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Viscoelasticity of coagulated alumina suspensions

Ashish Kumar, Anthony D. Stickland* and Peter J. Scales
Particulate Fluids Processing Centre, Department of Chemical & Biomolecular Engineering,
The University of Melbourne, Victoria 3010, Australia

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Abstract

The solid-to-liquid transition of a model coagulated alumina suspension at concentrations above the gel point was investigated to explore the critical parameter for describing network failure under shear forces. Static (creep and creep-recovery) and dynamic (small and large amplitude oscillatory) shear experiments were combined to examine shear softening in these systems and time-based dependence in the yielding dynamics. The particulate network structure exhibits failure and viscous dissipation under creep and oscillatory shear tests at stress values well below the conventionally defined yield stress. Results from strain recovery tests highlight a time-dependence for failure, where only partial recovery of strain energy was possible once a specific duration of creep was surpassed. The system was observed to fail at a common strain value across all methods of rheology testing. These results are self-consistent, showing a clear transition from the linear to non-linear viscoelastic region for a coagulated material under shear stress. It provides the starting point to incorporate mechanical viscoelastic models to extract time constants for yielding behaviour. This work also presents one of the first reported LAOS and creep results for particulate suspensions using a vane geometry.

Keywords **:** suspension rheology, viscoelasticity, alumina, yield stress, creep, Lissajous plot, Fourier transform rheology

1. Introduction

The rheology and flow behaviour of particulate suspensions has been the subject of extensive research aimed at predicting and optimising suspension transport and handling processes such as pipeline flow, mixing, solid-liquid separation and pumping. These suspensions encompass materials such as mineral slurries, biomass, pigments and mine tailings; the efficient processing of which is significant from economic, environmental and social standpoints. As the particulate concentration of these suspensions increases, they reach a critical concentration at which they become networked (the gel point concentration - ϕ_g) and are characterised by a yield stress in shear and compressional flows (Nguyen and Boger, 1983; Nguyen and Boger, 1985; Buscall and White, 1987).

Suspension rheology is the study of the flow and deformation of particulate suspensions. The shear properties are commonly described using generalised viscoplastic models, such as Herschel-Bulkley or Bingham fluids, both of which make use of a yield stress term to model viscosity behaviour as a function of shear rate. Arising from the presence of a networked structure, the yield stress is popularly defined as the stress at which a material transitions from solid-like behaviour to liquid-like flow. The application and existence of this term however, has been the subject of intense debate - early works by Barnes and Walters (1985) and Evans (1992) hinted at the possibility of flow eventually developing in a material, however slowly or small the applied stress. Characterisation experiments by several authors subsequently concluded that a measured yield stress corresponds to the transition between viscoelastic to fully viscous flow (Bird *et al.*, 1982; Hartnett and Hu, 1989; Liddell and Boger, 1995) and that the presence of a low-shear viscosity plateau is characteristic of a weakly flocculated material (Buscall *et al.*, 1993). However, the work presented herein pertains to strongly flocculated suspensions.

Despite these differing schools of thought, the concept of yield stress behaviour is widely exploited in the realm of engineering for the prediction and design of a range of industrial processes. For example, the shear yield stress is used to predict the start up of pipelines and compressive yield stress to predict the dewatering of suspensions (Nguyen and Boger, 1985; Stickland and Buscall, 2009). Yield stress materials have since been characterised with respect to particle physics, solids concentration and surface chemistry (Channel and Zukoski, 1997; Kapur *et al.*, 1997;

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*Corresponding author: stad@unimelb.edu.au

Zhou *et al.*, 1999) but more work to better understand the contributions of network rigidity and strength on yielding is still required.

Numerous works show a structural and time dependence for yielding and network failure, suggesting this transition is more complex and occurs over a range of stresses, rather than at a single point (Barrie *et al.*, 2004; Uhlherr *et al.*, 2005; Le Grand and Petekidis, 2008; Gibaud *et al.*, 2010). It has been suggested that the onset of yielding will depend strongly on the critical strain, γ_c as a descriptor of yielding – a parameter well known in the characterisation of polymer melts (Wilhelm *et al.*, 2000; Noirez *et al.*, 2009). Nonetheless, its measurement as the transition from linear to non-linear viscoelastic behaviour for coagulated particulate systems has not been reported systematically for a range suspension conditions. This problem is compounded by difficulties in accurately measuring aggregate deformation dynamics due to wall slip and machine sensitivity in rheometry and shear history-dependent behaviour.

