Shear and Compressive Rheology of Aggregated Alumina Suspensions

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The shear and compressive properties of aggregated alumina particles are determined as functions of volume fraction and the strength of the interparticle attraction. Over a range of volume fractions, yield stresses, τ_y, elastic moduli, the strain delimiting the extent of the linear elastic response, and compressive yield stress, P_y, are well described by power-law functions of volume fraction, while the role of interparticle attractions can be accounted for by expressing these mechanical properties as $(\phi/\phi_g - 1)^n$, where ϕ_g captures the strength of particle attractions and n the microstructure. The links between compressive and shear properties are well described by linear elastic models where the P_y and τ_y are a function of Poisson's ratio which, for the suspensions investigated, has a value near 0.49.

Introduction

Characterizing the filterability of suspensions of aggregated particles remains a difficult problem faced in solid–liquid separations and ceramic processing. In this work, we focus on the use of parameters derived from characterization of a slurry under shear to describe how suspensions will filter. Shear and compressive properties of suspensions composed of aggregated particles are both controlled by the strength of interparticle forces and suspension microstructure. Both shear and compaction require interparticle bonds to be distorted, broken, and reformed. Thus, for a given suspension microstructure, one would expect these two types of deformation to be intimately linked.

The compressive property of interest here is the compressive yield stress, P_y, which is a measure of the pressure required to compact a suspension in a uniaxial filter. When a load stress than P_y is applied, at times that are small compared to its relaxation time, the suspension responds in an elastic manner. For $P > P_y$, the bed compacts to a new volume fraction capable of supporting the applied load.

Assuming that suspensions respond in a linear elastic manner up to the yield point, Meeten (1994) proposed that τ_y and P_y at all volume fractions are linked through a single parameter, Poisson's ratio, which characterizes the stress transmitted orthogonal to the applied load in a uniaxial compaction. Buscall et al. (1988) take a different approach and suggest the elastic modulus, G, will have the same volume-fraction dependence as the bulk modulus, which is approximated as $K = -dP_y/d\ln\phi$. If the linear elastic models hold, both ratios (i.e., τ_y/P_y and G/K) will be independent of volume fraction. In this work we explore this prediction and investigate how the ratios vary with volume fraction and strength of interparticle attraction. Each of the four mechanical properties are found to have similar volume-fraction dependencies such that the preceding ratios are constants that are independent of volume fraction and strength of interparticle attraction, yielding a Poisson's ratio near 0.49.

Our investigations were carried out on aggregated alumina suspensions. Alumina was chosen due to its commercial significance and because the strength of the attraction between particles can be controlled by varying the continuous phase pH (Velamakanni and Lange, 1991). This property is used to advantage to explore the effects of both volume fraction and bond strength on suspension mechanics. By specifying continuous phase-ionic strengths and pHs, the strength of bonds between particles is fixed. As a result, the influence of variations in the density of interparticle bonds on mechanical properties can be probed through changes in volume fraction. On the other hand, if the microstructure could be held constant, the relationship between bond strength and mechanical properties can be explored through changes in continuous-phase pH and ionic strength.

Not surprisingly, even at a fixed volume fraction, suspensions display a variety of microstructures as the strength of the interparticle attractions is increased. This is most clearly seen by focusing on attractive strengths required to produce space-filling gels, which typically occurs at a well-defined volume fraction ϕ_g. For $\phi < \phi_g$, suspensions have no yield stress and are weakly elastic, while above ϕ_g, yield stresses and elastic moduli increase rapidly. If one fixes the suspension volume fraction and increases the strength of attraction, up to a critical bond strength, rheological properties will be dominated by discrete particles or aggregates, while for bond strengths above the critical value, mechanical properties of a continuous network are probed. These concepts suggest that descriptions of aggregated suspension rheology require incorporation of the gel transition to be complete.

Gel transitions are associated with a critical state where the first cluster percolates across the container of interest. At the gel point, suspensions have an infinite zero-shear-rate viscosity and an elastic modulus of zero (Stauffer, 1985; Martin et al., 1987). This state can, in principle, be achieved at any volume fraction by adjusting the strength of attraction to the appropriate level. An example of this behavior can be found in the studies of suspensions of octadecyl silica particles suspended in decalin that reversibly gel on decreasing temperature (Jansen et al., 1985a–d; Chen and Russel, 1991; Grant and Russel, 1993; Rueb and Zukoski, 1997). Here gel volume fractions ranging from a few volume percent to 0.6 have been reported. Near the gel point, however, independent of volume fraction, the suspensions have similar properties in that the modulus has the same dependence on temperature, and storage and loss moduli have equal values with both being power-law functions of frequency.

Due to the similarity of microstructural and mechanical properties of systems at the gel point, the gel volume fraction represents a natural starting point in describing the flow properties of gelled suspensions. This concept was used by Grant and Russel (1993), who studied the volume-fraction and interparticle bond-strength dependencies of the mechanical properties of octadecyl silica particles. They argue that as the elastic modulus increases with connectivity, moduli will scale on $(\phi - \phi_g)^m$, where ϕ_g incorporates the strength of the interparticle forces, $(\phi - \phi_g)$ represents the increase in bond density in the gel above ϕ_g, and m characterizes the microstructure. Working with a similar system, but preshearing the gel prior to measuring mechanical properties, Rueb (1994) and Rueb and Zukoski (1997) suggest a distinct scaling where moduli and critical strains scale as $(\phi/\phi_g - 1)^n$. Few systems have been investigated in sufficient depth to test these different attempts to incorporate bond strength into generalized descriptions of mechanical properties. Here we expand the number of systems by looking at mechanical properties of suspensions of alumina particles over a range of volume fraction under solution conditions for which suspensions show distinct values of ϕ_g.

