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Viscoelastic Properties of Concentrated Shear-Thickening Dispersions

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The viscoelastic properties of electrostatically stabilized concentrated dispersions of silica and of glass particles in a glycerol/water mixture are studied by oscillatory shear measurements. These dispersions are shear-thickening in steady shear flow. At most frequencies the loss modulus is found to dominate the storage modulus. At certain critical combinations of deformation amplitude and frequency the response signal becomes distorted, containing higher harmonics. This phenomenon can be ascribed to flow blockage, closely related to shear thickening in steady shear flow. When plotting the critical deformation against the frequency, three different regions can be detected. At low frequencies there is the steady shear flow limit, at intermediate frequencies double-layer overlap causes nonlinearity in the response signal, and at high frequencies there is a region where the critical deformation for flow blockage is a system-dependent function of the frequency, but is independent of the volume fraction. The magnitudes of the storage moduli are found to be in reasonable agreement with theoretical predictions. © 1992 Academic Press, Inc.

INTRODUCTION

Concentrated dispersions display a number of interesting rheological phenomena, examples of which are shear thinning (1, 2), shear thickening (3–7), thixotropy (8), and yield stress (9). Most investigations of these concentrated dispersions involved the steady shear properties, because of lack of sophisticated rheological measuring instruments. But lately the viscoelastic properties of dispersions received increasing attention (10–14). Reasons for this are, among others, the possibility of elucidating the molecular structure of materials and the use of material parameters in quality control of industrial products. For shear-thickening dispersions, however, still very little attention has been devoted to studying their viscoelastic properties. Also here most of the studies have dealt with the steady shear properties (see the recent review by Barnes (4)).

Strivens (14, 15) studied the viscoelastic properties of sterically stabilized dispersions

which were shear-thickening under steady flow conditions (16). In his results, a transition from a high dynamic viscosity, low elastic modulus (G') region at low frequencies to a low dynamic viscosity, high G' region at high frequencies can be observed. Strivens concludes that the transition is due to a reordering of particles into hexagonal sheets at low frequencies. With increasing flow the hexagonal sheets become increasingly closely packed until at close packing further increase of the flow leads to shear thickening. At high frequencies the particles have no time to reorder. The measurements also revealed nonlinearity in the strain wave form. Strivens attributed this to the interpenetration of steric barriers. Comparison with his steady flow data suggests that the transition to high G' and the nonlinear strain wave forms is not the same as the shear-thickening transition (14), because this last transition takes place at much higher shear rates. To our knowledge in other experiments the relation between shear thickening under steady flow and a similar phenomenon in the measurement of viscoelastic properties has also never been studied.

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Blockage of the flow of concentrated dispersions has, however, been observed in viscoelastic measurements. Schreuder *et al.* (17) showed that with highly concentrated pastes of glass particles in glycerol/water the response deformation to a sinusoidal oscillation shows a blockage phenomenon. A practically undeformable structure is formed which does not flow. It was also observed that when filling the apparatus by pushing the paste through a tube the flow blocked when the paste was pushed too fast. This probably is analogous to a shear-thickening transition. The experimental results have been explained by sheet formation at low frequencies, while at high frequencies the sheets are less developed and a more closely packed structure exists.

Gadala-Maria and Acrivos (18) found nonlinear response curves during oscillatory experiments on suspensions of polystyrene spheres in silicon oil. According to them an explanation of their findings is that, upon being sheared, the suspensions develop a structure which renders them anisotropic fluids. In steady shear measurements, however, no sign of shear thickening was found.

Finally, the work of Laun *et al.* (e.g., Ref. (19) and references therein) has to be mentioned. In a series of papers he carefully investigated the steady shear and viscoelastic properties of concentrated shear-thickening dispersions. Most of his work was concerned with the steady shear or linear viscoelastic properties. In his most recent paper (20), however, he also deals with the nonlinear viscoelastic properties of concentrated shear-thickening dispersions.

