

An experimental study of the first normal stress difference – shear stress relationship in simple shear flow for concentrated shear thickening suspensions

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Abstract: For many polymeric solutions in a simple shear flow a plot of the logarithm of the first normal stress difference N_1 , against the logarithm of the shear stress σ , for a range of temperatures results in a linear relationship. For such polymer solutions these plots yield a straight line of slope very close to 2 when measured at low shear rates. This relationship is tested against a polymer solution (polyacrylamide in a 50/50 mixture of glycerol/water), a polymer melt (polyethylene), and three concentrated suspensions. These are Superclay (supplied by English China Clays, Cornwall, U.K.) in water, polyvinylchloride in dioctylphthalate and polystyrene latex in water, at volume concentrations of 40%, 48% and 60% respectively. It was found that the $\log N_1 - \log \sigma$ relationship is applicable to the polymer solution and melt over a significant range of shear rates and temperatures. In the cases of concentrated suspensions the relationship holds to the point of onset of the shear thickening behaviour. Beyond this point a different relationship exists, however, flow instabilities are apparent. A comment on the contribution of N_1 and N_2 to the flow instabilities is made.

Key words: Normal force – shear thickening – suspensions – first normal stress difference – flow instabilities – second normal stress difference

Introduction

Solid in liquid suspensions at high solids volume fraction exhibit very complicated rheological behaviour. Many rheological phenomena, such as shear thickening and dilatancy, Bingham plasticity and viscoelasticity and attendant time-dependent complexities of thixotropy may appear within the same material (Barnes et al., 1987; Jomha et al., 1991). All these phenomena could be made less pronounced by decreasing the volume fraction of the solid phase. It is, however, desirable to handle suspensions in a concentrated form; more so if the suspension medium is non-aqueous. In the paint industry, for instance, there is a requirement to reduce the volatile organic component (VOC) of a paint product to become ecologically acceptable (Reynolds and Reid, 1991). Also transportation of suspensions in a concentrated form and its processing where drying is involved would be more efficient. Thus rheological control of concentrated suspensions is an important problem for many industrial products and processes (Barnes, 1980). Investigations of normal stresses are one

rheological aspect of concentrated suspensions which has received little attention in the literature, although there are numerous papers on this aspect for polymer melts and solutions (see references Ait-Kadi et al., 1989; Lodge et al., 1987; Meister and Biggs, 1969; Williams, 1967, for instance). The importance of studying normal forces is a reflection of the problems they present in many industrial processes, for example in the paper industry (Engstrom and Rigdahl, 1989), mixing processes (Jomha and Woodcock, 1990; Barnes et al., 1989) and co-extrusion processes (Cogswell, 1981). Normal stresses are not always undesirable effects. They could be advantageous, for instance, to provide load bearing between the parallel faces of a mechanical face seal or a plain thrust bearing (Bernd, 1968).

Despite its importance, there is a dearth of data for normal forces in concentrated suspensions. In practice, the quantities that can be evaluated are the normal stress differences. There are two types of normal stress differences separately denoted as the first normal stress difference, N_1 and the second normal stress difference, N_2 . In most situations the first nor-

mal stress difference is considered to be of prominent importance and the second normal stress difference is deemed to be negligible (Walters, 1980). This, as shown later, may not be a good approximation. Thus the main concern of this paper is the investigation of the first normal stress difference and its correlation with the shear stress for a polymer solution, a polymer melt and three concentrated suspensions in a simple shear flow. The polymer solution and melt were used to confirm the measurement capability of the instrument and extend the same measurements to suspensions under the same conditions.