Several models have been developed to describe the scaling properties of aggregated suspensions on volume fraction based on the fractal nature of suspension microstructure. These models, developed to describe the behavior of suspensions that gel at all volume fractions (de Rooij et al., 1993, 1994; Potanin et al., 1995; Shih et al., 1990), predict that material properties such as the shear and compressive yield stress, elastic modulus, and the strain limiting the extent of the linear region are written as power-law functions of ϕ. The power-law exponents are associated with a variety of fractal dimensions describing the microstructure of the suspension and the stress-transmitting structures within the suspension. In this work we investigate suspensions that, like those containing octadecyl silica particles, display well-defined gel volume fractions that are sensitive to the strength of interparticle attraction. Power-law dependencies on volume fraction are observed for many mechanical properties, in keeping with previous studies. However, predicted and experimentally derived exponents are not in good agreement.

In this article, experimental setup and results are described as well as data-gathering techniques. Then, shear and compressive properties are compared with previous experimental studies and the microstructural models of de Rooij et al. (1993, 1994), Potanin et al. (1995), and Potanin and Russel (1996). These comparisons prove only partially satisfactory. The connection between P_y, τ_y, K, and G is also discussed and Poisson's ratio near 0.49 extracted for the materials investigated.

Experimental Procedure

Particle characterization and suspension preparation

Shear and compressive rheology experiments were carried out using suspensions of conventional α-alumina particles (AKP-15, Sumitomo Chemical, New York). The alumina particles have a density of 3.984 g/cm^3, as determined by helium pycnometry, and a median particle diameter of 1.3 μm. Velamakanni and Lange (1991) measured the zeta potential of AKP-15 powders and determined that the zeta potential reaches a plateau at a pH of approximately 4.0 and that the isoelectric point of these particles is at pH 9.0. Suspensions were prepared at three different pHs (4.0, 7.0, and 9.0), and all of the suspensions studied were flocculated by the addition of 1.0-M NH_4Cl. All of the pH adjustments were made using HNO_3 and NH_4OH.

Two different sample preparation methods were used for the compressive experiments. One set of suspensions was prepared by starting with a stock suspension at high solids loading ($\phi \approx 0.45-0.50$), a pH of 4.0, and a salt concentration of 1.0-M NH_4Cl. This stock solution was mixed under high shear conditions (20,000 rpm) for 15 min using a Power Gen homogenizer in order to provide a uniform microstructure. The suspensions were then diluted with 1.0-M NH_4Cl to various initial volume fractions above the gel point, and the pH was adjusted to the desired value (4.0, 7.0, or 9.0).

The other set of suspensions was prepared at a volume fraction below the gel point ($\phi \approx 0.10$) so that the particles in suspension would consist of individual particles or flocs. These suspensions were dispersed in 1.0-M NH_4Cl at a pH of 4.0 and then homogenized under very high shear conditions (20,000 rpm) using a Power Gen homogenizer for 15 min. The pH of the suspension was then adjusted using NH_4OH to the desired pH (4.0, 7.0, or 9.0), and the suspension was again homogenized.

The suspensions for the shear experiments were also prepared via two different methods. The procedure for the first set of suspensions is identical to that for the first set of compressive samples as described earlier. Since direct comparison of shear and compressive data requires the measurements to be performed on suspensions with the same microstructure, a second set of suspensions was prepared. As with the second set of compressive samples, these suspensions were prepared at a pH of 4.0 at a volume fraction below the gel point. The suspensions were homogenized for 15 min and then adjusted to the proper pH and rehomogenized. In order to provide a more accurate comparison with the compressive samples, these suspensions were concentrated to the desired volume fraction using a uniaxial filter. The filter consisted of a cylindrical sample chamber approximately 2.5 cm in diameter, a movable piston, and a 0.1-μm cellulose nitrate membrane. A known mass was placed on the piston, and the suspension was given 24 h to reach equilibrium. The side of the membrane outside the sample chamber was kept in contact with a solution identical in pH and ionic strength to the continuous phase of the suspension in order to prevent diffusion of the species into the filtrate. Since each position in a uniaxial filter experiences the same stress, the microstructure of the resulting suspension should be uniform, and the volume fraction corresponds to the density of interparticle bonds necessary to support the applied load.

Measurement of suspension rheology

Both filtration and centrifugation were used to measure the compressive yield stress. In filtration, the entire suspension experiences the same stress. Therefore, at equilibrium, the suspension has a uniform volume-fraction profile. The volume fraction of the final bed at a series of increasing pressures was measured during the preparation of the shear rheology suspensions, providing a measure of the compressive yield stress as a function of volume fraction.

Centrifugal loads were applied to the suspensions using a Beckman J2-21M/E centrifuge. Samples were loaded into a JS-13.1 swinging bucket rotor, and spun at a constant speed until equilibrium was reached. The beds were then manually dissected to determine the volume-fraction profiles (Meeten, 1993). Using a spatula constrained so that only material above a selected height was removed, the final bed was sectioned into slices of thickness 0.5 mm–2.0 mm so that 15–20 total slices were obtained. The volume fraction of each slice was measured by weight loss upon drying, and the stress that each height experienced was determined. At each point in the bed, the suspension must support the weight of all material of smaller s, where s is the distance from the top of the bed:

$$P_y = \int_0^s \Delta \rho g(s)\, \phi(s)\, ds. \qquad (1)$$

This method allows the measurement of the $P_y(\phi)$ for a wide range of pressures with a single experiment.

The shear properties were measured using a Bohlin variable rate of strain rheometer (VOR) fitted with a Couette geometry. The bob had a diameter of 25.0 mm, while the cup had a diameter of 27.2 mm. The shear yield stress, τ_y, was determined from the extrapolation of the shear-stress plateau in the low shear-rate regime. Oscillation experiments were conducted at several frequencies to determine the shear modulus G. The breaking strain, γ_b, was determined by measuring the shear modulus as a function of the amplitude of the oscillations. The breaking strain was then defined as the strain at which the modulus fell below 90% of its plateau value.