In a recent study (3) we showed that the shear rate at which shear thickening in dispersions starts can be predicted from a balance of forces between the particles at small interparticle distances: stabilizing repulsive forces and hydrodynamic forces which induce disorder in the dispersion. In this paper we present measurements of the viscoelastic properties of these concentrated dispersions and show that the steady-state shear-thickening transition is reflected in a transition in the visco-

elastic properties. The occurrence of the latter transition depends on volume fraction, angular frequency, and deformation amplitude. From the measurements interesting information can be extracted about the mechanisms in the dispersion that are responsible for shear thickening.

MATERIALS AND METHODS

Sample Preparation and Characterization

Measurements were performed on dispersions of silica (SiO_2) particles in a glycerol/water mixture and on dispersions of glass particles in a glycerol/water mixture. The preparation and characterization of these dispersions were described elsewhere (3). In Table I the most important characteristics of the two different particles are presented. The SiO_2 particles were prepared by the method of Tan *et al.* (21) while the glass particles were obtained from Potters Ballotini (soda lime glass). The dispersion medium was a 86.1/13.9% w/w glycerol/water mixture. Glycerol (Merck, reinst) was used as supplied and the water was double-distilled. The density of the glycerol/water mixture was 1224 kg/m^3 and the viscosity was $140 \text{ mPa} \cdot \text{s}$, both at 20°C .

Steady Shear Rheology

Continuous shear measurements were carried out with a Contraves Rheomat 115 shear-rate-controlled rheometer, supplied with a personal computer. During all measurements the rheometer was kept at $20.0 \pm 0.1^\circ\text{C}$. Measurements were made as quickly as possible. This means that a value for the torque at a

TABLE I
Characteristics of the Used Particles

Particle	Radius (μm)	a_W/a_N	Density (3) (kg/m^3)	ζ -potential (mV)
SiO_2	0.955	1.06	1457	-50
Glass	1.2	2.08	2550	-75

constant shear rate was taken as soon as the torque reached its maximum value in order to minimize thixotropic and other time-dependent effects. A comparison of this way of measuring with other methods and with the literature has been published elsewhere (22).

After the measuring system was filled, with care being taken not to include air in the system, the system was fitted into the rheometer. There it was first kept at rest for 30 min in order to equilibrate thermally and to restore possible structures that might have been destroyed during the filling of the system. The system was closed by a Teflon cover in order to prevent evaporation of the dispersion medium. Checks for wall slip were made using the Couette two-measurement method (23). Up to the onset of shear thickening no significant wall slip was measured. At higher shear rates dependence of the torque on the size of the measuring geometry was detected. The results with the largest geometry were taken to be the most reliable (22).

Oscillatory Measurements

All oscillatory measurements were performed on a Weissenberg Rheogoniometer Model R-18 supplied with a concentric cylinder system. The amplitude and phase of the oscillation (strain) and response (stress) were determined using a SE frequency response Analyzer SM2001A. The Couette device consisted of an oscillating cup and a concentric bob with diameters 5.5 and 5.2 cm, respectively. The movement of the bob was constrained by a torsion bar and both the movements of the cup and the bob were registered in time. The system was kept at $20.0 \pm 0.1^\circ\text{C}$.

For the oscillations a frequency range of 0.05–50 Hz and thus an angular velocity range of $0.314\text{--}314\text{ s}^{-1}$ were used. The deformation (strain) amplitude was varied between 0.004 and 0.13. For the transformation of the measured phase and amplitude differences into rheological quantities use was made of the formulae given by Walters (24). When above a critical deformation or frequency the response

became nonlinear; the amplitude and phase of the higher harmonics of the bob movement were also determined with the frequency response analyzer. They were compared with the amplitude and phase of the first harmonic of the cup movement. From this, rheological quantities were calculated, using the same formulae as for the first harmonic of the stress. As phase difference we took the difference between the zero passage of the first harmonic of the cup movement and the nearest zero passage of the higher harmonic of the bob movement. In our Weissenberg the minimum oscillation amplitude at which higher harmonics in the oscillatory drive unit are negligible is approximately 0.002.