Viscoelastic behaviour can be observed using static rheometry. In creep tests, a fixed value of stress is applied and the strain measured. An elastic response is fixed strain whilst a viscous response is constant strain-rate. Viscoelastic behaviour can manifest as instantaneous and retarded elastic responses, and either elastic or viscous behaviour at long times depending on whether the material has yielded. Non-linear viscoelastic behaviour can be observed at applied stresses below the yield stress using this technique. An alternative static test is stress relaxation, which involves applying a fixed strain and measuring the stress.

Dynamic rheometry incorporating oscillatory shear measurements also offer a suitable means to investigate the deformation of complex materials. The onset of a non-linear viscoelastic response in a particulate system marks the diminishing proportionality between the input and output rate of sinusoidal deformation (Nguyen and Boger, 1992; Uhlherr *et al.*, 2005), providing a glimpse into bond strengths and distributions. While the yielding dynamics of material exhibiting linear viscoelasticity is well documented with sound mathematical theory (Macosko, 1994), the yielding processes of more complex particulate systems such as mineral slurries and suspension gels are non-linear even at very low strains. Henceforth, the sole use of linear viscoelastic measurements is insufficient to fully characterise yielding behaviour – the yielding process is potentially a combination of non-linear and transient dynamics.

A more suitable, albeit less common, technique of large amplitude oscillatory shear (LAOS) tests can be used to explore the yielding mechanics of complex systems - due in part to the contribution of higher order harmonics (Nguyen and Boger, 1992; Wilhelm *et al.*, 1998). The presence of these harmonics is a contributor to the breakdown of the linear viscoelastic equations as discussed by Wilhelm *et al.* and can be analysed using Fourier Transforms (FT). While the basic principle of FT rheology has been discussed (Giacomin and Dealy, 1993), it's application to the full range of non-linear properties was investigated by Wilhelm *et al.*, (1998).

The basic approach involves the decomposition of the output waveform for a function in the time domain to obtain a frequency dependent spectrum (Wilhelm *et al.*, 1998). LAOS measurements deform the test material into the non-linear viscoelastic region, causing harmonic distortions of the shear stress response. These higher order harmonics can be analysed using FT rheology with respect to their frequencies, applied stress or strain amplitudes, and phase angles (Wilhelm, 2002). A sensitivity analysis on FT rheology outputs makes it an excellent technique for determining the linear viscoelastic limits of structured yield stress materials.

In this work, the transient dynamics and non-linear process by which a model networked particulate structure (coagulated alumina) fails before yielding are investigated using static (creep and creep-recovery) and dynamic (small and large amplitude oscillation) rheological techniques. Creep and creep-recovery data was analysed by plotting the change in strain as recorded by the rheometer, as a function of time. Fourier Transforms (FT) were employed to process LAOS data, uncovering microscopic network contributions to non-linear viscoelasticity. The oscillatory shear data is presented graphically in the form of Lissajous curves or plots as a means of distinguishing strain hardening or softening within these systems (Ewoldt and McKinley, 2010). The tests use a four-bladed vane, favoured over other configurations (*e.g.* parallel plate or cup-and-bob) as it is able to eliminate the errors associated with wall slip phenomena. Direct measurement also eliminates errors associated with the extrapolation of viscosity measurements (Liddell and Boger, 1995; Johnson *et al.*, 2000). This work presents, for the first time, the use of the vane geometry in oscillatory shear experiments of a suspension to elucidate a yield criterion for suspensions.

2. Experimental Materials and Methods

2.1. Sample preparation

The alumina used in this study has been characterised in detail by Zhou *et al* (1999; 2001). The alumina (AKP-30, Sumitomo Chemicals Pty. Ltd, Japan) was characterised by nearly spherical particles with a density of 4.0 g.cm^{-3} and a mean diameter of 360 nm.