Results

Shear flow properties

Determination of meaningful parameters that characterize the flow properties of flocculated suspensions requires that the stress has reached a steady value prior to moving to the next shear rate. The stresses determined in this manner reflect steady-state microstructures. For the AKP-15 suspensions investigated here, the structure rapidly achieved steady state, and if the shear rate was held constant for 5 min at each shear rate, stresses on increasing and decreasing shear rates were experimentally indistinguishable. In addition, 5 min after the cessation of flow, the shear modulus (G) became independent of time.

Figures 1a–1c show typical flow curves for flocculated alumina suspensions at various concentrations for pH 9, 7, and 4, respectively. All of the curves for suspensions above the gel point exhibit a low shear-rate plateau in shear stress, while those for suspensions below ϕ_g exhibit a constant, finite viscosity at low shear rates. By extrapolating the low shear plateau to a zero shear rate, the shear yield stress was determined. The length of the plateau region tends to increase with concentration, as does the value of the yield stress. AKP-15 alumina has an isoelectric point near a pH of 9.0. Thus we expect the interparticle bond strength to increase as the pH moves from 4 to 9 (Velamakanni and Lange, 1991). Supporting this hypothesis, the shear yield stress increases with increasing pH.

The continuous shear and modulus data measured on the samples that were prepared by starting at an elevated volume fraction, diluting and homogenizing were, within experimental uncertainty, the same as those prepared below the gel point and compressed to the proper volume fraction (Figure 2). As discussed below, this was not true for compressive properties that were sensitive to preparation technique. As a result, comparisons are made on samples prepared below the gel point and compressed to the volume fraction of interest. The lack of sensitivity of shear properties to preparation technique indicates that the preshear used after the suspension was loaded into the rheometer is effective at resetting the microstructure to a uniform state.

A summary of the yield stress as a function of volume fraction for the three pHs studied is given in Figure 2. The yield stress is well described by a power-law dependence on volume fraction: $\tau_y \approx A\phi^x$. The exponent does not appear to depend on pH and has a value of $x = 5.0 \pm 0.1$. Similar exponents have been reported on a variety of aggregated suspensions (Shih et al., 1990; Buscall et al., 1988; de Rooij et al., 1994).

The shear modulus and breaking strain are determined through oscillatory shear experiments. The amplitude (strain) of the oscillations is increased, and the shear modulus is measured at each amplitude. Typical curves for two concentrations are shown in Figure 3. The shear modulus is determined by extrapolating the low strain plateau to zero, and the breaking strain is defined as the strain at which the shear modulus falls to 90% of the plateau value. As shown with typical results in Figure 4, the value of the plateau shear modulus is independent of the oscillation frequency for the range that could be explored.

Figure 5 summarizes the effect of particle concentration

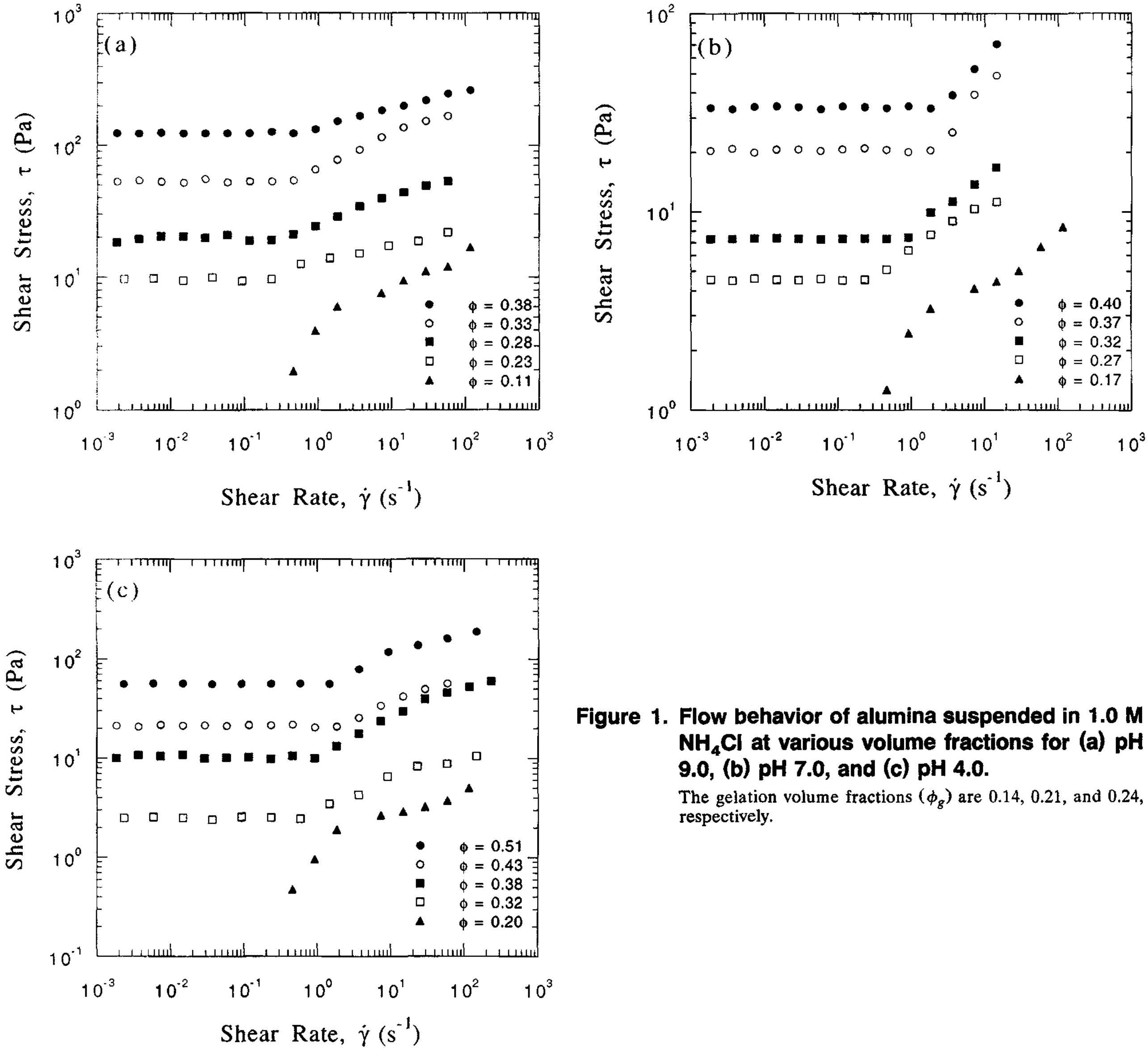

Figure 1. Flow behavior of alumina suspended in 1.0 M NH_4Cl at various volume fractions for (a) pH 9.0, (b) pH 7.0, and (c) pH 4.0.

