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Dynamic and rate-dependent yielding in model cohesive suspensions

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ABSTRACT

An experimental system has been found recently, a set of coagulated $CaCO_3$ suspensions, which shows very variable yield behaviour depending upon how it is tested and, specifically, at what rate it is sheared. At Péclet numbers (Pe) > 1 it behaves as a simple Herschel–Bulkley liquid, whereas at Pe < 1 highly non-monotonic flow curves are seen. In controlled stress testing it shows hysteresis and shear banding and in the usual type of controlled stress scan routinely used to measure flow curves, it can show very erratic and irreproducible behaviour. All of these features appear to arise from a dependence of the solid phase, or yield stress, on the prevailing rate of shear at the yield point. Stress growth curves obtained from step strain-rate testing showed that rate-dependence was a consequence of Péclet number dependent strain softening. At very low Pe, yield was cooperative and the yield strain was order-one, whereas as Pe approached unity, the yield strain reduced to that needed to break inter-particle bonds, causing the yield stress to be greatly reduced.

It is suspected that rate-dependent yield could well be the rule rather than the exception for cohesive suspensions more generally. If so, then the Herschel–Bulkley equation can usefully be generalized to read $\sigma = \sigma_0 g(\dot{\gamma}) + \sigma_{iso} + k\dot{\gamma}^n$ (in simple shear). The proposition that rate-dependent yield could be general for cohesive suspensions is amenable to critical experimental testing by a range of means and along lines suggested.

1. Introduction

An earlier paper [1] described the shear flow of two strongly cohesive suspensions showing highly non-monotonic flow curves, one of which was a 40% v/v suspension of 4.5 μm $CaCO_3$ in water, coagulated by taking its pH close to the iso-electric point. Here the rheology of the $CaCO_3$ system is examined in more detail with an emphasis on transient behaviour and how it controls the steady state. The effect of solids concentration on the shear rheology will also be reported.

The way in which the original 40% v/v $CaCO_3$ system presented itself as a yield stress liquid was found to depend upon how it was caused to flow [1], as is summarised in Table 1 below. With regard to the table, please note that 'CR' denotes 'controlled rate', that 'CS' means 'controlled stress' and that Pe_0 is the so-called 'bare' Péclet number, $6\pi\bar{a}^3\mu\dot{\gamma}/k_B T$ $\bar{a}$ where is the mean particle radius, μ the viscosity of the liquid phase, T is absolute temperature, k_B is Boltzmann's constant and $\dot{\gamma}$ is the shear-rate.

Table 2 summarises the variation of the apparent yield stress with test type and compares it with a pattern reported earlier by Pham et al. [3] for a weakly-cohesive but very concentrated (60% v/v) non-aqueous dispersion of PMMA particles, depletion-flocculated with dissolved polystyrene. Pham et al. did not see shear-rate dependent yield, but that apart, their variation in apparent yield stress follows a pattern not dissimilar to that seen for $CaCO_3$, qualitatively-speaking.

In [1] it was suggested that the Herschel–Bulkley equation [4] be modified as follows in order to account for the flow curves obtained by controlled rate testing,

$$\sigma = \sigma_s + k_1\dot{\gamma}^n \Rightarrow \sigma_0 g(\dot{\gamma}) + \sigma_{iso} + k_1\dot{\gamma}^n. \quad (1.1)$$

In Eq. (1.1) the yield stress has been split into two parts, a shear-rate dependent part, taken to decrease with increasing shear-rate and to decay to zero at some point, together with a second fixed solid-phase stress term, σ_{iso}, included to recover Herschel–Bulkley as limiting behaviour at higher shear rates.

The flow curve and the fits are re-plotted in Fig. 1 with some additions. Please note also that an error made in the original plot in [1] has been corrected and doing so has changed the position of the falling part of the curve on the abscissa somewhat. It

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Table 1
Yield behaviour depends upon test type.

	Test protocol	Test type	Behaviour
A	An ascending "staircase" of shear rates in time, all at $Pe_0 > 1$	CR	Herschel–Bulkley [1]
B	As above but starting from $Pe_0 \ll 1$	CR	Non-monotonic flow curve [1]
C	Creep testing at a series of stresses	CS	Time-dependent yield over a modest range of stress [2]
D	An ascending "staircase" of stresses in time (CS flow curve)	CS	Erratic yield and shear banding [1]
E	As above but with a return down the staircase of stresses	CS	Hysteresis between ascending and descending branches [1]

Table 2
Approximate variation in apparent yield stress by method compared with that seen by Pham et al. [3].

Method	Pham et al. PMMA [3] $\varphi = 0.6$	$CaCO_3$ [1] $\varphi = 0.4$
Peak stress on flow start-up @ constant shear-rate	1	0.5–1 (rate-dep^t)
Strain sweep or staircase	0.67	>0.5
Stress sweep or staircase	0.56	0.26–0.36
Extrapolation from flow curve	0.13	~0

The stress values have been scaled on the largest value measured.

improves the fit to the peak stress on the rising branch too. In the case $CaCO_3$ at 40% v/v, the residual yield stress, σ_{iso}, could be taken as zero for fitting purposes, although it need not be more generally; indeed, it was substantial for the other suspension described in [1], for example, and it becomes significant for the $CaCO_3$ system herein at concentrations >40% v/v.

