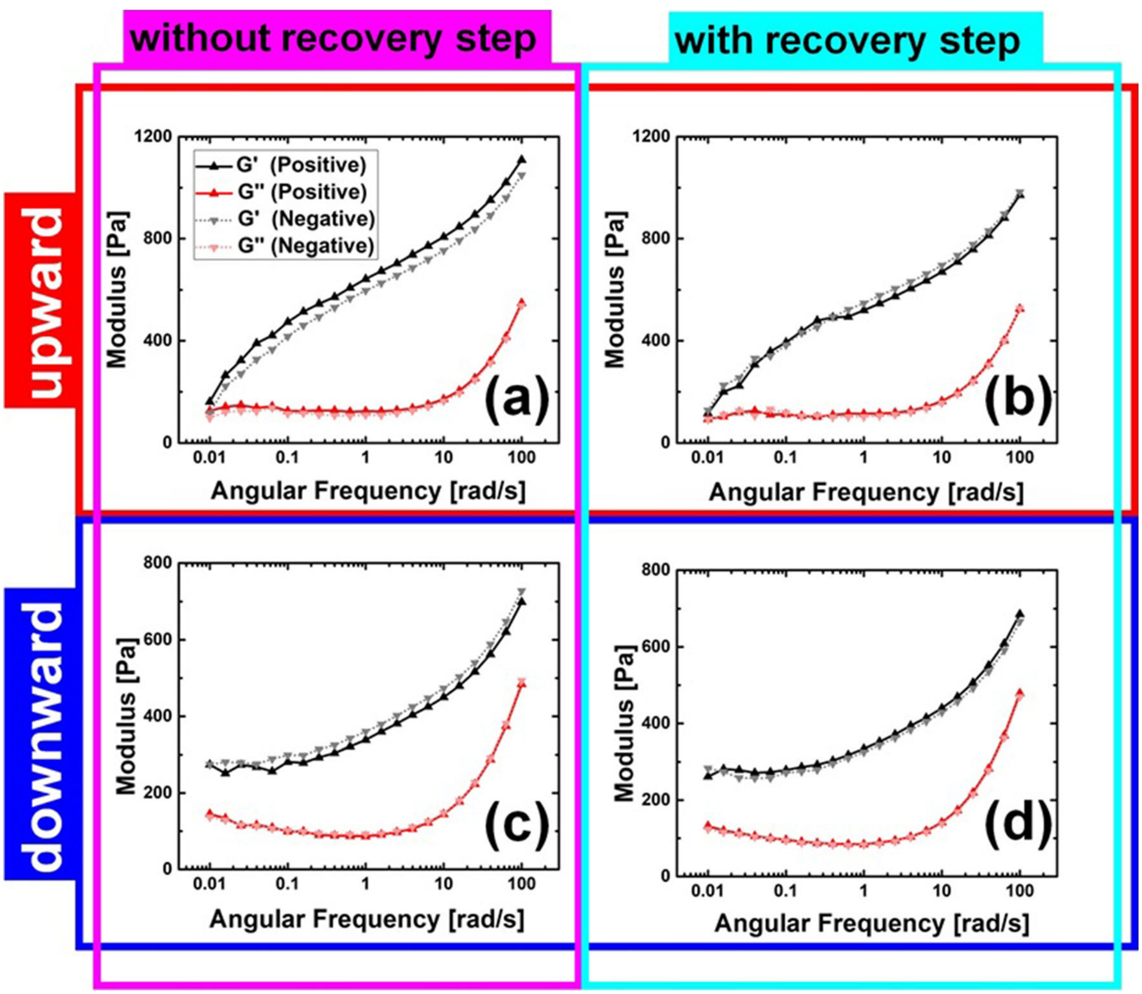

Fig. 12 **a** Frequency sweep measured from low shear rate to high shear rate without recovery step, **b** frequency sweep measured from low shear rate to high shear rate with recovery step, **c** frequency sweep measure from high shear rate to low shear rate without recovery step, and **d** frequency sweep from high shear rate to low shear rate with recovery step

The overall shapes are similar regardless of pre-shear protocols but have a strong dependence on whether high or low frequencies are probed first. Even though the shapes are similar, the values of moduli differ significantly according to the different pre-shear protocols. These results are, in some ways, not surprising. The application of any shearing to a structured thixotropic suspension is going to affect the rheology, and the rate at which the shearing is applied dictates the magnitude of those effects. The choice of high or low frequencies to begin the frequency sweep will therefore impart different shear histories, which one must expect will lead to different rheology, as observed here.