Theoretical background

The most general form that the total stress tensor π can have for a simple shearing flow (Bird et al., 1987) is:

$$\pi = \begin{bmatrix} P + \sigma_{xx} & \sigma_{yx} & 0 \\ \sigma_{xy} & P + \sigma_{yy} & 0 \\ 0 & 0 & P + \sigma_{zz} \end{bmatrix} \quad (1)$$

As it is not possible to separate the pressure (P) and the normal stress contributions in normal force measurements on surfaces, the only quantities of experimental interest are the shear stress, $\sigma = \sigma_{yx}$, the first normal stress difference $N_1 = \sigma_{xx} - \sigma_{yy}$, and the second normal stress difference, $N_2 = \sigma_{yy} - \sigma_{zz}$. The normal stress differences are usually expressed as functions of the shear rate in a way analogous to the shear stress (i.e. $\sigma = \eta \dot{\gamma}$) such that:

$$N_1 = \Psi_1 \dot{\gamma}^2 \quad (2)$$

$$N_2 = \Psi_2 \dot{\gamma}^2, \quad (3)$$

where Ψ_1 and Ψ_2 are respectively the first and second normal stress coefficients. Thus a plot of N_1 versus σ could be expected to give a slope of 2 on logarithmic scales at low shear rates in the so-called second order region. This was verified experimentally for polymeric systems (Ait-Kadi et al., 1989; Lodge et al., 1987) particularly at low shear rates. Furthermore, it was found that this plot is independent of temperature as a unique relationship applied over the whole range of shear rates and temperature utilised. It was, however, argued (Barnes et al., 1989) that there is no obvious fundamental justification for the plot to be independent of the temperature, nor is there any obvious fundamental justification of the unique relationship to apply outside the second order regime.

In this work we have tested the above dependency of the first normal stress difference on the shear stress (Eq. (2)) using a polymer solution and a polymer melt. Additionally, we present some novel data testing the same dependency using concentrated suspensions. To our knowledge, this represents the first attempt at measuring this phenomenon for suspensions dispersed in simple (Newtonian) fluids.

Experimental

Materials used

The polyacrylamide (PAA) and polyethylene (PE) polymers were commercial samples taken off the shelf and used as found. The solids used in the concentrated solid in liquid suspensions were Superclay, polyvinyl chloride (PVC) and polystyrene latex (PS).

The Superclay was supplied by English China Clays, Cornwall, UK. Its mean particle size and specific gravity were respectively 7.8 μm and 2.6. The PVC was supplied by ICI plc, Runcorn, UK. Its mean particle size and specific gravity were respectively 3.4 μm and 1.62. The Superclay particles were platelets and the PVC particles were spheroids with a broad particle size distribution. The polystyrene latex was monosized spheres, produced by dispersion polymerisation of styrene in a reaction medium comprising ethanol, polyvinyl pyrrolidone and Aliquat 336 (as a surfactant). The reaction was initiated by AIBN (2,2 azobisisobutyronitrile) dissolved in the styrene monomer (Almog, 1982). The product was collected by centrifugation of the reaction mixture, washed twice with doubly distilled water and centrifuged again. Further purification was attained by dialysis against doubly distilled water. Various techniques were utilised for the characterisation of the latex. GPC was used for molecular weight, Coulter Counter for particle size, NMR and IR for analysing monomer residue and confirming surfactant presence (Merrington, 1991). The particle size, molecular weight (Mw) and specific gravity of the latex were respectively 2.25 μm , $\sim 10^6$ and 1.03.

Some physical properties of the latex as well as Superclay and PVC are given in Table 1.

Sample preparation

The polymer solution was made from 1.2 wt% of polyacrylamide (PAA) dissolved in a mixture of 50/50 w/w of water and glycerol. The samples for polymer melt experiments were taken from a thin sheet of polyethylene (PE). The suspensions used were:

Table 1. Physical properties of the dispersed phases

Sample	SG	Mean particle size	Mw
Polystyrene*	1.03	2.25 + 3%	10 ⁶
Superclay [†]	2.6	7.8	—
Polyvinyl chloride [#]	1.62	3.4	Not available

[†] 80% of the particles fall in the size range 3.3–13 μm

[#] 70% of the particles fall in the size range 1.2–10 μm

* Refractive index is 1.591 and Mw/Mn = 1.47

- i) Superclay in water stabilised with Dispex (Allied Colloids, Bradford, UK) and adjusted to pH of about 7 using sodium hydroxide. The Superclay in water suspension was used at a volume concentration of 40%.
- ii) PVC in dioctyl phthalate (DOP). This dispersion was prepared at a volume concentration of 48%.
- iii) PS in water at a volume concentration of 60%.