RESULTS

In Figs. 1 and 2 the steady shear flow curves for the various measured dispersions are shown. All dispersions show severe shear-thickening behavior. The rise in viscosity is much more pronounced at the higher volume fractions and also the shear rate at which shear thickening starts is lower for the higher volume fractions. The shear-thickening transitions for the glass dispersions take place at higher shear rates than those for the silica dispersions. This can be explained using a force balance between hydrodynamic and electrostatic forces (3). A definition of the transition in steady shear measurements, and how to obtain the value of the critical shear rate from experiments are also given in the referenced paper.

The linear viscoelastic region can be determined by measuring, at a fixed frequency, the stress response to a varying oscillatory deformation. This region is that at which the deformation is small enough for the moduli to be independent of the deformation. In specific measurements (high volume fraction ϕ , high frequency ω) the response signal became non-sinusoidal at higher deformations. This coincided with the limit of the linear viscoelastic region. A similar behavior occurs if the deformation is kept constant and the frequency is increased. In Fig. 3 typical evolutions of the

FIG. 1. Relative viscosities for dispersions of SiO₂ in glycerol/water (86.1% w/w) at 20°C.

response signals at various amplitudes are shown. These signals were all measured with the silica dispersions at the highest volume fraction, at $\omega = 6.28 \text{ s}^{-1}$. With the frequency being varied at a fixed deformation similar results were obtained for all volume fractions investigated. As will be discussed later, this behavior can be ascribed to the flow blocking already observed in the steady flow measurements (3). In some cases the flow blockage was also observed as a drastic increase of G' with increasing deformation γ or frequency ω . This was detected especially with the higher volume fractions. An example is plotted in Fig.

4. The oscillation frequency was 1 Hz and it can be seen that at a distinct deformation amplitude ($\gamma \approx 0.09$) the moduli of the most concentrated dispersion suddenly increase strongly. For the two less concentrated dispersions no flow blockage in oscillation was observed within the deformation range investigated. Although in principle a superposition of curves of the steady-state viscosity versus shear rate and the dynamic viscosity versus maximum oscillatory shear rate would be interesting, it will not be done here. This is because, as will be shown further on, the critical shear rate for shear thickening depends

FIG. 2. Relative viscosities for dispersions of glass in glycerol/water (86.1% w/w) at 20°C.

FIG. 3. Typical evolution of the response signal with increasing deformation amplitude or frequency. This example: SiO_2 in glycerol/water (86.1% w/w), 20°C , $\phi = 0.598$, $\omega = 6.28 \text{ s}^{-1}$ (1 Hz). $\gamma = 0.01$ (a), $\gamma = 0.07$ (b), $\gamma = 0.08$ (c), $\gamma = 0.10$ (d). Amplifications are different for the different signals.

strongly on the oscillation frequency and the maximum deformation. Only in the case of large deformation do we expect the steady shear and the oscillatory shear measurements

to coincide, but unfortunately it was not possible to measure at these large deformations. It can be noted, however, that in general the magnitudes of the steady shear and the dynamic viscosities before the shear-thickening transition were in reasonable agreement.

In Figs. 5 and 6 for two different deformations the viscous and elastic moduli are plotted as a function of frequency at a fixed deformation amplitude. From the plot of G' and G'' at the lower deformation ($\gamma = 0.03$) no blockage can be extracted. From the shape of the response signal (same shape as, e.g., in Figs. 3b and 3c) it could be observed, however, that for all volume fractions there was flow blockage at $\omega \geq \sim 80 \text{ s}^{-1}$ (12.5 Hz). For the higher deformations flow blockage is more distinctly seen with all volume fractions in the range investigated. This shows especially in the elastic modulus G' , which starts to increase more steeply with frequency at the same frequency at which the response signal becomes deformed. The frequency at which the flow blocks at this higher deformation is, however, different for the different volume fractions.

Another way to detect nonlinearity in the response signal is to measure higher harmonics. We found that with our dispersions a third harmonic (referred to with G'_3 and G''_3) could be observed. Sometimes also the fifth harmonic was detectable. In Figs. 7a and 7b we show the first and third harmonic of the two most concentrated dispersions at a relatively high deformation amplitude. Only the values of the third harmonic which were measurable

FIG. 4. Elastic modulus G' (a) and viscous modulus G'' (b) as a function of deformation amplitude at an angular velocity of 6.28 s^{-1} (1 Hz) for dispersions of SiO_2 in glycerol/water (86.1% w/w) at 20°C with volume fractions $\phi = 0.598$ (Δ , $\blacktriangle$), $\phi = 0.562$ ($+$, $+$), and $\phi = 0.524$ ($\circ$, $\bullet$).