The gelation volume fractions (ϕ_g) are 0.14, 0.21, and 0.24, respectively.

on the shear modulus. As with the shear yield stress, the shear modulus follows a power-law dependence ($G \approx B\phi^y$) with an exponent of $y = 5.0 \pm 0.1$, again in agreement with the scaling observed for a variety of aggregated suspensions. The stiffness of the suspensions increases (G increases) as suspension pH is increased toward the particle's isoelectric point.

The breaking strain, a measure of suspension brittleness, is a decreasing function of volume fraction and decreases with increasing pH (Figure 6). Power-law fits accurately describe the concentration dependence ($\gamma_b \approx C\phi^z$) with exponents of $z = -2.9 \pm 0.1$. Table 1 summarizes the volume-fraction dependence for the various shear properties.

Compressive properties

The concept of the compressive yield stress was formalized by Buscall and White (1987), who argue that P_y represents the ability of a particle network to support a static load. The compressive yield stress is analogous to the shear yield stress in that it is a critical stress below which the network is able to store the stress elastically. Above the compressive yield stress, the network undergoes an irreversible deformation. Unlike the shear properties, however, the compressive properties are highly dependent upon the method used to prepare the samples (Miller et al., 1995).

When the samples are prepared below the gel point, the particles in suspension exist as individual particles or flocs, with no interconnected structure. Bodies compressed at a slow rate should therefore have a homogeneous microstructure, and the compressive yield stress of these suspensions is termed the uniform suspension compressive yield stress. In these studies, we measured P_y on samples prepared below ϕ_g, which had been compressed to $\phi > \phi_g$, as well as samples made from dense suspensions, which had been diluted and exposed to high shear prior to the determination of P_y. The compressive yield stress of suspensions prepared by these dis-

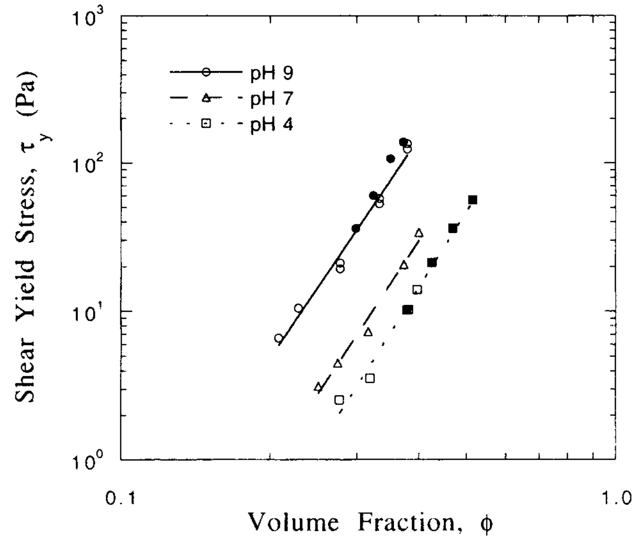

Figure 2. Shear yield stress of flocculated AKP-15 suspensions.

The solid symbols represent suspensions prepared below the gel point and compacted to the desired volume fraction. The open symbols represent suspensions prepared at high concentration and diluted.

tinct methods were, within experimental uncertainty, the same, suggesting that compaction from below ϕ_g, and high shear of samples prepared above ϕ_g produce similar microstructures (Figure 7). Without high shear mixing, samples prepared above ϕ_g displayed preparation method dependencies. The agreement of P_y measured on samples prepared by the two distinct methods gives confidence that the compressive and shear properties were measured on suspensions with similar microstructures.

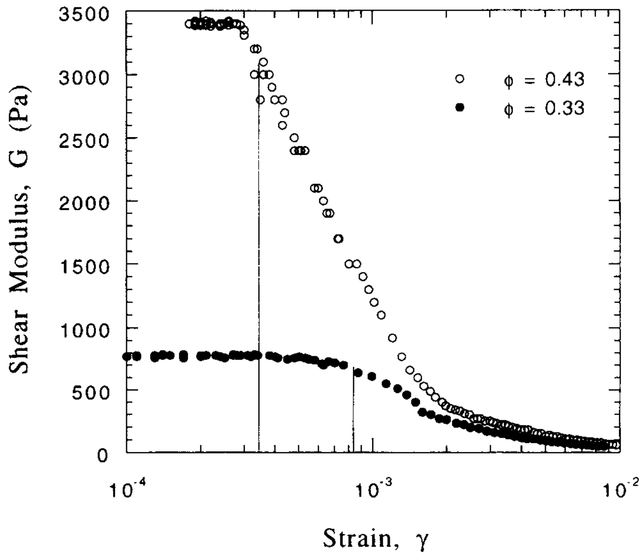

Figure 3. Strain sweep data at 1 Hz displaying the linear elastic region.

Extent of the linear response was estimated from the strain where the modulus drops to 0.9 times the low strain plateau modulus (vertical lines). Samples were at a pH of 9.0.