The three suspensions were prepared such that the solid phase was added gradually to a mechanically stirred liquid. The suspensions were then placed in an ultrasonic bath for an hour, and then left at rest for several hours before the commencement of the rheological measurements.

Measurements

The rheological measurements were performed with a Weissenberg Rheogoniometer model R-18. This rheometer utilised cone and plate geometries. Three cones were used, for which the shear rates were determined at known, well defined, angular velocities. The specifications are given in Table 2. The resultant torques and forces were measured using one of three torsion bars and either of the two normal springs respectively. The appropriate choice was made according to the particular response monitored at the defined shear rates. The measurements were carried out at three temperatures in the range of 20–40 °C for the polymer solution and the suspensions, and 135–175 °C for the polymer melt. The

Table 2. Measuring geometry parameters

	Radius (cm)	Angle (deg)	Truncation (μm)
Cone 1	3.75	1.0	46
Cone 2	2.5	0.5	22
Cone 3	2.0	0.5	22

data were treated using the following relationships (Walters, 1975):

$$\text{first normal stress difference } N_1 = 2F/\pi R^2 \quad (4)$$

$$\text{shear stress} \quad \sigma = 3M/2\pi R \quad (5)$$

$$\text{shear rate} \quad \dot{\gamma} = \Omega/\theta, \quad (6)$$

where F is the normal force, M is the torque, Ω is the angular velocity, and R and θ are the cone radius and angle respectively. For the work with the particulate materials a minimum gap width to particle size ratio of 5:1 was maintained.

Results and interpretation

PE melt and PAA solution behaviours

Typical viscosity-shear rate data for polyacrylamide in water/glycerol and polyethylene melt are shown in Fig. 1. The data show shear thinning behaviour, a characteristic of polymer melts (Jacovic et al., 1979) and solutions (Graessley and Segal, 1970) at high molecular weights.

Figures 2 and 3 display the data of the first normal stress difference as a function of the shear stress on log-log scale at various temperatures for PAA and PE respectively. It is clearly shown that there is a unique relationship between the first normal stress difference and the shear stress over the whole range of shear rates 10^{-3} to 10^3 s^{-1} and is independent of the temperature within the range studied. Furthermore, this relationship yields a straight line of slope 2 in the

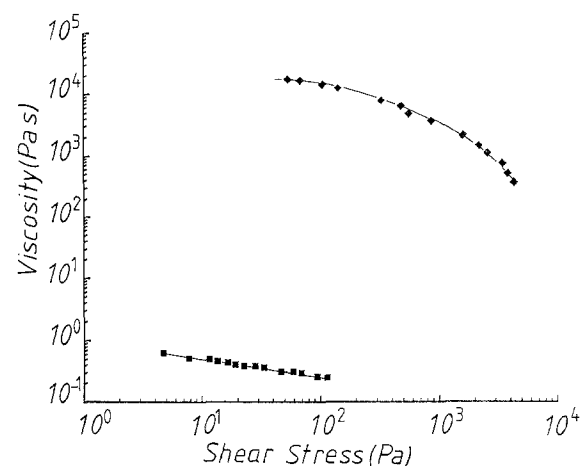


Fig. 1. Viscosity – shear rate data for polyethylene (♦) at 135 °C and polyacrylamide solution (■) at 20 °C. Lines are drawn through the data to guide the eye