FIG. 5. Elastic modulus G' (a) and viscous modulus G'' (b) as a function of angular velocity at the deformation amplitude $\gamma = 0.03$ for dispersions of SiO_2 in glycerol/water (86.1% w/w) at 20°C with volume fractions $\phi = 0.598$ (Δ , $\blacktriangle$), $\phi = 0.562$ ($+$, $+$), and $\phi = 0.524$ ($\circ$, $\bullet$).

with reasonable accuracy are shown. At lower frequencies the third harmonics were too small to measure. It is clear that at a certain frequency the third harmonics suddenly increase in magnitude. This occurs almost at the same ω at which the first harmonic indicates flow blockage.

From the preceding results it can be concluded that all these concentrated dispersions have conditions under which the flow blocks. This critical condition for flow blockage is a combination of deformation amplitude and oscillation frequency. In Fig. 8 we plotted all the “critical deformations” for our dispersions. It can be seen that at high frequencies all dispersions show flow blockage at the same deformations, independent of ϕ . At lower frequencies, however, the critical deformation for flow blockage decreases with increasing volume fraction. At these lower frequencies the

critical deformation amplitude is more sensitive to the frequency with the less concentrated dispersions.

To obtain some additional information the same range of measurements of viscoelastic properties was also performed with the glass-in-glycerol/water dispersions, for which the flow curves were shown in Fig. 2. The results resembled the results for the silica dispersions, with the exception that the combination of frequency and deformation at which flow blockage occurred was shifted to higher frequencies. An example of the results for G' and G'' at a fixed (relatively small) deformation amplitude ($\gamma = 0.025$) is shown in Fig. 9. In Fig. 10 the critical deformation points for flow blockage are plotted.

Finally, it should be noted that the nonlinear response signals are definitely not artifacts. This can, in the first place, be concluded from

FIG. 6. Elastic modulus G' (a) and viscous modulus G'' (b) as a function of angular velocity at the deformation amplitude $\gamma = 0.09$ for dispersions of SiO_2 in glycerol/water (86.1% w/w) at 20°C with volume fractions $\phi = 0.598$ (Δ , $\blacktriangle$), $\phi = 0.562$ ($+$, $+$), and $\phi = 0.524$ ($\circ$, $\bullet$).

FIG. 7. Elastic modulus G' and viscous modulus G'' calculated from the first and third harmonics as a function of angular velocity at the deformation amplitude $\gamma = 0.13$ for dispersions of SiO_2 in glycerol/water (86.1% w/w) at 20°C with volume fractions $\phi = 0.562$ (a) and $\phi = 0.598$ (b). (a) G'_1 (+), G''_1 (+), G'_3 (▽), G''_3 (▼), (b) G'_1 (Δ), G''_1 (▲), G'_3 (□), G''_3 (■).

the large range of deformations and frequencies over which they occur with the different dispersions. Moreover, checks were made with viscous calibration oils. When determining the viscoelastic properties of these oils no nonlinear response signals were observed, indicating the absence of artifacts.

DISCUSSION

When analyzing the values of G' and G'' resulting from the measurements one immediately notices that the value of G'' is almost always higher than the value of G' . This indicates that the dispersions have a predomi-

nantly viscous character and it is likely that at rest no closely connected structures (e.g., aggregates) exist in the dispersions. With these well-stabilized dispersions flocculation is not expected and the low values of G' , compared to measurements on flocculated dispersions (25), indicate that our dispersions are not flocculated. Only when the dispersion is subjected to high frequencies or high deformations does the magnitude of G' increase and sometimes G' even becomes higher than G'' . This only takes place above the critical deformation point. Note that when this happens the shape of the response curve is not sinusoidal any-

FIG. 8. Critical deformation for flow blockage as a function of angular velocity for dispersions of SiO_2 in glycerol/water (86.1% w/w) at 20°C with volume fractions $\phi = 0.598$ (Δ), $\phi = 0.562$ (○), and $\phi = 0.524$ (□). Calculated results from Table A.1 (+) and the expected form of the curves (solid and dashed lines) are also indicated.