Because of the difficulty of converting angular velocity to shear rate in the case of such a complex flow curve, it was expedient to fit the raw flow curve of stress versus angular velocity in the first instance, using, by analogy to Eq. (1.1),

$$\sigma = \sigma_s + k'\Omega^n = \sigma_0 g_{app}(\Omega) + \sigma_{iso} + k'\Omega^n. \tag{1.2}$$

This in turn is tantamount to fitting using the apparent, Newtonian shear rate $\dot{\gamma}_N$ thus,

$$\sigma = \sigma_s + k'\dot{\gamma}_N^n = \sigma_0 g_{app}(\dot{\gamma}_N) + \sigma_{iso} + k\dot{\gamma}_N^n. \tag{1.3}$$

since $\dot{\gamma}_N$ is proportional to Ω. Such a fit gives a true value for the power-law index n and apparent values for the consistency index and the softening function. The problem of estimating the true shear rate will be addressed in section 2.

It can be seen from Fig. 1 that solid phase stress drops to zero logarithmically, thus the overall fit to the stress took the functional form,

$$\sigma \approx \sigma_{fit} = k_0 \ln(\dot{\gamma}_N^0/\dot{\gamma}_N) + k\dot{\gamma}_N^n. \tag{1.4}$$

where $\dot{\gamma}_N^0$ is the value of $\dot{\gamma}_N$ at which the fitted stress appears to extrapolate to zero. From the upper axis in Fig. 1 it can be seen that σ_s does so at an apparent bare Pe_{0N}, calculated from the Newtonian shear-rate at the vane (hence Pe_{0N}), of order unity. The observation that the solid-phase stress decreases with Pe is unprecedented, so far as we are aware. Koumakis and Petekidis [5], working on the same system as Pham et al. [3], did not see any such effect at values similar to Pe_{0N}, for example. They did however suggest that an effect of Pe was to be expected, but that it should be seen at very high $Pe_0 \gg 1$. They proposed that it should be controlled by a re-scaled Péclet number, $Pe_{dep} \sim F\, Pe_0$, where F is the magnitude of the dimensionless inter-particle cohesive force. For the $CaCO_3$ suspensions of interest here, Pe_{dep} is conservatively estimated to be at least 10^5 Pe_0 (from a consideration of the Van der Waals forces); hence it is clear that Koumakis and Petekidis' expectation is not borne out in practice. Indeed, from the left-hand side of Fig.1, it can be seen that softening is already underway at Pe_{0N} values ca. eight orders of magnitude lower. Possible reasons why Koumakis and Petekidis' experimental system did not show softening at $Pe_{0N} < 1$, whereas the $CaCO_3$ system does, will be suggested later.

The scaling rule of Koumakis and Petekidis, $Pe_{dep} \sim F\, Pe_0$, was based on the idea that there is a competition between shear disrupting the local environment, or 'cage' and diffusion and re-bonding trying to re-form it, which is entirely reasonable so far as it goes, of course. It is suspected though, that they might

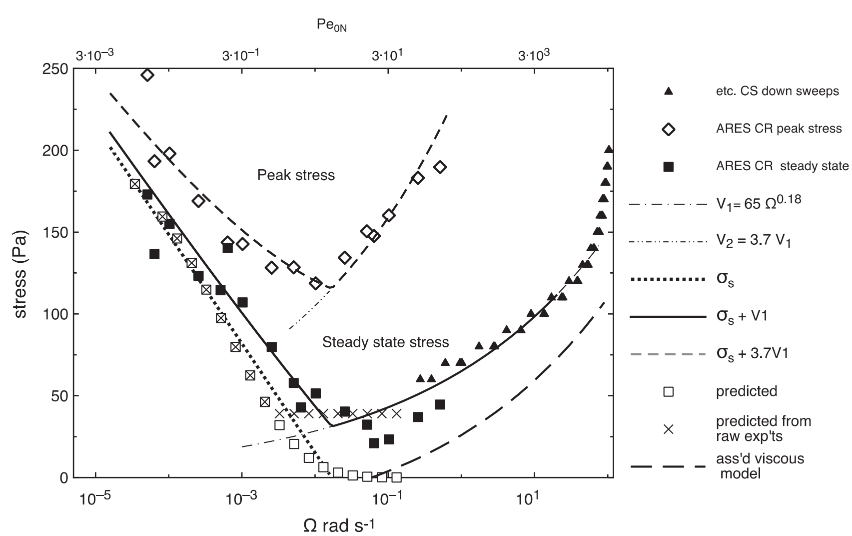

Fig. 1. Flow curves re-plotted from [1] for 40% v/v coagulated $CaCO_3$ with a numerical error in [1] corrected, which inter alia improves the peak stress fit. The larger filled squares come from controlled rate measurements. The smaller triangles to the right are from controlled stress testing, stepping the stress downwards from the highest value. The total steady-state stress can be fitted by using the sum of a solid-phase term $\sigma_s = \sigma_0 g(\dot{\gamma})$, assumed to decrease logarithmically, and a power-law viscous term V_1: note also that a shear-thickening region at the extreme right [1] has been ignored in the fit. The peak stress measured in start-up can be modelled using the same value of σ_s but with a larger viscous term = 3.7 V_1. The crosses and unfilled squares represent predicted values for the solid-phase stress σ_s calculated from the strain-softening exponents discussed in section 3.3 using Eq. (3.8) (see text for details). The upper axis shows the apparent 'bare' Péclet number calculated from the apparent, or Newtonian shear-rate at the vane, the subscript N denoting this.