Alumina suspensions were prepared at a volume fraction, ϕ, of 0.20 by mixing the alumina powder in a 0.01M KNO_3 background electrolyte solution; this corresponded to a nominal yield stress of 85.0 Pa as measured using the Nguyen and Boger (1985) vane technique. The mixture was acidified using 1M HNO_3 to an approximate pH of 5 at which the suspension was fully dispersed. The mixture was then sonicated with a high intensity sonic probe (Misonix™ S4000 Sonicator and 12.5 mm horn, 20 kHz, 800 W) to break up any remaining lumps or granules, and then left to rest for 24-48 hours to establish physical and chemical equilibrium.

Before measurements, the pH was adjusted using 1M KOH to the isoelectric point (IEP) of approximately pH 9.2 (Fisher *et al.*, 2007) and allowed to rest for a minimum of 2 hours. All reagents were made using water from a Milli-Q system (Millipore™ Synergy®, 0.22 μm filter) and pH measurements made using a Sensorex® Combination pH electrode (Denver Instrument Company).

2.2. Experiments

Creep, creep-recovery and oscillatory shear experiments were performed in a stress-controlled rheometer (AR-G2, TA Instruments) using a vane (d_v = 28.0 mm, h_v = 42.0 mm) in cup (d_c = 30.0 mm, h_c = 80.0 mm) geometry. Vane yield stresses were measured on a rate-controlled rheometer (Haake VT550, Thermo Scientific) according to the method presented by Nguyen and Boger (1983; 1985). The sample was sheared between successive applied stresses, thereby negating thixotropy effects.

During creep, a constant stress was applied to the sample and the resulting increase in strain, γ, measured as a function of time. The rebound of material structure after removing this applied stress was then recorded in creep-recovery tests.

Small and large amplitude oscillatory shear (SAOS and LAOS) tests in this work were limited to dynamic time sweeps at specific shear stresses ranges between 10 – 100 Pa, applied at a frequency, ω, of 10 rad.s^{-1} over a duration of 5 minutes. The resulting strain was logged for further analysis.

3. Results and Discussion

3.1. Creep compliance

Fig. 1 shows the results of creep experiments performed on the coagulated alumina sample when subjected to increasing values of applied stresses, *i.e.* 1, 10, 50, 80 and 100 Pa. The results are plotted in the form of creep compliance, $J = \gamma/\tau$, which allows easy identification of nonlinear viscoelasticity (*i.e.* strain that is not linear with stress) and time dependent yielding. The material response as a function of time is described in terms of instantaneous elasticity, retarded elasticity and viscous flow (Barnes *et al.*, 1993; Barnes, 2000). Below the vane yield stress, measured previously at 85 Pa using the method of Nguyen and Boger (1985), the compliance response can be categorised into three regions.

Initially, for t < 0.005 s, creep ringing was observed and attributed to the rotational inertia in the system (Barnes, 2000). Next, an elastic region (0.005 < t < 0.05 s) followed by material creep, with increasing contributions of viscous behaviour manifesting at long time periods. The relaxation times for the initial deformation were approximately 10 s at the low stresses. This region of creep diminished to less than 1 s at the highest stress. The long term retarded elasticity time constant also decreased with stress from approximately 10^4 s to 100 s. The results generally indicate a time-dependent yielding process.

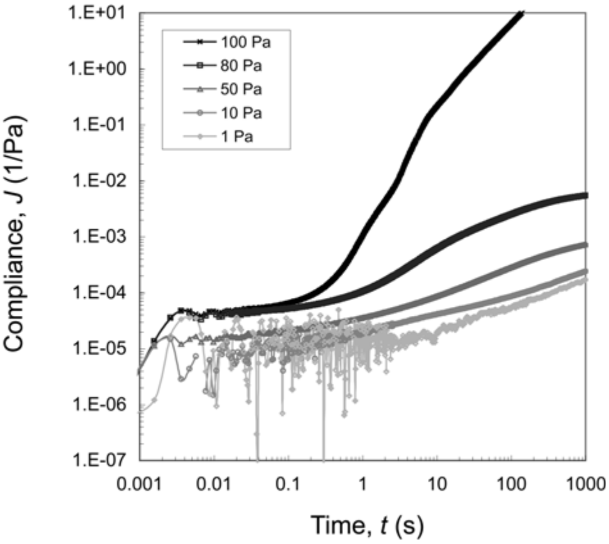

Fig. 1. Compliance behaviour of coagulated alumina (ϕ = 0.20 at IEP) under increasing applied stresses.