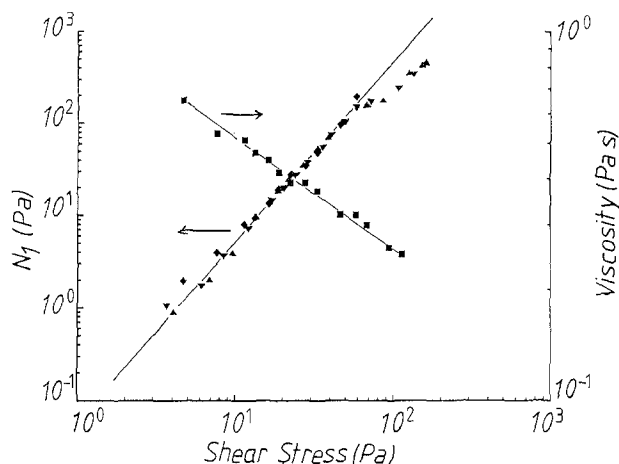


Fig. 2. N_1 - σ data for polyacrylamide solution at (\diamond) 20°C, (\blacktriangle) 27°C and (\blacktriangledown) 35°C. The solid line has a slope of 2. Viscosity data (\blacksquare) at 20°C is shown

region corresponding to low shear rates (hence low stresses), that is, the second order region. This is in accordance with previous observations (Ait-Kadi et al., 1989; Lodge et al., 1987). These data confirm the validity of our experimental technique to be applied to the suspensions. The degree of scatter in the data sets in the figures is relatively small and reassuring, particularly since the data were collected from three cone angles, three torsion bars and two normal force springs, over the entire shear stress range.

Concentrated suspension behaviours

All three suspensions, Superclay/water, PVC/DOP and PS/water at volume fractions of 0.4, 0.48 and 0.6

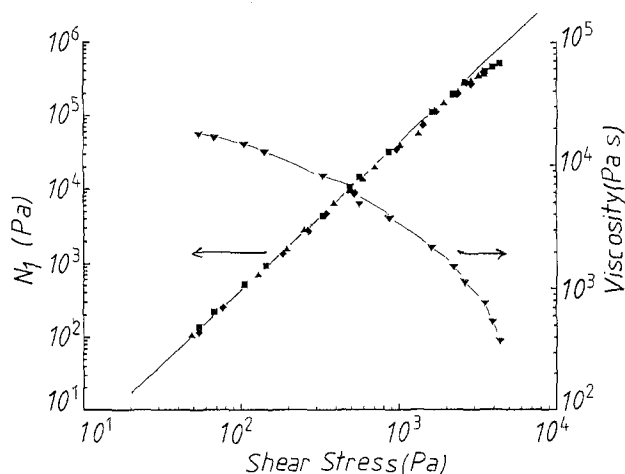


Fig. 3. N_1 - σ data for polyethylene melt at (\blacksquare) 135°C, (\blacklozenge) 145°C and (\blacktriangle) 175°C. The solid line has a slope of 2. The viscosity data (\blacktriangledown) at 135°C is shown

respectively, exhibited shear thickening behaviour, which is defined in this context as an increase in the viscosity of the suspension with increasing shear rate over a limited range (Barnes, 1987). The viscosity of these suspensions is plotted as a function of shear rate and shear stress at a temperature of 20°C and shown in Figs. 4A and 4B respectively.

The first normal stress difference-shear stress data at the various temperatures are shown in Figs. 5–7 for the suspensions of 40% Superclay/water, 48% PVC/DOP and 60% PS/water. The viscosity data are also shown for comparison purposes.

Inspection of these figures reveals a number of features. Firstly, the unique relationship of the first

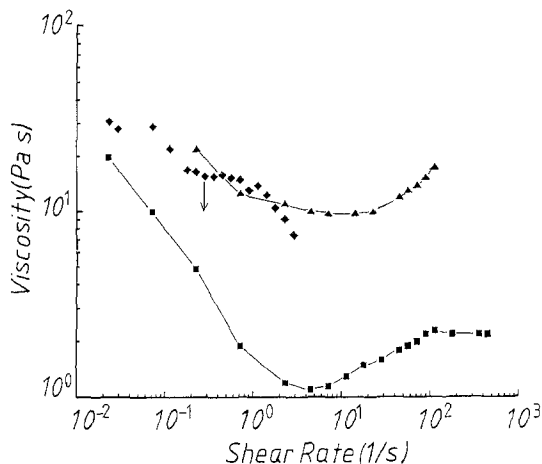


Fig. 4A. Viscosity – shear rate data for (\blacksquare) Superclay, (\blacklozenge) polystyrene latex and (\blacktriangle) PVC suspensions. The arrow indicates the point at which polystyrene latex fractured. Lines are drawn through the data to guide the eye