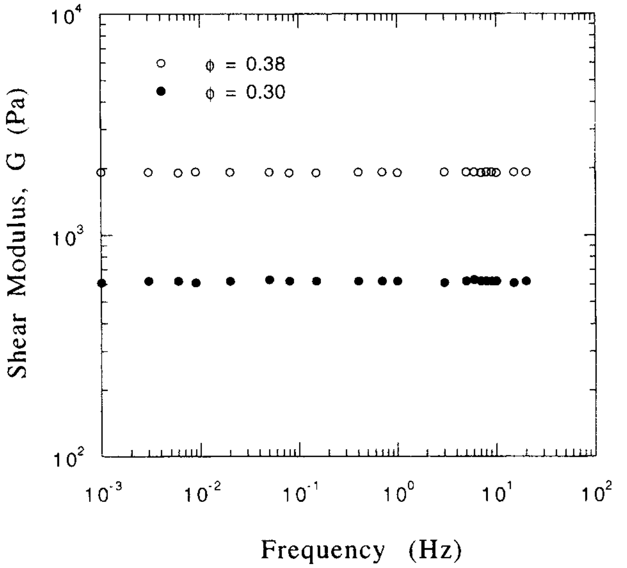

Figure 4. Shear modulus as a function of the frequency of oscillations for two flocculated alumina samples at pH 9.0.

Confirming the result of Miller et al. (1996), we find the compressive yield stress is independent of loading mechanism where the same $P_y(\phi)$ curves are measured through filtration and centrifugal techniques. The results of the three pHs investigated are summarized in Figure 7. At low concentrations ($\phi \leq 0.45-0.50$), $P_y^u \sim \phi^w$ (Table 1). However, as the particles approach a maximum packing fraction, a more rapid divergence is observed, and the simple power-law behavior fails. Landman et al. (1991) suggest that the compressive yield stress can be described by

$$P_y = k\left[\frac{\phi}{\phi_g} - 1\right]^n, \tag{2}$$

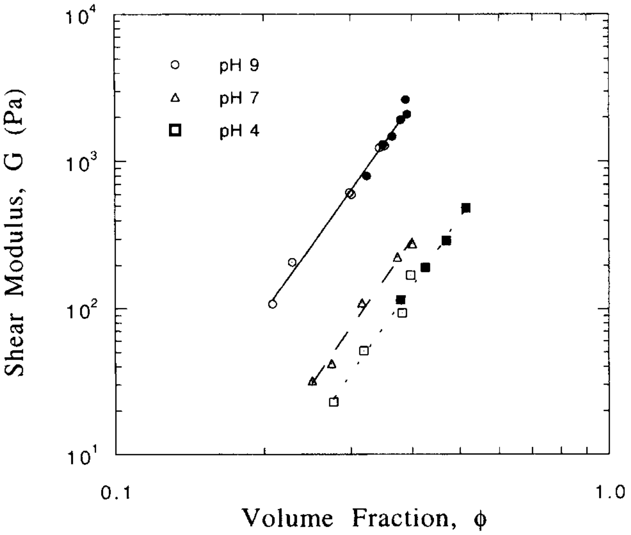

Figure 5. Effects of volume fraction and interparticle potential on the shear modulus for flocculated AKP-15 suspensions.

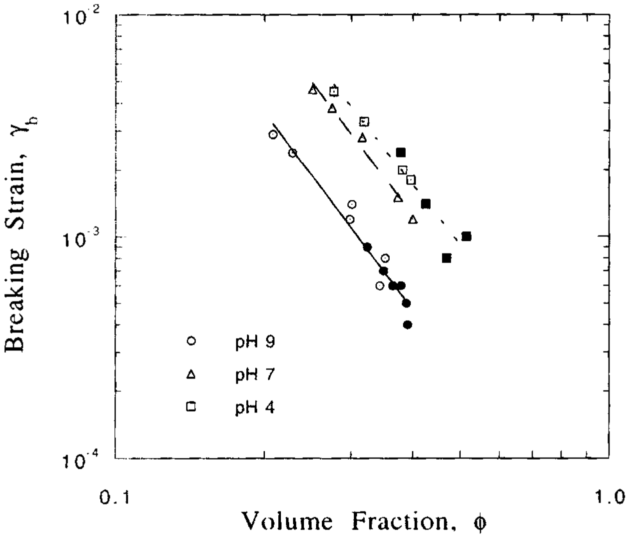

Figure 6. Summary of the breaking strain (γ_b) as a function of concentration for the three pHs studied.

where ϕ_g is the gel point. The gel point varies with the ionic conditions of the solvent, indicating that increasing attractions lowers ϕ_g (Table 2). These gel points were determined by curve fits to $P_y(\phi)$ and were qualitatively confirmed by observing the settling behavior of the suspensions.

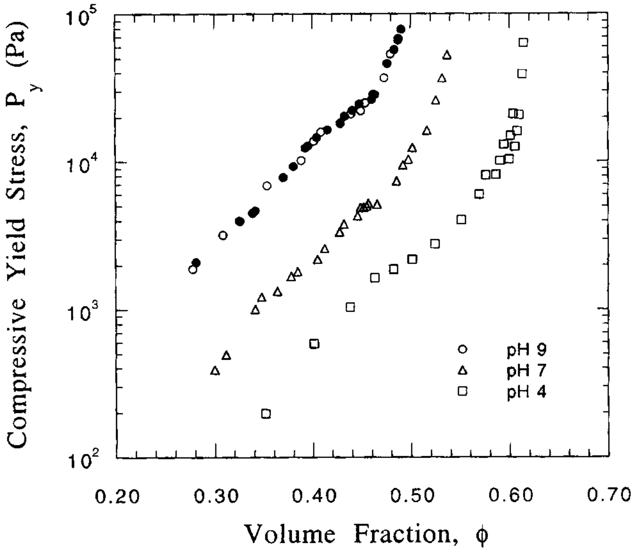

Figure 7. Compressive yield-stress curves for the three pHs studied.

The closed symbols represent a sample that was prepared at high ϕ, diluted, and subjected to high shear prior to testing. The samples represented by the open symbols were prepared below ϕ_g and compressed to $\phi > \phi_g$.

