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# Universal behaviour of silica suspensions gelled under shear\*

H J M Hanley<sup>1,2</sup>, C D Muzny<sup>3</sup>, J Bartlett<sup>1</sup> and E Drabarek<sup>1</sup>

<sup>1</sup> Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW 2234, Australia

<sup>2</sup> Australian National University, Canberra, ACT 0200, Australia

<sup>3</sup> Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, CO 80305, USA

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## Abstract

The shear-influenced gelation of three aqueous suspensions consisting of silica particles of nominal diameter 7, 12 and 24 nm, respectively, is reported. It is shown that the viscosity/stress of a gelling system increases with time after gel initiation, reaches a maximum, then falls to a plateau value. A very simple relation between this maximum stress and the precursor volume fraction is verified experimentally.

(Some figures in this article are in colour only in the electronic version)

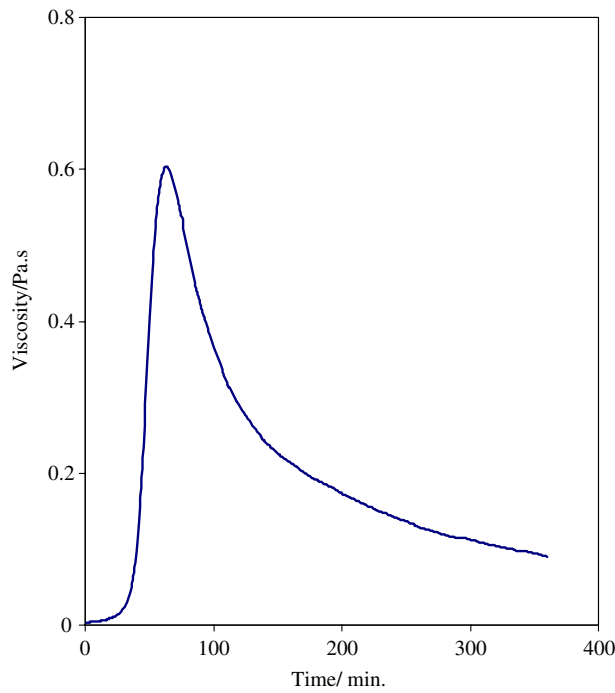
A few years ago we discussed how an applied shear affects the gelation process in a dispersion of colloidal silica [1, 2]. As reported in that work we initiated gelation in a given suspension of volume fraction,  $\phi$ , subjected the system to a steady shear rate,  $\gamma$ , and recorded the viscosity/stress as a function of time. In the limit when the shear rate approached zero the viscosity,  $\eta$ , increased as the gelation advanced until, as expected, it became essentially infinite at a time defined loosely as the gel time,  $t_m$ . At finite shear rate, however, we found that the final gel state was postponed; specifically, that the viscosity initially increased with time but then peaked at a time  $\sim t_m$  until finally decreasing to a plateau value, figure 1<sup>4</sup>. This relatively low viscosity state could be held indefinitely by maintaining the shear, but the system gelled once the shear was removed<sup>5</sup>. Some preliminary results from other systems gelling under shear hint strongly that the behaviour of the silica dispersion could be general [3].

The stress corresponding to the peak viscosity is a critical stress  $\Pi_c$  which, for a given sample, appeared to be constant to within the experimental uncertainties over a wide range of applied shear rates, and was independent of the gel time,  $t_m$ . An argument can be made,

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<sup>4</sup> Small angle neutron scattering and dynamic light scattering indicated that the drop in viscosity is explained by a structural densification of the growing clusters when the stress corresponding to the peak viscosity value is reached.

<sup>5</sup> However, oscillatory experiments and the SANS studies indicate that this final gel has a short range order different from that of the gel formed in the absence of a shear. See [2].