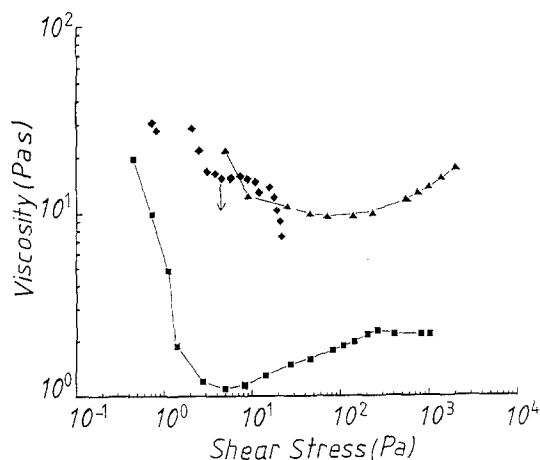


Fig. 4B. Viscosity-shear stress data for the suspensions (keys are given in Fig. 4A)

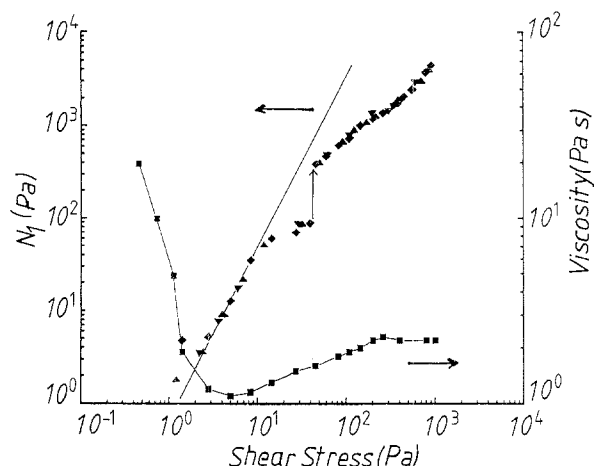


Fig. 5. $N_1 - \sigma$ data for Superclay/water suspension at (♦) 20°C, (▲) 27°C and (▼) 36°C. The straight line has a slope of 2. The viscosity data (■) at 20°C is shown

normal stress difference-shear stress of the polymer systems is found to apply for suspensions reasonably well, and the second order region is well defined, as shown in Figs. 5–7. Secondly and perhaps more strikingly, this unique relationship is still valid in the shear thickening region. This is clearly exemplified in Figs. 5 and 6. It is interesting to note that the onset of shear thickening precedes the discontinuity by a small magnitude of shear stress, at least for the PVC and Superclay dispersions. This implies that the suspensions have to be in the shear thickening region before a discontinuity in the flow process occurs. The lower values of viscosity after the discontinuity seen for polystyrene were due to the loss of some sample resulting in an under-filled gap. The third feature of

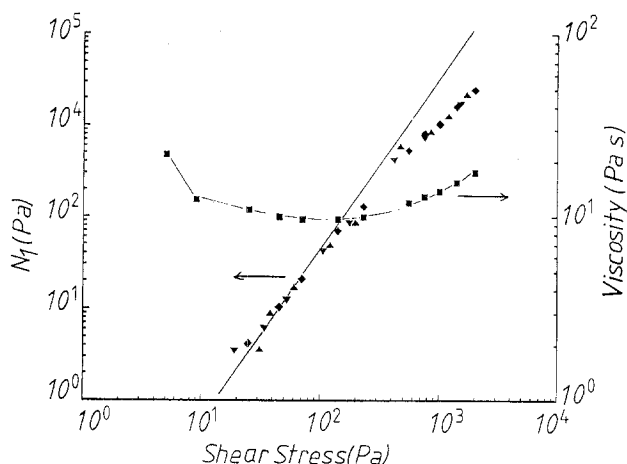


Fig. 6. $N_1 - \sigma$ data for PVC/DOP suspension at (♦) 20°C, (▲) 27°C and (▼) 36°C. The straight line has a slope of 2. The viscosity data (■) at 20°C is shown