However, at no time was truly viscous flow attained even at extended test durations, *i.e.* the compliance curve does not attain a slope of unity (on a log-log plot) (Barnes *et al.*, 1993; Barnes, 2000), and the network strain continued to drift for as long as the test persisted (maximum of 24 hours). Should the applied stress deform the network structure sufficiently to reach a particular strain, the material is expected to fail irrespective of the applied stress. Only when the alumina system was subjected to an applied stress of 100 Pa ($\tau > \tau_y$) does viscous flow manifest within the timeframe under observation. Creep at long periods below the nominal yield stress of 85 Pa may eventually flow, slowly creep, or cease completely; each case provides critical information about the microstructure, but are beyond the measurement times in this work. The results indicate the material simply rearranges according to the inter-particle forces, rather than yielding into viscous flow.

Note that the scatter of results ($J < 10^{-4}$) is a consequence of instrument measurement limitations when attempting to record extremely small strain values.

3.2. Creep-recovery

Creep-recovery tests saw the application of 10 Pa creep test at 1, 5, 10, 100, and 1000 s durations (see Fig. 2). This value of applied stress was chosen in order to probe the

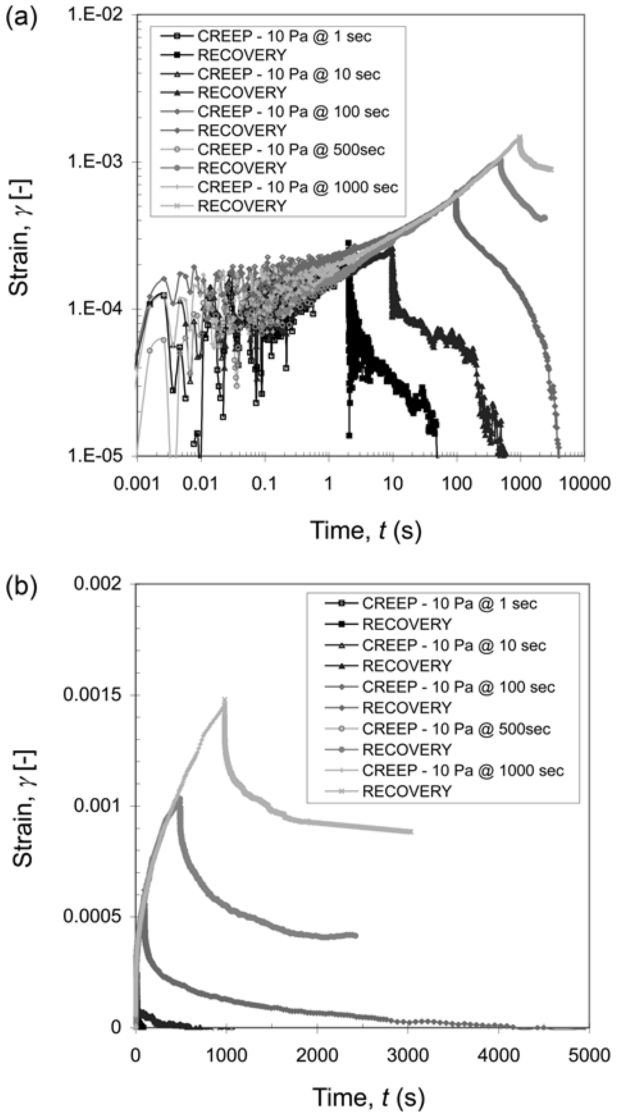

Fig. 2. (a) Log-log plot and (b) linear-linear plot of creep-recovery behaviour of coagulated alumina (ϕ = 0.20 at IEP) under increasing durations of creep, applied at 10 Pa.

yielding dynamics of the system rather than cause immediate network failure. This test was followed by the removal of the applied stress to allow the strain to recover, providing information surrounding the elasticity of the coagulated alumina network. Once again, the instrument feedback-control mechanism affects low strain values.