FIG. 9. Elastic modulus G' and viscous modulus G'' as a function of angular velocity at the deformation amplitude $\gamma = 0.025$ for dispersions of glass in glycerol/water (86.1% w/w) at 20°C with volume fractions $\phi = 0.54$ (G' , $\circ$; G'' , $\bullet$) and $\phi = 0.57$ (G' , $+$; G'' , $+$).

more and the precise physical interpretation of G' and G'' becomes unclear. Nevertheless, the pictures of the response curves also clearly indicated that the phase difference between oscillation and response became smaller, indicating that the elastic component became stronger.

The increase in magnitude of G' is probably due to a type of flow blockage, closely related to the shear-thickening phenomenon observed

in the steady shear measurements (Figs. 1 and 2; see also Ref. (3)). This is also indicated by the form of the response curves in Fig. 3. In the distorted response curves it can be seen that there is a sudden blockage of the flow, until the direction of shear is reversed (Fig. 3b). At higher frequencies or deformations the blockage occurs at a smaller deformation ("earlier" in the oscillation) and is followed by some kind of a relaxation process (Fig. 3c).

FIG. 10. Critical deformation for flow blockage as a function of angular velocity for dispersions of glass in glycerol/water (86.1% w/w) at 20°C with volume fractions $\phi = 0.54$ ($\blacklozenge$) and $\phi = 0.57$ ($\blackplus$). Calculated results from Table A.1 ($+$) and the expected form of the curves (solid and dashed lines) are also indicated.

At the highest frequencies and/or deformations the blockage can be complete and the oscillation and response are nearly in phase (Fig. 3d), indicating a solid-like behavior. The reported behavior can most easily be explained by the formation of large particle clusters, due to the hydrodynamic interaction forces between the particles in a concentrated dispersion. These clusters can span the whole gap and give rise to flow blockage and higher values of G' . In another study (22) we showed that in steady shear flow the presence of large clusters and plug-flow in the gap could be visualized using a photographic technique.

When comparing the results with other studies on stabilized dispersions it can be noticed that we do not see a transition at a certain volume fraction as is seen with some sterically stabilized dispersions (10, 13). In these studies it is observed that in the linear viscoelastic range at low volume fractions the loss modulus G'' is larger than the storage modulus G' , while at volume fractions above a certain "transition volume fraction" (which usually lies between 0.4 and 0.5) the storage modulus dominates the flow behavior. The interpretation of this transition is mostly sought in the interpenetration of the stabilizing steric barriers. The gel-like behavior of the sterically stabilized dispersions is hard to imagine with our electrostatically stabilized dispersions. So even at the highest volume fractions there are no signs of flocculation with our dispersions.

Strivens (14) also investigated viscoelastic properties of concentrated sterically stabilized dispersions. As mentioned before he observed nonlinear response signals and a transition to a high G' level. Although the phenomena he observed may be related to the phenomena we found, in our opinion they are not the same, because of the fact that his anomalous viscoelastic results occur in the same ω -range as ours while his dispersions only shear thicken at much higher $\dot{\gamma}$ -values ($>500 \text{ s}^{-1}$) than our dispersions.

In a similar range of deformations, a transition from linear viscoelastic flow behavior to flow blockage was reported previously by

Schreuder *et al.* (17). They found no distinct difference between strongly coagulating and noncoagulating dispersions. It should be remarked, however, that their dispersions contained particles in a size range (30–100 μm) in which colloidal forces are dominated by viscous and body forces (e.g., gravity). In the case of Schreuder's dispersions, the predominance of viscous forces was evidenced by arguments from energy dissipation (26) and from the viscosity at high shear rates. Because our dispersions contain smaller particles with much higher stabilizing forces the effects seen in our measurements are more severe and can also be studied in a wider range. It is interesting to observe, however, that the same type of flow blockage phenomenon can occur with dispersions that are quite different in particle size and interaction strength, probably indicating the general validity of the order-disorder concept. This is in agreement with the statements made by Barnes (4) that shear thickening, and related phenomena, can occur over a wide range of particle sizes, shear rates, and interaction strengths.