Appendix 5. Determination of linear regime based on amplitude sweeps

We performed strain amplitude sweeps for 0.1 rad s^{-1} and 100 rad s^{-1} to determine linear regime, because we compare frequency sweeps with consecutive and separated ways from 0.1 to 100 rad s^{-1} in "Comparison between consecutive and separated frequency sweep."

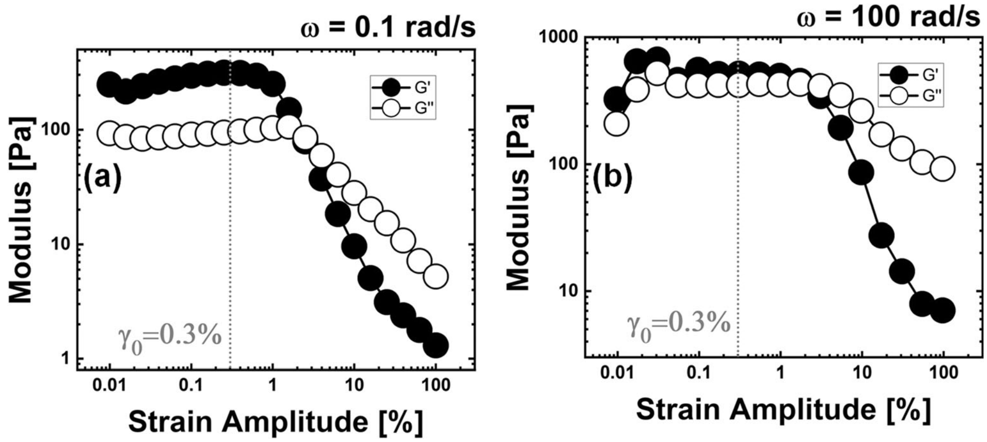

Fig. 13 Strain amplitude sweeps of fumed silica suspension for **a** 0.1 rad/s and **b** 100 rad/s

References

Armstrong MJ, Beris AN, Rogers SA, Wagner NJ (2016) Dynamic shear rheology of a thixotropic suspension: comparison of an improved structure-based model with large amplitude oscillatory shear experiments. J Rheol *60*(3):433–450. https://doi.org/10.1122/1.4943986

Ballauff M, Brader JM, Egelhaaf SU, Fuchs M, Horbach J, Koumakis N, Krüger M, Laurati M, Mutch KJ, Petekidis G, Siebenbürger M, Voigtmann T, Zausch J (2013) Residual stresses in glasses. Phys Rev Lett 110(21):1–5. https://doi.org/10.1103/PhysRevLett.110.215701

Bandyopadhyay R, Liang D, Yardimci H, Sessoms DA, Borthwick MA, Mochrie SGJ, Harden JL, Leheny RL (2004) Evolution of particle-scale dynamics in an aging clay suspension. Phys Rev Lett 93(22):2–5. https://doi.org/10.1103/PhysRevLett.93.228302

Baudez JC (2008) Physical aging and thixotropy in sludge rheology. Appl Rheol 18(1). https://doi.org/10.1515/arh-2008-0003

Bot A, Van Amerongen IA, Groot RD, Hoekstra NL, Agterof WGM (1996) Large deformation rheology of gelatin gels. Polym Gels Network *4*(3):189–227. https://doi.org/10.1016/0966-7822(96)00011-1

Bouchaud JP (1992) Weak ergodicity breaking and aging in disordered systems. J Phys I France 2:1705–1713. https://doi.org/10.1051/jp1:1992238

Cipelletti L, Ramos L (2005) Slow dynamics in glassy soft matter. J Phys Condens Matter 17(6). https://doi.org/10.1088/0953-8984/17/6/R01

Cloitre M, Borrega R, Leibler L (2000) Rheological aging and rejuvenation in microgel pastes. Phys Rev Lett 85(22):4819–4822. https://doi.org/10.1103/PhysRevLett.85.4819