Creep durations at $t < 100$ s ($\gamma < 7\times10^4$) appear to deform the material elastically, as shown by the nearly complete strain recovery after the removal of the applied stress. The recovery shows instantaneous and retarded elastic behaviour. For longer creep times, viscous deformation was observed, characterised by the irreversible conversion of mechanical creep to internal energy. This manifests as partial strain recovery, as summarised in Table 1, where approximately 60% of the strain was recovered after 500 s of creep, and only 40% recovery after 1000 s of creep.

Table 1. Summary of total strain recovered following increasing durations of applied creep

Applied Stress, τ (Pa)	Creep duration, t (s)	Strain recovered, γ (%)
10	1	100
10	10	100
10	100	100
10	500	60.6
10	1000	39.3

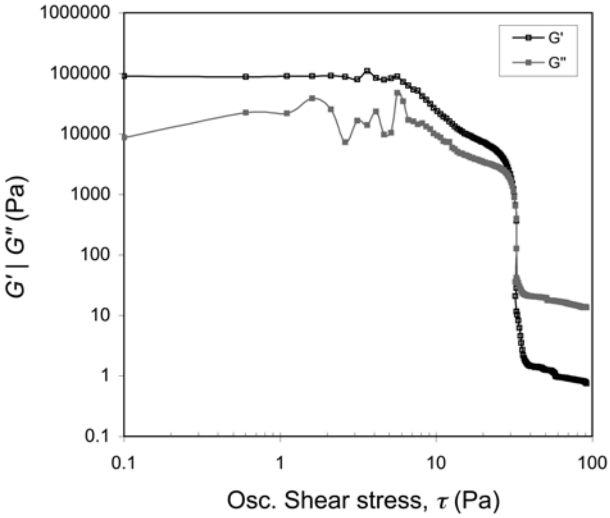

Fig. 3. Elastic and storage moduli as functions of shear stress for coagulated alumina suspension (ϕ = 0.20 at IEP) at ω = 10 rad/s.

The reduced recoverable strain indicates a time-dependence for network fracture at applied stress values well below the conventional yield stress.

3.3. Fourier transform rheology

The non-linear strain response of a material is commonly detected using a dynamic strain or stress sweep (Barnes, 2000), uncovering the regime in which the elastic moduli (G' or G'') begin to break down (Fig. 3). The results indicate that coagulated alumina at 0.20 v/v begins to show non-linear behaviour at approximately 7 Pa. G' and G'' are, however, only the 1st harmonic of the non-linear response. FT rheology, on the other hand, provides deeper insight into the dynamics of yielding when a LAOS is applied outside the linear viscoelastic region.

Fig. 4 shows the normalised harmonic spectrum $I(\omega_n)/I(\omega_1)$ of the coagulated alumina system under increasing

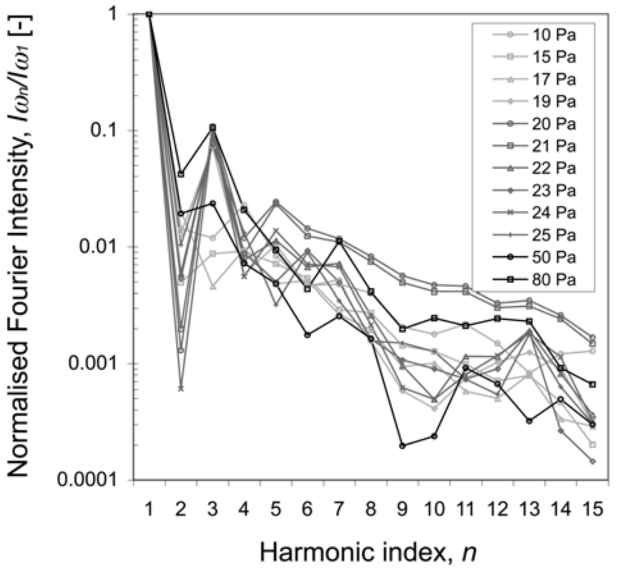

Fig. 4. Normalised power spectrum as a function of applied oscillatory stress for a coagulated alumina system (ϕ = 0.20 at IEP) at ω = 10 rad/s.