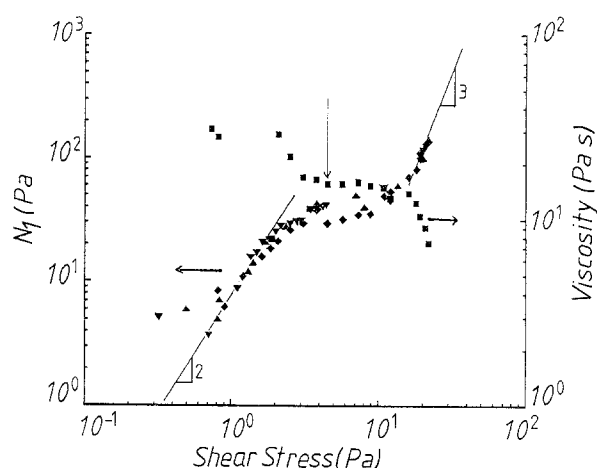


Fig. 7. $N_1 - \sigma$ data for polystyrene latex suspension at (♦) 20°C, (▲) 26°C and (▼) 35°C. The straight lines have slopes of 2 and 3 as indicated. The arrow indicates the point at which the sample fractured. The viscosity data (■) at 20°C is shown

particular interest is the shape of the $N_1 - \sigma$ curves in Figs. 5–7 before and after the onset of the shear thickening behaviour. At low shear stress in the second order region the slope is clearly 2, however, with increasing shear stress up to its critical value the dependence becomes somewhat less than 2. After the critical point and again with increasing shear stress, the slope of the plot increases dramatically to give a value greater than 2. The implications of this are discussed later.

The final feature of particular interest is that in the case of PVC/DOP and Superclay dispersions at the point of discontinuity in N_1 there does not appear a corresponding discontinuity in viscosity. This is not true of the polystyrene dispersion, where a discontinuity in both curves is coincident. This is attributed to the expulsion of the material from the gap.

Discussion

The novel data for the suspensions reveal useful information about their behaviour in simple shear. It is shown in this work, Fig. 4, and in the work of others (e.g., Hoffman, 1972), that a concentrated suspension often exhibits a shear thinning region followed by a second Newtonian region prior to the onset of shear thickening behaviour.

The transition to the shear thickening region can be a gradual one as shown in the case of PVC and Superclay suspensions, or abrupt, as in the case of the latex. Although the comparison is somewhat flawed as the packing fraction of the three suspensions is not

the same, these differences can be explained in terms of particle size and its distribution (Keller and Keller, 1991) and the gross particulate structure (Hopkins and Woodcock, 1990). Keller and Keller (1991), for instance, found that narrow size distribution particles exhibited abrupt, discontinuous shear thickening. As the size distribution increased, the transition to the shear thickening became gradual, and moved to higher shear rates than that obtained for narrow size distribution at the same packing fraction. The first normal stress difference, N_1 in the shear thinning and Newtonian regions of the suspensions behaves in a similar manner to the polymer systems. N_1 increases as a function of σ^2 at low shear stresses (or shear rates). At higher rates of shear, prior to the onset of shear thickening in the case of suspensions, the rate of increase in N_1 slows down, giving an exponent lower than 2. After the onset of shear thickening, the rate of increase in N_1 exceeds that of the shear stress, thus giving a curve of increasing slope.

After the onset of shear thickening, however, a step jump was observed in $N_1 - \sigma$ curves for PVC and Superclay suspensions, Figs. 5 and 6. This indicates that N_1 increases as the shear stress raised to an exponent greater than 2. Unfortunately, the exponent could not be determined due to the gradual expulsion of the sample from the measuring geometry, although an exponent of 3 is obtained for polystyrene latex at the high rates of shear utilised in this work, Fig. 7. It should be noted that the step-jump is not observed in the curve of polystyrene latex suspension because the fracture of the latex resulted in a significant loss of the sample from the measuring geometry. It is, however, obvious a critical change has occurred.