Buscall *et al.* (27) deduced a simple model based on the theory of interaction between electrical double layers for the prediction of the shear modulus G_∞ in electrostatically stabilized dispersions. This shear modulus is defined as

$$G_\infty = \lim_{\omega \rightarrow \infty} G'. \quad [1]$$

As can be concluded from the results in Fig. 5, in our experiments this high frequency limit is not reached, but in the linear viscoelastic region we may be able to compare the magnitude of our G' values at the highest frequencies with the theoretically predicted magnitude of G_∞ . The total energy of interaction between particles, V_T , can be written as (3, 28)

$$V_T = 2\pi\epsilon_r\epsilon_0 a\psi_0^2 \ln \{1 \pm \exp[-\kappa(R - 2a)]\} \quad [2]$$

because in our case $\kappa a > 10$. We assume that the electrostatic stabilization dominates the

Van der Waals attraction. Then Buscall's theory for the theoretical value of G^∞ leads to

$$G_\infty^{\text{th}} = \frac{2\pi\alpha\epsilon_0\epsilon_r\psi_0^2a}{R} \times \left(\frac{\kappa^2 \exp[-\kappa(R-2a)]}{\{1 \pm \exp[-\kappa(R-2a)]\}^2} \right). \quad [3]$$

Here ϵ_r is the relative dielectric constant of the medium and ϵ_0 is the permittivity of vacuum; ψ_0 is the surface potential, which can be approximated by the ζ -potential of the particles in the medium; $1/\kappa$ is the Debye double-layer thickness (29); a is the particle radius; R is the center-to-center distance between two particles; and $\alpha = (3/32)\phi_m n$, with ϕ_m the maximum packing fraction and n the number of neighbors. For a face-centered cubic structure (a reasonable choice for our dispersions at rest) α reduces to 0.833 and R is given by $R = 2a(0.74/\phi)^{1/3}$. The + and - signs in Eqs. [2] and [3] correspond to constant surface potential and constant surface charge, respectively.

Several improvements can be made on the theory for G_∞^{th} . An example is the modification suggested by Russel and Benzing (30) to allow for changes in the counterion concentration in a dispersion sample at finite volume. Also the use of ζ -potentials instead of ψ_0 can be questioned. Elsewhere (3) we discussed that in our dispersions these modifications have only a small influence and especially for a first estimate they can be neglected.

When using the dispersion parameters mentioned before, we arrive at values of G_∞^{th} of 18.5 Pa ($\phi = 0.524$), 33.7 Pa ($\phi = 0.562$), and 53.7 Pa ($\phi = 0.598$), using the constant surface potential approximation, and of 22.3 Pa ($\phi = 0.524$), 48.1 Pa ($\phi = 0.562$), and 101.0 Pa ($\phi = 0.598$), using the constant charge approximation. From Fig. 5 it can be seen that at $\gamma = 0.03$ and at 20 Hz ($\omega = 126 \text{ s}^{-1}$) the values of G' are approximately 5 Pa ($\phi = 0.524$), 32 Pa ($\phi = 0.562$), and 800 Pa ($\phi = 0.598$). The agreement is qualitatively reasonable, indicating that the theory is likely to be valid for our dispersions, and gives rea-

sonable results even with our relatively large particles.