Discussion

Shear properties

The shear properties of a wide variety of flocculated suspensions exhibit power-law dependencies on volume fraction similar to the flocculated AKP-15 suspensions (Chen and Russel, 1991; Buscall et al., 1988; de Rooij et al., 1993, 1994; Shih et al., 1990). To describe this behavior, de Rooij et al. (1994) developed a microrheological model in terms of fractal microstructures. This model, extended by Potanin et al. (1995), describes the suspension in terms of particle chains where interparticle bonds can be soft or rigid. Only rigid bonds transfer elastic stress such that under equilibrium conditions, the elastic modulus is written in terms of the density of rigid chains, which is in turn determined by the rates particles form soft and rigid bonds by thermal agitation. In this model, shear thinning results from the shear degradation of chains. The volume-fraction dependence of the shear modulus, shear yield stress, and breaking strains are predicted to follow power-law dependencies with power-law exponents, α_G, $\alpha_{\sigma h}$, and α_{cr}, respectively, that were related to the fractal dimensions by

$$\alpha_G = (7 + 2d_1 - 2d_f)/(3 - d_f) \tag{3}$$

$$\alpha_{\sigma h} = 3/(3 - d_f) \tag{4}$$

$$\alpha_{cr} = -\,d_1/(3 - d_f), \tag{5}$$

where d_1 ($1 < d_{ch} < 1.6$) is the chemical dimension, and d_f is the fractal dimension of the flocs within the suspension.

Previous studies on a variety of systems have reported α_G to be between 3.7 and 5.0 (Shih et al., 1990; Buscall et al., 1988). De Rooij et al. (1994) report values of 4.6 ± 0.3 for weakly aggregated latex suspensions, while Rueb (1994) reports α_G to be 5.0 ± 0.2 for presheared suspensions of octadecyl silica particles. For the dense, presheared alumina systems investigated here we find $\alpha_G = 5.0 \pm 0.1$. Buscall et al. (1988) find values of $\alpha_{\sigma h}$ in the range of 4–5, while de Rooij et al. (1993) report values of 3.0 ± 0.1, and our dense suspensions have a uniform value of $\alpha_{\sigma h}$ of 5.0 ± 0.1. Finally, de Rooij et al. (1993) report α_{cr} of -2.5 ± 0.3, while Shih et al. (1990) report α_{cr} values of -2.1 and -2.3 for low volume-fraction boehmite and alumina gels. For dense octadecyl silica gels, Rueb (1994) finds α_{cr} ranges from -0.7 to -4.0 as the strength of the attraction increased. Note that for the alumina systems investigated here, $\alpha_{cr} = -2.9 \pm 0.1$. From this comparison we conclude that the systems investigated here have power-law dependencies similar to previously investigated aggregated suspensions.

Table 1. Power Law Dependence for the Suspensions Properties

	$\tau_y = A\phi^x$		$G = B\phi^y$		$\gamma_b = C\phi^z$		$P_y = D\phi^w$	
pH	A	x	B	y	C (10^{-4})	z	D (10^5)	w
4.0	1,740	5.2	12,900	4.9	1.50	−2.8	0.941	5.3
7.0	2,980	5.1	29,100	5.0	0.99	−2.9	1.96	5.0
9.0	23,500	5.1	221,000	4.9	0.32	−2.9	15.1	5.1

Predicted Values	$\alpha_{\sigma h}$	α_G	α_{cr}
$d_f = 2.3\text{–}2.4$, $d_1 = 1.3$	4.3–5.0	6.7–7.0	−1.4–1.6
$d_f = 1.8$, $d_1 = 1.3$	3.0	3.3	−1.0

Note that power-law dependence for the compressive yield stress is only observed for $\phi < 0.4\text{–}0.5$.
All prefactors are in units of Pa except C which is dimensionless.

Table 2. Parameters for Compressive and Shear Properties when Fit to the Form $k(\phi/\phi_g - 1)^n$

		$\tau_y = A'(\phi/\phi_g - 1)^{x'}$		$G = B'(\phi/\phi_g - 1)^{y'}$		$\gamma_b = C'(\phi/\phi_g - 1)^{z'}$		$P_y = D'(\phi/\phi_g - 1)^{w'}$	
pH	ϕ_g	A'	x'	B'	y'	C' (10^3)	z'	D'	w'
4.0	0.24	40.4	2.5	533	2.6	1.34	−0.67	2,470	2.6
7.0	0.21	41.7	2.4	528	2.4	1.46	−0.72	2,170	2.6
9.0	0.14	42.5	2.6	565	2.4	1.28	−0.69	2,320	2.4

Again, all the prefactors are in Pa, except C' which is dimensionless, and the compressive data were fit over the low-volume fraction region.

De Rooij et al. (1993, 1994) and Rueb and Zukoski (1997) conclude that the presheared suspensions have fractal dimensions of 2.3–2.4. Using this value for d_f, $\alpha_{\sigma h}$ is predicted to be 4.3–5.0, while setting d_1 to a lower bound of 1.0 yields $\alpha_{cr} = -(1.4\text{–}1.6)$ and $\alpha_G = 6.7\text{–}7.0$. [Potanin et al. (1995) prefer $d_1 = 1.3$, which is expected for percolation clusters. Under these conditions $\alpha_{cr} = -(1.7\text{–}2.1)$ and $\alpha_G = 7.1\text{–}8.0$.] On the other hand, Potanin et al. (1995) assumes that γ_b and G reflect quasi-equilibrium structures yielding values of $d_f = 1.8$ and $d_1 = 1.3$. From these values, using Eqs. 3–5, we predict $\alpha_G = 3.3$, $\alpha_{\sigma h} = 3.0$, and $\alpha_{cr} = -1.0$. While the use of $d_f = 2.3\text{–}2.4$ provides the best approximation, the overprediction of α_G is severe and well outside the experimental range. For ease of comparison, these predictions are reproduced in Table 1.