Divoux T, Grenard V, Manneville S (2013) Rheological hysteresis in soft glassy materials. Phys Rev Lett 110(1):1–5. https://doi.org/10.1103/PhysRevLett.110.018304

Dullaert K (2005) Constitutive equations for thixotropic dispersions. Katholieke Universiteit Leuven

Dullaert K, Mewis J (2005) Stress jumps on weakly flocculated dispersions: steady state and transient results. J Colloid Interface Sci 287(2):542–551. https://doi.org/10.1016/j.jcis.2005.02.018

Erwin BM, Cloitre M, Gauthier M, Vlassopoulos D (2010) Dynamics and rheology of colloidal star polymers. Soft Matter 6(12):2825–2833. https://doi.org/10.1039/b926526k

Ewoldt RH, Clasen C, Hosoi AE, McKinley GH (2007) Rheological fingerprinting of gastropod pedal mucus and synthetic complex fluids for biomimicking adhesive locomotion. Soft Matter 3(5):634–643. https://doi.org/10.1039/b615546d

Fernandes RR, Andrade DEV, Franco AT, Negrão COR (2017) Influence of pre-shearing on rheometric measurements of an oil-based drilling fluid. Rheol Acta 56(9):743–752. https://doi.org/10.1007/s00397-017-1027-y

Fielding SM, Sollich P, Cates ME (2000) Aging and rheology in soft materials. J Rheol 44(2):323–369. https://doi.org/10.1122/1.551088

Fritschi S, Fuchs M, Voigtmann T (2014) Mode-coupling analysis of residual stresses in colloidal glasses. Soft Matter *10*(27):4822–4832. https://doi.org/10.1039/c4sm00247d

Gonçalves G, Graça B, Campos AV, Seabra J, Leckner J, Westbroek R (2015) Formulation, rheology and thermal ageing of polymergreases—Part I: influence of the thickener content. Tribol Int *87*:160–170. https://doi.org/10.1016/j.triboint.2015.02.018

Holroyd GAJ, Martin SJ, Graham RS (2017) Analytic solutions of the Rolie Poly model in time-dependent shear. J Rheol *61*(5):859–870. https://doi.org/10.1122/1.4990639

Kitade S, Ichikawa A, Imura N, Takahashi Y, Noda I (1997) Rheological properties and domain structures of immiscible polymer blends under steady and oscillatory shear flows. J Rheol *41*(5):1039–1060. https://doi.org/10.1122/1.550871

Laun HM (1986) Prediction of elastic strains of polymer melts in shear and elongation. J Rheol 30(3):459–501. https://doi.org/10.1122/1.549855

Lee JCW, Porcar L, Rogers SA (2019a) Recovery rheology via rheo-SANS: Application to step strains under out-of-equilibrium conditions. *AIChE Journal*, *September*, pp 1–15. https://doi.org/10.1002/aic.16797

Lee JCW, Weigandt KM, Kelley EG, Rogers SA (2019b) Structure-property relationships via recovery rheology in viscoelastic materials. Phys Rev Lett 122(24):248003. https://doi.org/10.1103/PhysRevLett.122.248003

Leonov AI (1976) Nonequilibrium thermodynamics and rheology of viscoelastic polymer media. Rheol Acta 15(2):85–98. https://doi.org/10.1007/BF01517499

Lescanne M, Grondin P, D'Aléo A, Fages F, Pozzo JL, Mondain Monval O, Reinheimer P, Colin A (2004) Thixotropic organogels based on a simple N-hydroxyalkyl amide: rheological and aging properties. Langmuir 20(8):3032–3041. https://doi.org/10.1021/la035219g

Lodge AS (1958) A network theory of constrained elastic recovery in concentrated polymer solutions. Rheol Acta 1(2–3):158–163. https://doi.org/10.1007/BF01968859

Mewis J, Wagner N (2011) Thixotropy. In Colloidal suspension rheology (Cambridge Series in Chemical Engineering, pp. 228–251). Cambridge: Cambridge University Press. https://doi.org/10.1017/CBO9780511977978.010

Mewis Jan;Wagner NJ (2012) Colloidal suspension rheology. In *Cambridge University Press*. https://doi.org/10.1017/CBO9780511977978