The results for the critical points for flow blockage (Fig. 8) show some interesting phenomena. In the first place it can be seen that above a certain oscillation frequency (and below a certain deformation) the critical points for blockage become independent of volume fraction (for these high volume fractions). It is not completely clear to what this behavior can be ascribed, but a possible explanation can be that at these small deformations and high frequencies the particles oscillate only around their equilibrium positions. Nonlinearity of the response signal can then arise from double-layer effects, such as the particles moving out of their double layer. This can be estimated from the ion-Péclet number $\text{Pe}_{\text{ion}} = u/(m\kappa kT)$, where u is the velocity of the particle and m is the ionic mobility (31). If $\text{Pe}_{\text{ion}} \ll 1$ distortion of the double layer due to shear can be neglected. u can be approximated by $\dot{\gamma}a$, whereby $\dot{\gamma}$ in oscillatory experiments is given by $\gamma_{\text{max}}\omega$, with γ_{max} the deformation amplitude. If m in glycerol/water is taken to be $5 \times 10^9 \text{ s/kg}$ (32), the maximum value of Pe_{ion} is 0.005, so the double layer will probably always stay intact. Van der Werff and De Kruif (1) give a particle Péclet number, $\text{Pe} = 6\pi\eta_0 a^3 \dot{\gamma}/kT$, where η_0 is the dispersion medium viscosity and kT is the thermal energy. If $\text{Pe} \gg 1$ the shear forces dominate the Brownian forces and then the Brownian forces can be ignored. It could be argued that for viscoelastic measurements $\dot{\gamma}$ should be replaced by ω , but since in our measurements the values of ω are, in general, higher than the values of $\dot{\gamma}$ the latter provide a more stringent criterion for the neglect of Brownian forces. The minimum Péclet number that can be reached in our measurements is ~ 60 , and so we will not consider Brownian forces to be of importance. Since these two Péclet numbers cannot be held responsible for the observed behavior, it is still not clear what causes the critical points for flow blockage to become independent of volume fraction. More study is needed to clarify this point.

At the other end of the scale we find the low frequency, high deformation region, which finally ends in steady shear flow (∞ deformation, zero frequency). It seems reasonable to assume that there the critical combination of deformation and angular velocity (frequency) will be equivalent to the critical shear rate for deformation. This comparison can be made by calculating the maximum shear rate attained in a certain experiment by $\dot{\gamma} = \gamma_{\max} \cdot \omega$, where $\gamma_{\max}$ is the deformation amplitude. In this low frequency region the behavior of the dispersion is probably the same as that in steady shear flow. We showed in another paper (3) that a dispersion orders at low shear rates, due to the electrostatic repulsion. At higher shear rates the hydrodynamic forces become larger in magnitude, inducing cluster formation (33, 34) and higher viscosities.

From Fig. 8 it can be seen that especially at the highest volume fractions there seems to be a region at intermediate values of $\log(\omega)$ where the critical deformation is almost independent of the frequency. In the Appendix we show that this can be explained by overlap of the double layers in ordered flow. The dispersion has no time for a complete order-disorder transition, but above a certain deformation the double layers of the particles in two adjacent layers start to overlap and the flow blocks.

In Figs. 8 and 10 we also indicated these transition points between the steady shear limit and the region where double layer overlap occurs, according to the Appendix. At frequencies below and deformations above this point, the steady shear limits are indicated by solid lines. Solid lines also indicate the high frequency regions where the critical points become independent of volume fraction. The connections between these two regions are indicated by dashed lines. Here double-layer overlap should occur. It can be seen from Figs. 8 and 10 that the measurements coincide well with the dashed lines, indicating that the given explanation seems reasonable.

Finally we can compare our results with those obtained by Laun (20). He also found

a transition to nonlinearity at a critical combination of deformation and frequency. He did not, however, find three regions, but only two, corresponding to our two regions at the lower critical frequencies. These are a region where the same behavior as in steady shear flow occurs and a region where the critical deformation amplitude becomes (nearly) independent of the oscillation frequency. The reason why Laun did not find the third region where the critical points for flow blockage become independent of volume fraction is not clear. It could be that this region can only be seen with certain dispersions or that Laun did not measure at high enough frequencies to see it with his dispersions. More study is needed to clarify this point.

CONCLUSIONS

When measuring the viscoelastic properties of shear-thickening dispersions, in the linear viscoelastic region the loss modulus dominates the storage modulus, indicating the absence of flocculation. At a critical combination of frequency and deformation a transition to nonlinear response signals can be observed which is closely related to the flow blockage observed in steady shear flow. Three different regions can be determined.