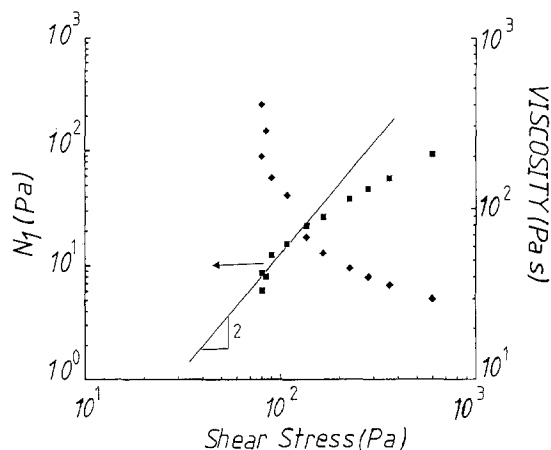


Fig. 8. N_1 and viscosity versus shear stress for 54% PVC plastisol. Data were obtained from Willey and Macosko (1978) J. Rheol. 22:525

Willey and Macosko (1978) reported N_1 data for PVC plastisols. Some of these data were extracted (from their Figs. 6 and 7) for shear stress ($= \eta \dot{\gamma}$) and N_1 respectively, and plotted here in Fig. 8. It is interesting to note that the general form of the $N_1 - \sigma$ curve is very similar to the curves reported here in that the slope is very close to 2 at low rates of shear whereas it is less than 2 at higher rates of shear. They also report that a shear thickening "discontinuity" is observed. Figure 8 is plotted up to this discontinuity. Given that the slope of 2 was obtained in the shear thinning region (Fig. 8), a plot of N_1 against the shear rate $\dot{\gamma}$ is expected to give a slope of less than 2 according to the following power law analysis. Since N_1 is proportional to σ^2 and that σ is proportional to $\dot{\gamma}^n$ for a power law fluid (n is the power law index). It follows that N_1 is proportional to $\dot{\gamma}^{2n}$. Thus:

$$\log N_1 = 2n \log \dot{\gamma} + \text{constant}$$

and the log-log plot of N_1 and $\dot{\gamma}$ yields as slope of $2n$.

The mechanism of abrupt shear thickening is explained by Hoffman (1972). In his study, he attributed the discontinuity in the viscosity/shear rate curve to a flow instability in which surfaces of spheres, packed in a two-dimensional hexagonal packing at low shear rates, break up into less ordered arrays of spheres. The order-disorder transition at the instability point was confirmed by light diffraction (Hoffman, 1974) and small-angle neutron scattering (SANS) (Laun et al., 1992) investigations. Laun (1988) further conjectured that the long range particle structure induces co-operative flow of particles into string-like or ordered layer structures. These break-down abruptly when the shear forces dominate the interparticle forces and strong shear thickening is observed. Other workers (Wagstaff and Chaffey, 1977) explained the abrupt shear thickening in terms of the time scales over which the applied shear rates were accelerated. They explained that acceleration to the steady shear rates, using a Weissenberg rheogoniometer like the one used here, was complete in a few milliseconds. This time may be insufficient to allow re-ordering of the particles to facilitate laminar simple shear flow at the higher shear rates to continue. This is perhaps supported to an extent by the observation of Laun et al. (1992) that a metastable low viscosity can be measured in a high viscosity shear thickening region by gradually increasing the stress of a controlled stress instrument.

Another explanation for this behaviour has been given by Woodcock (1986). Here abrupt shear thickening discontinuities have been predicted on the

basis of the inertial forces between the disperse particles determining an effective thermo-rheological state via the shear perturbation of the osmotic pressure tensor. The anisotropy of the osmotic pressure tensor, caused by the heterogeneous shear of inertial particles, sets up regional osmotic pressure differences giving rise to concentration gradients. Thus particle migration and complex structures result. Computer simulations of dense suspension in Couette flow, using a soft sphere model with interparticle inertial forces only, predicts the flow properties including instabilities such as an abrupt shear thickening.