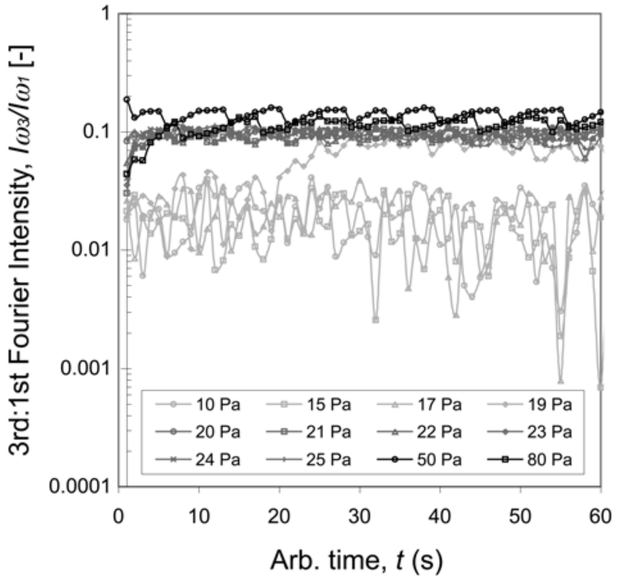

Fig. 5. Plot of the 3rd:1st harmonic intensity as a function of time for a coagulated alumina system (ϕ = 0.20 at IEP) at ω = 10 rad/s.

values of applied stress. Fig. 5 shows the FT intensity spectrum of the normalised 3rd harmonic against the fundamental harmonic, $I(\omega_3)/I(\omega_1)$, as a function of test time at increasing applied stress amplitudes. This harmonic ratio is most dominant and the first to exhibit the presence of higher order harmonics (Wilhelm *et al.*, 1998; Wilhelm *et al.*, 2000). For this reason, $I(\omega_3)/I(\omega_1)$ will be used to detect the limits of the linear viscoelastic region from the FT analysis of oscillatory shear data.