Moghimi E, Jacob AR, Koumakis N, Petekidis G (2017a) Colloidal gels tuned by oscillatory shear. Soft Matter 13(12):2371–2383. https://doi.org/10.1039/c6sm02508k

Moghimi E, Jacob AR, Petekidis G (2017b) Residual stresses in colloidal gels. Soft Matter 13(43):7824–7833. https://doi.org/10.1039/c7sm01655g

Mohan L, Bonnecaze RT, Cloitre M (2013) Microscopic origin of internal stresses in jammed soft particle suspensions. Phys Rev Lett 111(26):1–5. https://doi.org/10.1103/PhysRevLett.111.268301

Mohan L, Cloitre M, Bonnecaze RT (2015) Build-up and two-step relaxation of internal stress in jammed suspensions. J Rheol 59(1):63–84. https://doi.org/10.1122/1.4901750

Møller PCF, Mewis J, Bonn D (2006) Yield stress and thixotropy: on the difficulty of measuring yield stresses in practice. Soft Matter 2(4):274–283. https://doi.org/10.1039/b517840a

Mours M, Winter HH (1994) Mours and Winter_1994_Time-resolved rheometry. *Acta*. Rheol Acta 33:385–397 https://link.springer.com/content/pdf/10.1007%2FBF00366581.pdf

Negi AS, Osuji CO (2010) Physical aging and relaxation of residual stresses in a colloidal glass following flow cessation. J Rheol 54(5):943–958. https://doi.org/10.1122/1.3460800

Osuji CO, Kim C, Weitz DA (2008) Shear thickening and scaling of the elastic modulus in a fractal colloidal system with attractive interactions. Phys Rev E Stat Nonlinear Soft Matter Phys 77(6):8–11. https://doi.org/10.1103/PhysRevE.77.060402

Petekidis G, Vlassopoulos D, Pusey PN (2004) Yielding and flow of sheared colloidal glasses. J Phys Condens Matter 16(38). https://doi.org/10.1088/0953-8984/16/38/013

Philippoff W, Gaskins FH, Brodnyan JG (1957) Flow birefringence and stress. V. Correlation of recoverable shear strains with other rheological properties of polymer solutions. J Appl Phys 28(10):1118–1123. https://doi.org/10.1063/1.1722590

Pipkin AC (1986) Lectures on viscoelasticity theory. Springer

Radhakrishnan R, Fielding SM (2018) Shear banding in large amplitude oscillatory shear (LAOStrain and LAOStress) of soft glassy materials. J Rheol 62(2):559–576. https://doi.org/10.1122/1.5023381

Reiner M (1958) Encyclopedia of physics VI. Springer-Verlag

Rogers SA, Callaghan PT, Petekidis G, Vlassopoulos D (2010) Time-dependent rheology of colloidal star glasses. J Rheol 54(1):133–158. https://doi.org/10.1122/1.3270524

Rogers SA, Vlassopoulos D, Callaghan PT (2008) Aging, yielding, and shear banding in soft colloidal glasses. Phys Rev Lett 100(12):1–4. https://doi.org/10.1103/PhysRevLett.100.128304

Rogers SA, Erwin BM, Vlassopoulos D, Cloitre M (2011) A sequence of physical processes determined and quantified in LAOS: application to a yield stress fluid. J Rheol 55(2):435–458. https://doi.org/10.1122/1.3544591

Smith TL, Tschoegl NWT (1970) Rheological properties of wheat flour doughs. Rheol Acta:339–344

Sollich P, Lequeux F, Hébraud P, Cates ME (1997) Rheology of soft glassy materials. Phys Rev Lett 78(10):2020–2023. https://doi.org/10.1103/PhysRevLett.78.2020

Sun W, Yang Y, Wang T, Huang H, Liu X, Tong Z (2012) Effect of adsorbed poly(ethylene glycol) on the gelation evolution of Laponite suspensions: aging time-polymer concentration superposition. J Colloid Interface Sci 376(1):76–82. https://doi.org/10.1016/j.jcis.2012.01.064

Wei Y, Solomon MJ, Larson RG (2016) Quantitative nonlinear thixotropic model with stretched exponential response in transient shear flows. J Rheol 60(6):1301–1315. https://doi.org/10.1122/1.4965228

Weissenberg K (1947) A continuum theory of rheological phenomena. Nature 159:310–311