The lack of agreement between our results and the predictions of the model of Potanin et al. (1995) is disappointing, as this description appears to capture much of the essential physics of the mechanical properties of aggregated suspensions. The failure may arise from microstructures that are not well described by the models. In the first place, our suspensions have been subjected to high shear prior to measuring mechanical properties. Second, the alumina suspensions tend to be of higher volume fraction than those of de Rooij et al. (1994) and Shih et al. (1990). Third, our suspensions have well-defined gel volume fractions below which they are liquidlike. The models of de Rooij et al. (1993, 1994) and Potanin et al. (1995) were developed for suspensions that gel at all volume fractions, and thus there might be substantially different microstructures for dense gelling systems than for dilute systems that gel in the limit of $\phi = 0$.

Rueb (1994) and Rueb and Zukoski (1997) found that the shear properties of colloidal silica gels could be described as functions of (ϕ/ϕ_g). This approach correctly captures the pH and volume fraction dependencies of the shear properties of the flocculated AKP-15 suspensions, suggesting that the changes in microstructure in presheared suspensions are buried in the exponent, while the influence of interaction potential is associated with ϕ_g. In agreement with the studies here on alumina, in extensive studies of gelled octadecyl silica suspensions, Rueb and Zukoski (1997) found that $G \sim (\phi/\phi_g)^5$. Thus, for at least these two systems where ϕ_g is finite, the details of the interaction potential appear to weakly influence scaling exponents, while the strength of the attraction is largely buried in ϕ_g.

Compressive properties

Recently, Potanin and Russel (1996) presented a model for the compressive properties of beds of aggregated particles that accounts for a transition from viscous to plastic deformation mechanisms as the load is increased. In this approach, for $P < P_y$, the suspension will respond in a viscous manner at times longer than the suspension's characteristic relaxation time, t_c. Potanin and Russel (1996) estimate this crossover time for a suspension of spheres of radius a, aggregated due to an attractive well of depth U_c, as

$$t_c \approx \frac{\delta}{k_0^{1/2} U_c} 6\pi\eta_c a^2 \exp\left(\frac{zU_c}{k_bT}\right)\phi^{d_1/(3-d_f)}, \tag{6}$$

where δ is the surface-to-surface spacing of particles in the network; η_c is the continuous phase viscosity; z is the average number of bonds per particle; d_1 is the dimension of the chain bearing the load ($1 \le d_1 \le 1.6$); and d_f is the fractal dimension of aggregated structure (typically, $1.6 \le d_f \le 3$). The dimensionless curvature of the potential energy well when the particle surfaces are spaced by a distance δ, k_0, is a poorly characterized parameter, but may be large. Potanin and Russel (1996) use a value of $k_0 = 100$ to describe the compressive rheology of aggregated suspensions. Choosing $a = 0.65$ μm, $\eta_c = 10^{-3}$ Pa·s, $\phi = 0.3$, $d_1 = 1.6$, $d_f = 2.0$, $\delta = 5$ nm, $z = 3$, and $U_c = 5\text{–}10$ k_bT, we estimate t_c ranges from several hours to several thousand years. If the attractions arise from van der Waal's forces, $U_c \approx Aa/12\delta$, where A is the Hamaker coefficient that is 5–10 k_bT. This approximation yields $U_c/k_bT = 40\text{–}80$, indicating that for the systems studied here, t_c is extremely large. Based on these estimates, even though the compression experiments used here required several days to reach equilibrium, we conclude the samples deformed in a plastic manner and, in further discussions, we will neglect viscous deformation during compaction.

Systematic investigations of the dependence of P_y on process variables are limited. However, a recent investigation on alumina, zirconia, and clay suspensions shows that P_y is independent of loading mechanism (Miller et al., 1996). Bergström et al. (1992) and Green et al. (1994) show that the compressive yield stress is sensitive to the particle interaction potential, and several studies suggest P_y is well described by a power-law function of volume fraction near ϕ_g, but diverges more rapidly at volume fractions approaching close packing (Green et al., 1996; Meeten, 1994; Buscall et al., 1988). Recently, for particles at their isoelectric points, P_y was found to scale as a^{-2} where a is the particle size (Miller et al., 1996). This result parallels the work of Leong et al. (1994) for the shear yield stress, which also demonstrated an inverse parabolic dependence on particle size.

Figure 8 shows the compressive and shear yield stresses the AKP-15 suspensions as a function of ϕ/ϕ_g. Data are only

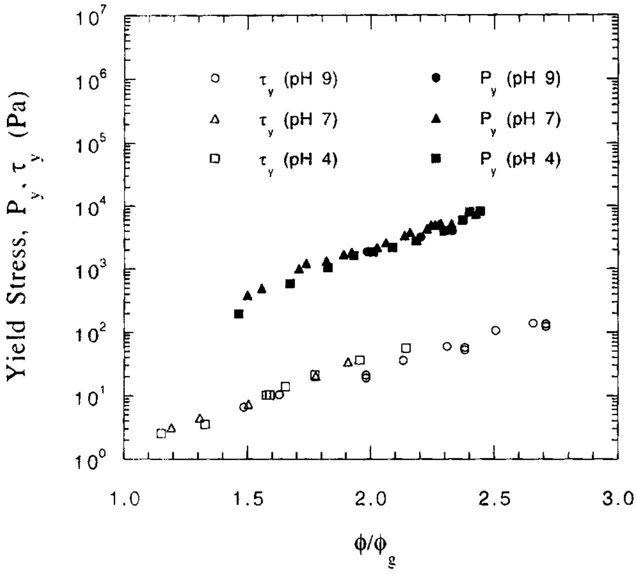

Figure 8. Comparison of the compressive and shear yield stresses normalized by the gel point (from Table 2).

shown over the volume-fraction range where suspensions could be loaded into the rheometer for determination of τ_y. For $\phi/\phi_g > 2.5$, this scaling fails for P_y as the suspensions approach close packing at different rates. In the range of volume fractions shown, P_y and τ_y are both well described by a power-law model with an exponent of 5.0. The ratio of the compressive yield stress to the shear yield stress is therefore independent of concentration and strength of interparticle attraction (as reflected in ϕ_g), yielding $P_y/\tau_y = 55$. Buscall (1982) followed by Buscall et al. (1988) argue that the elastic modulus should have the same volume-fraction dependence as the bulk modulus of the particle network. Not surprisingly, as P_y and G are both well described by the same power-law exponent for the systems we investigate here, we find that $K/G \approx 46$ independent of volume fraction or particle interaction potential (Figure 9).