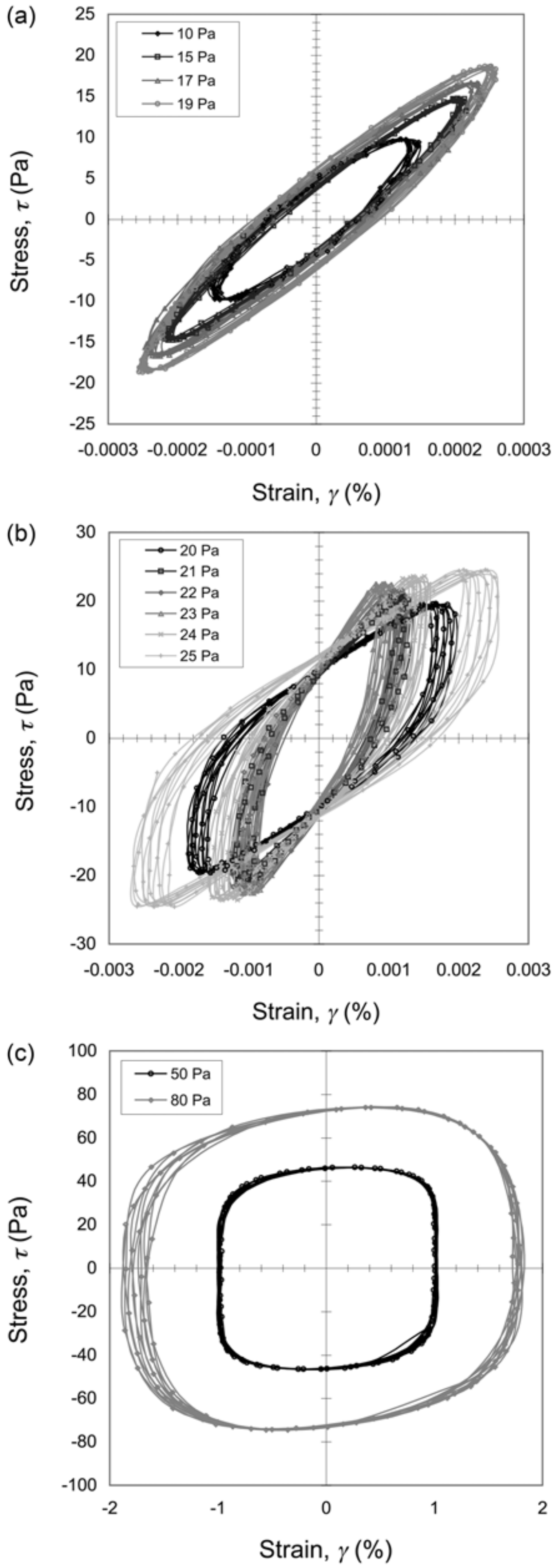

Fig. 6. Lissajous plots showing the stress-strain response for coagulated alumina at applied stresses between (a) 10- 19 Pa, (b) 20-25 Pa, and (c) 50-80 Pa; frequency of 10 rad/s (1.6 Hz), ϕ = 0.20 at IEP.

These results show higher order harmonics developing after a critical stress amplitude, $\tau_c = 20.0$ Pa, and continues to burgeon with increasing applied stresses. This coagulated material was no longer able to exhibit a linear viscoelastic response because of changes in the microstructure, where incremental increases in shear stresses result in increasingly greater deformations within the particulate network.

3.4. Lissajous curves

Lissajous plots for a range of applied stresses are shown in Fig. 6. In the linear viscoelastic regime, a Lissajous curve approximates an ellipse, while increasing non-linearity in the material strain response causes deformations to the ellipsoidal shape. This transition was observed to occur at 20-25 Pa, during which the curves were no longer ellipsoidal and show strain deformations of an order of magnitude larger than those in the linear regime (10-19 Pa applied stress).

This transition coincides precisely with the burgeoning ratio of the 3rd:1st harmonic, from the FT analysis previously, over the same applied stress range. This indicates an approximate critical stress, τ_c, of 19.0 Pa, with the corresponding critical strain, γ_c, estimated as 2.5×10^{-4} %, for this frequency.

Combined, the creep and oscillation results provide evidence of the gradual weakening of the microscopic structure within networked particulate systems. When subjected to applied stresses during creep, a gradual increase in strain is observed before the strain rate eventually slows down, and then drifts indefinitely. This behaviour suggests a wide distribution of bond strengths in the system, with the weakest bond components progressively disrupted during the creep procedure. The slowing of the strain rate at long times may be a result of inter-particle forces such as van der Waals interaction and the associated particle dynamics as a result of Brownian motion continually regenerating the network structure, therefore preventing fully viscous flow from developing. Creep-recovery and LAOS experiments provide further evidence of this, showing a clear transition to a non-linear material response when subjected to a critical stress value, highlighting the systems inability to recovery its strain energy once deformed beyond a critical strain in a given time (in this case 1.6 Hz).

4. Conclusions

The yielding dynamics of a model coagulated alumina system was investigated through a combination of static and dynamic rheological experiments. Creep results offer insight into the distribution of bonding strengths within this system, suggesting that they appear to fail continuously for all values of applied stress due to the failure, reformation and rearrangement of inter-particle bonds associated with weakly aggregated systems. Creep-recovery experiments highlight a strong time-dependence for network failure, with only partial strain recovery at small applied stresses. LAOS measurements analysed via FT-Lissajous plots allowed for the clear distinction between linear and non-linear viscoelasticity manifesting in these systems at sufficiently small stresses.

The failure of a particulate network can therefore take place at stress values well below the conventional yield stress, provided sufficient time is allowed, although below a characteristic time for a given stress, full recovery is possible. This characteristic time reduces as the applied stress increases.

These results provide the basis for further understanding critical yielding behaviour of coagulated systems. In addition, comparisons with the yielding dynamics of polymer-flocculated systems will provide insight into both types of aggregated particulate suspensions.

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List of Symbols

d_c	Cup diameter, mm
d_v	Vane diameter, mm
ϕ	Solids volume fraction, v/v
γ	Strain
γ_c	Critical strain
h_c	Cup height, mm
h_v	Vane height, mm
$I(\omega_n)$	Intensity of nth harmonic.
J	Compliance, (1/Pa)
M	Molar, mol/L
ω	Angular velocity, rad/s
t	Time, s
τ	Shear stress, Pa
τ_c	Critical stress, Pa
τ_y	Vane yield stress, Pa

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