1. At high deformations and low frequencies the same order-disorder transition as that in steady shear flow occurs.

2. In an intermediate region the flow blockage is relatively independent of frequency. Here overlap of double layers from particles in adjacent layers can be held responsible for the nonlinear response signals.

3. At the high frequency, low deformation end, the critical point for nonlinearity becomes independent of volume fraction.

The values of the storage moduli for the different dispersions were found to be in qualitative agreement with the theory developed by Buscall *et al.* (27) for the high frequency limit. The constant surface potential approximation gives slightly better results than the constant surface charge approximation, but the differ-

ences are small. Glass dispersions which shear thicken at a higher shear rate in steady shear flow showed the same behavior at higher angular velocities, indicating once more the close relation between nonlinearity in oscillatory measurements and shear thickening under steady shear.

APPENDIX

In steady-state shear flow the mechanism for flow blockage is hydrodynamic disruption of individual particles out of the electrostatically induced layers. This occurs beyond a critical shear rate $\dot{\gamma}_c$. In oscillatory shear, we expect this to occur beyond a critical value of $(\omega\gamma)_c = \dot{\gamma}_c$. This, however, requires enough total deformation to induce "clusters," which is not always the case in oscillatory shear. Thus, below a specific value of γ , this criterion fails. Here we propose a blockage mechanism for oscillatory shear at low deformations.

When a dispersion undergoes oscillatory shear at small amplitudes of oscillation the dispersion will organize itself in layers as depicted in Fig. A.1a. As we showed elsewhere (3) it is most likely that the distance h between two layers equals the distance between two particles in the same layer. The relation between dimensionless distance and volume fraction is then given by

$$h/a = \left(\frac{8\pi}{3\sqrt{3}\phi} \right)^{1/3} - 2. \quad [\text{A.1}]$$

FIG. A.1. Typical particle configuration at rest (a) and under oscillatory shear (b). At the deformation shown in (b) flow blockage occurs.

TABLE A.1

Critical Values for Flow Blockage

Dispersion	ϕ	γ_c	$\dot{\gamma}_c$	ω_c
SiO ₂ in glycerol/water	0.524	0.52	0.63	1.22
SiO ₂ in glycerol/water	0.562	0.34	0.25	0.74
SiO ₂ in glycerol/water	0.598	0.21	0.06	0.29
Glass in glycerol/water	0.54	—	5.6	—
Glass in glycerol/water	0.57	0.74	1.8	2.4

In Fig. A.1a the double-layer thickness $(1/\kappa)$ is also depicted, which is for our SiO₂ dispersion $0.079a$ and for our glass dispersions $0.028a$ (3). The maximum packing fraction for a freely flowing structure in this arrangement is 0.605 (touching layers, see also Ref. (17)). Even then in the situation shown in Fig. A.1a no considerable double-layer overlap will occur for our dispersions. When, however, the dispersion is subjected to an oscillatory deformation the situation can, for large enough deformation amplitudes, change to the arrangement depicted in Fig. A.1b. Then double-layer overlap starts to occur and the flow will block. In Fig. A.1 we also indicated the important distances in these structures, all scaled by the particle radius a . It is now possible to calculate the critical deformation for flow blockage as a function of h and $1/\kappa$. As can easily be checked the result is

$$\gamma_{\text{crit}} = \frac{1 + 0.5h - \sqrt{8/\kappa + 4/(\kappa^2) - 4h - h^2}}{1 + 0.5h}. \quad [\text{A.2}]$$

Values of γ_{crit} for the different dispersions investigated are given in Table A.1. This is the deformation at the left end of the less steep part of the curve for the critical points. At higher critical deformations, and thus lower frequencies, the dispersion blocks at a certain shear rate value. This shear rate is given by

$\gamma \cdot \omega$ and equals the critical shear rate for shear thickening in steady shear flow. In Table A.1 we give the critical deformations and the shear rates at which shear thickening starts in steady shear flow for our dispersions. From this it is then possible to also calculate the critical angular frequency where the less steep part in Fig. 8 (see under Results) should start. In the Discussion section we indicate in Figs. 8 and 10 the critical points from Table A.1.

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