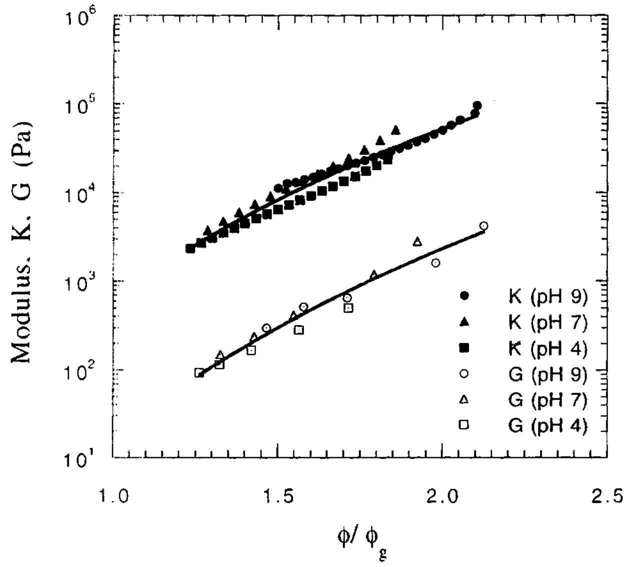

Figure 9. Comparison of the bulk and snear moduli normalized by the gel point.

Meeten (1994) developed a model based on linear elasticity to relate the various rheological parameters, which assumes that the response to any stress is a linear deformation until yield. In linear elastic theory, any stress on a body can be written in terms of the principal stresses (σ_1 and σ_2). Since both compression and shear can be written in terms of the same normal stresses, these two mechanical properties are directly related through Poisson's ratio (Chou and Pagano, 1967). If the principal axes are set up so that the axis of compression lies along one of the principal axes, $P = \sigma_1$, the maximum shear stress in the bed acts on a plane at 45° from this compressive axis with a magnitude of $\tau = (\sigma_1 - \sigma_2)/2$. In a pressure filter the walls of the container and thus the material do not deform perpendicular to the compressive axis such that $\sigma_2 = \sigma_1 \nu/(1-\nu)$, where ν is Poisson's ratio (Chou and Pagano, 1967). As a result, although the measured compressive yield stress is equal to σ_1 (the applied normal load), the bed deforms as if it were subjected to an isotropic pressure σ_2 and an excess compressive load of $\sigma_1 - \sigma_2 = 2\tau$. If the material deforms like a linear elastic solid up to the yield point,

$$\frac{P_y}{\tau_y} = \frac{2(1-\nu)}{1-2\nu}, \tag{7}$$

where the assumption has been made that τ_y is independent of P up to the yield point. Experimentally, P_y/τ_y is independent of volume fraction or strength of interparticle potential with a value near 55. From this we estimate $\nu = 0.491 \pm 0.001$.

Linear elastic theory can also be used to relate the bulk and shear moduli to Poisson's ratio:

$$\frac{K}{G} = \frac{2(1+\nu)}{3(1-2\nu)}. \tag{8}$$

When the values obtained for the suspensions investigated are used, Poisson's ratio is calculated to be 0.489 ± 0.002. The agreement between the value of Poisson's ratio calculated from the yield-stress data and that calculated from the modulus data suggests that despite the uncertainties associated with the bulk modulus, it is a reasonably accurate measure of the elastic behavior of the suspensions. Meeten (1994) reports values of ν ranging from 0.474 to 0.497 for aggregated suspensions of inorganic materials, while the soil mechanics literature reports Poisson's ratio to lie in the same range (Terzaghi et al., 1996).

These results suggest that the shear and compressive properties of the alumina suspensions studied are linked through a single parameter, Poisson's ratio, which is found to have a value near 0.49. Indeed, our investigations suggest ν is independent of volume fraction and strength of interparticle attraction. Knowledge of Poisson's ratio therefore allows prediction of the compressive properties from the shear properties. Unfortunately, given τ_y, small changes in ν produce large changes in P_y. As a result, blind application of Eq. 7 may result in large errors in predicting P_y from τ_y.

Conclusions

In this work we present a detailed investigation of the shear and compressive properties of weakly aggregated, alumina suspensions. The shear properties of these materials are similar to broad classes of gelled suspensions showing power-law dependencies on volume fraction for yield stress, modulus, and strain limiting the extent of a linear response. While power-law exponents are weakly dependent on strength of attraction, master curves of these parameters and the compressive yield stress can be generated by scaling volume fraction with ϕ_g. Models developed to link power-law exponents to microstructure are only partially adequate. However, the scaling of mechanical properties on ϕ/ϕ_g reported here is independent of microstructural models, suggesting that alternative descriptions for linking microstructure to flow properties must be sought. The master curves produced by plotting mechanical properties against ϕ/ϕ_g are similar to those reported for gelled octadecyl silica particles, providing some hope that broad classes of materials can be described with a limited set of parameters. We note, however, that power-law fits to the data are difficult to test due to the limited range of volume fractions and measured material properties that could be investigated.

A central goal of this work was to link compressive and shear properties of suspensions. Over the range of volume fractions where both shear and compressive properties could be measured, P_y and τ_y had the same power-law dependencies on volume fraction. Using a model where the suspension responds like a linear elastic solid up to the yield point, Poisson's ratio is found to lie near 0.49. Values in the range of 0.474 and 0.495 have been reported for a variety of aggregated suspensions and soils, offering hope that P_y can be predicted from τ_y. However, the success of this model is tempered by the fact that given τ_y, P_y is extremely sensitive to small changes in ν such that a decrease of ν to 0.485 produces a decrease in P_y of an order of magnitude. Nevertheless, given a slurry, measurement of τ_y at different volume fractions above ϕ_g provides a useful characterization tool for how the compressive properties will vary with increasing volume fraction.

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