**Figure 1.** Plot of the viscosity behaviour of a gelling aqueous system of 12 nm colloidal silica particles subjected to a shear rate of  $500 \text{ s}^{-1}$ . The maximum corresponds to the critical stress,  $\Pi_c$  discussed in the text.

therefore, that the critical stress is a universal parameter that depends to a first approximation on only the precursor volume fraction. In fact, a heuristic relationship between these variables is immediately apparent. Assume colloidal particles of radius  $r_p$  coalesce on gelation to form clusters of radius  $R_c$  with fractal dimension  $d_f$  at a volume fraction  $\Phi$ . Define a reduced length  $\zeta = R_c/r_p$ . If the primary particles remain unchanged during the process, we can write the standard relation between the volume fractions [1, 4]:

$$\Phi \approx \phi \zeta^{3-d_f}. \quad (1)$$

Provided the energy is constant during the gelling process which, as discussed in [1], is in practise true, we have by dimensional arguments that the stress  $\Pi$  must vary as  $\zeta^{d_f-3}$ . Hence

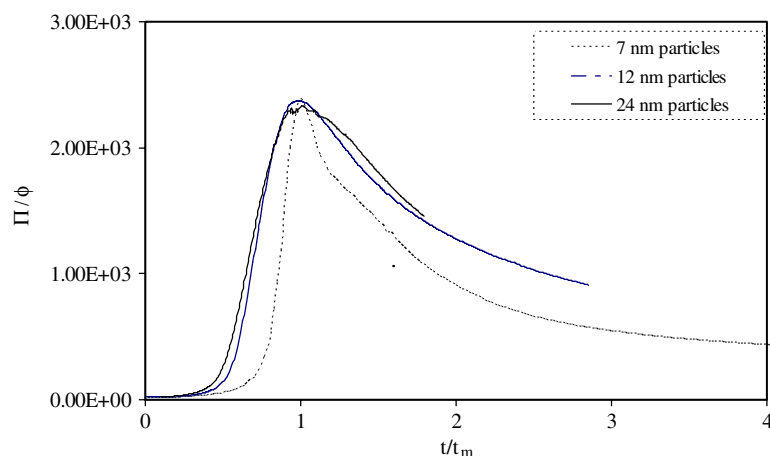
$$\Pi \approx \phi/\Phi. \quad (2)$$

But  $\Phi$  tends to 1 as the stress approaches the critical value  $\Pi_c$ , since the gel spans the container. Whence

$$\Pi_c/\phi \approx C \quad (3)$$

where  $C$  is a constant.

This short note reports a test of this expression. We gelled three precursor aqueous dispersions of colloidal  $\text{SiO}_2$  particles of nominal diameter 7, 12 and 24 nm—corresponding to volume fractions of 0.170, 0.228 and 0.307, respectively. Gelation was induced in a given dispersion by adding HCl following the procedure outlined in [1]. Immediately after gel initiation the dispersion was placed in a commercial Couette rheometer thermostatted to 298 K,



**Figure 2.** Test of equation (3) using three suspensions containing silica particles of diameter 7, 12 and 24 nm, respectively. The systems were subjected to an applied shear of  $1000 \text{ s}^{-1}$ . Shown is a plot of the term  $\Pi/\phi$  as a function of reduced time. The term  $\phi$  is the precursor suspension volume fraction and  $t_m$  is an effective gelation time for the static system.

kept at ambient pressure, and subjected to an applied shear. The stress and viscosity were recorded as a function of time,  $t$ . All systems were subjected to shear rates in the range  $5 \leq \dot{\gamma}/\text{s}^{-1} \leq 1600$ . The majority of the runs were then repeated using a cone-on-plate rheometer.

The most complete comparative data set was obtained from the three systems subjected to the shear rate  $\dot{\gamma} = 1000 \text{ s}^{-1}$ . Figure 2 depicts the evaluation of equation (3): shown is the plot of  $\Pi_c/\phi$  as a function of  $t/t_m$ . Similar curves were obtained at shear rates of 200 and  $500 \text{ s}^{-1}$ . For all runs, representing the three systems over the range of shear rates studied, we have the overall result that

$$10^3(\Pi_c/\phi)_{\text{couette}} = 2.37 \pm 0.08$$

$$10^3(\Pi_c/\phi)_{\text{cone-on-plate}} = 2.34 \pm 0.25.$$

It is thus clear that equation (3) is justified. As figure (2) indicates, the curves deviate when  $t/t_m \neq 1$ , since the equation requires that the cluster volume fraction be constant, but other approximations—including the very obvious simplification that the stress is independent of the shear—do not appear significant. In short, although the relation does not address any details of the gel structure, and changes to that structure due to a shear, the equation appears very robust and could well be system independent. We intend to investigate this hypothesis.

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