The expulsion of material from the gap of the cone and plate can be explained by proposing that the inertial forces exceed the capillary forces. Thus according to Tanner and Keentock (1983)

$$\frac{\text{Re} R \Omega \eta}{\Gamma} < \frac{80}{3} \quad (7)$$

for the material to remain in the gap. Re is the Reynolds number and Γ is the surface tension of the fluid. This condition alone, however, does not seem adequate even in a qualitative way to explain the difference between a gradual expulsion of material, PVC and Superclay, to an "instantaneous" fracture with attendant loss of material, polystyrene latex, from the geometry gap.

For polymer melts and solutions, the problem of the abrupt onset of flow discontinuities has been the subject of many studies. The problem of edge fracture or flow irregularities in curvilinear flows, such as occurs in a cone and plate geometry used here for instance, has been known and recorded for some time. Hutton (1963, 1965, 1969) determined that this was not due to a secondary flow and proposed that the elastic component of the viscoelastic material was responsible for the instability. An expression relating N_1 to the fluid surface tension predicts instabilities on exceeding a critical value. Tanner and Keentok (1983) produced a similar expression in which N_2 would produce flow instabilities on exceeding a critical value. The general area of flow instabilities in viscoelastic fluids has recently been reviewed by Larson (1992) but the review does not cover colloidal materials. It is, however, worth noting that a non-zero N_2 is predicted to play a major role in controlling the stability of viscoelastic flows whereas N_1 is the driving force for the instabilities, for non-entangled or moderately entangled polymers at least. For large negative values of N_2 edge fracture in cone and plate flows is promoted. Kuliche and Wallbaum (1985) ob-

served for polystyrene samples that for shear flow in cone and plate geometry the ratio $-N_2/N_1$ decreased with increasing shear rate and ultimately reached a constant value. It was found that if this constant, shear rate dependent, value of the ratio was greater than 0.3 flow instabilities would result. A more recent study (Lee et al., 1992) demonstrated that for a series of polymer solutions it is on exceeding a critical value of N_2 , as predicted by Tanner and Keentok, that produces the edge fracture instability in cone and plate flow.

It is necessary to note that there exist many different types of flow instability, as reviewed by Larson (1992), but that it is our intention here to note that N_2 can, under a variety of circumstances, be seen to be non-zero and have a critical effect on flow instability. Thus a comparison with polymer rheology suggests that N_2 is likely to be important in the rheology of dense suspensions at high rates of shear. The question that naturally arises is: do critical values of N_1 , N_2 or indeed $-N_2/N_1$ exist for concentrated colloidal (viscoelastic) dispersions.

Our work here shows that indeed some critical behaviour does occur and is coincident with a step change in N_1 . It is tempting to propose that this is also coincident with a phase change of the colloidal dispersions as discussed above, however, this has not been experimentally verified.

Perhaps an indicator of the importance of N_2 is seen in the recent work of Ohl and Gleissle (1992), who have measured the second normal stress difference for a highly concentrated limestone dispersion in polyisobutene. Although a considerable experimental spread of data was observed for the suspension, the disperse system was found to have a larger N_2 than N_1 , in contrast to the pure polymer. Thus since N_1 would be expected to be greater than the shear stress at high shear rates, the influence of N_2 would dominate both in this case.

The influence of both N_1 and N_2 on the high shear properties of highly concentrated dispersions may well dominate these viscoelastic materials which are of commercial importance and are often subjected to high shear flows.

Conclusions

The behaviour of the normal stresses in concentrated solid in liquid suspensions was found to obey similar relationships to those found in polymer solutions and melts. This is particularly true for suspensions prior to the onset of shear thickening. The rela-

tionship between the first normal stress difference and shear stress was found to be independent of the temperature. Moreover, the data fitted a straight line of slope 2 for regions corresponding to low rates of shear. At the onset of shear thickening and beyond, it is evident that the slope of the first normal stress difference-shear stress curve can show dramatically different behaviour. Most notably for the dispersions a discontinuity in N_1 can be observed whilst at the same time a discontinuity in the viscosity is not necessarily seen.

This preliminary work has shown the importance of the first normal stress differences in concentrated suspensions and it is hoped that it will trigger more in-depth studies on this topic.

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