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The relationship between particle aggregation and rheology in mixed silica–titania suspensions

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Abstract

The rheological behaviour of concentrated suspensions of coarse SiO_2 particles containing various amounts of fine TiO_2 has been studied using a viscometer which prevents settling of the suspended material. At a volume fraction of 0.468 the mixed SiO_2/TiO_2 suspensions exhibit shear thinning behaviour, with the yield stress and viscosity being strongly dependent on pH and the TiO_2 content of the suspension. Four different TiO_2 samples are investigated, each having different inorganic surface coatings. The TiO_2 particles adsorb on the surface of the SiO_2 particles and coat them, resulting in suspensions with isoelectric points corresponding to those of suspensions containing TiO_2 alone. The changes in yield stress as a function of pH are influenced by the TiO_2 content of the suspension, and when the silica:TiO_2 volume ratio is greater than $\sim$0.03, the yield stress vs pH curve resembles that of a pure TiO_2 suspension. The maximum yield stress is observed at a pH corresponding to the isoelectric point of the TiO_2 component, and at this pH, networks of TiO_2 aggregates can form. The formation and breakdown of these aggregates has been monitored in concentrated suspensions using focused beam reflectance measurement (FBRM). FBRM results clearly demonstrate that increases in the yield stress of the suspensions are accompanied by an increase in aggregate size. At a given pH, changes in plastic viscosity with increasing TiO_2 content in the suspensions appear to result from an increase in the maximum packing density due to the corresponding change in the particle size distribution.

Keywords: Rheology; Aggregation; Silica; Titanium dioxide; Concentrated suspensions; Focussed beam reflectance measurement

1. Introduction

The transport of concentrated suspensions is an important consideration in many mineral processing operations, particularly with regard to the disposal of process tailings. Economic and environmental considerations usually dictate that solid waste be transported as a slurry of high solids concentration. However, this often presents problems, because the flow properties of a slurry can change drastically as the solids concentration is increased, and if the slurry is to be transported by pumping through a pipeline, increased power consumption becomes a major concern. If particle–particle interactions in the suspension lead to aggregation, the effects on the viscosity can be dramatic, since not only are the aggregates bigger than the individual particles, and hence more resistant to flow, but they also enclose, and so immobilise some of the liquid phase. This increase in the apparent solids volume fraction, results in a higher than expected viscosity at low shear rates, with the suspension exhibiting non-Newtonian shear-thinning behaviour.

Suspensions encountered in processing industries typically contain a number of mineral components of various particle sizes and, although most mineral slurries have average particle sizes well in excess of colloidal dimensions, there is usually a sufficient number of sub-micron particles for electrostatic interparticle forces to be significant. Attractive electrostatic interactions are more likely to occur between particles when the surfaces are dissimilar, so mutual aggregation of the components of mixed suspension systems, known as heteroaggregation, is an important factor influencing their flow properties. The most commonly observed rheological behaviour for such slurries is pseudoplasticity, since the aggregates of particles can withstand small shear stresses, but are frequently broken down by larger stresses.

Heteroaggregation in mixed colloid suspensions has been extensively studied [1] and the conditions required for colloid stability (i.e. dispersion) in such systems are well understood [2]. However, the link between aggregation

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conditions and overall suspension rheology, particularly in concentrated suspensions [3,4] has received less attention. This may be a consequence of the difficulty in observing such aggregation in a concentrated slurry. For dilute suspensions, aggregate size can be measured by optical techniques such as light scattering, [5] or inferred from sedimentation behaviour [6], but such sizing techniques are not suited to the study of suspensions at the high solids concentrations usually associated with mineral processing schemes.

Focused beam reflectance measurement (FBRM) offers the possibility of in situ characterisation of particles and aggregates over a wide range of solids concentrations [7]. In this technique, a highly focused laser beam is projected through a sapphire window and rapidly scans at a fixed velocity (2 m s^{-1}) across any particle or aggregate flowing past the window. The beam will cross on a straight line between any two points on the edge of the particle or aggregate, the distance between these points being a *chord length* (Fig. 1). Light is then reflected back to the probe and, given that the duration of the reflection and the laser scanning speed are known, the chord length can be calculated. Thousands of chords may be counted per second, producing a chord length distribution over the range 0.8 to 1000 μm, which may be updated at short intervals. As can be seen from Fig. 1, for a spherical particle a distribution of chord lengths will be measured between zero and the particle diameter. Such distributions will shift in response to changes in particle or aggregate size, and the form of the distribution will also be influenced by the shape of the particles or aggregates.

FBRM relies solely on laser reflection rather than scattering and, as such, is much less sensitive to multiple scattering and coincidence effects. It is therefore, a technique which can be used at much higher solids concentrations than particle sizing instruments based on laser diffraction. FBRM is also ideally suited to the study of weakly aggregated systems, as it does not require sample dilution or result in significant aggregate disruption.

While attempts have been made to calibrate FBRM against laser diffraction measurements for particle standards [8], the sensitivity of FBRM to shape makes such calibrations of little value for non-spherical particles and, in particular, for aggregating systems. FBRM is therefore not used to obtain absolute measurements, but to provide a direct, real-time indication of changes (permanent or transitory) in particle or aggregate size.

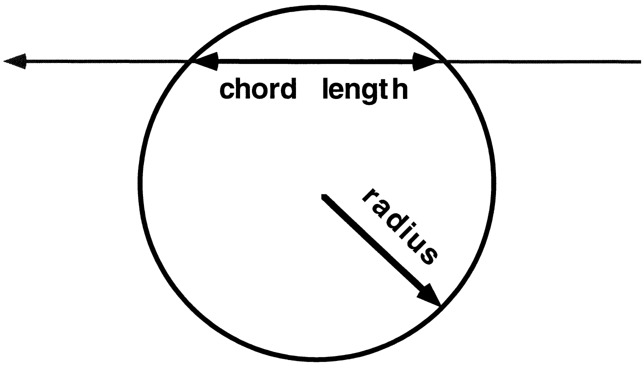


Fig. 1. Definition of a chord length.

A mixed aqueous slurry containing coarse silica as the major component, with much finer titania present in quantities up to 10% by weight has been chosen as a model system. Silica is the principal component in many mineral process tailings, but a number of minor components, including other metallic oxides, may also be present, depending on the particular mining and processing operations [9,10]. Titania was chosen as the minor constituent for the experiments described here due to the ready availability of samples having different inorganic surface treatments, while still having very similar densities and particle size distributions. This meant that the effects of surface properties on the overall aggregation characteristics of the system could be studied while maintaining almost constant particle size and volume fractions of the suspended solids.

2. Materials and methods

2.1. Materials

SiO_2 (grade 100G, Commercial Minerals) was 99.5% pure and composed of quartz crystallites having irregular prismatic shapes. The density of the SiO_2 was 2.65 g cm^{-3}. The TiO_2 was a pigment-grade rutile product with a density of 4.27 g cm^{-3}, kindly provided by Tiwest. Four samples were supplied, each having a different inorganic surface treatment. The four samples will be referred to here as **T1**, **T2**, **T3** and **T4**, and their surface treatments and particle size distributions are outlined in Table 1. The particle size distributions of the SiO_2 and TiO_2 samples were determined by laser diffraction on a Malvern Mastersizer, and the size distributions for the four TiO_2 samples were confirmed to be very closely matched. Only sample **T4** had a significant content of particles greater than 1 μm in diameter (~8%). The SiO_2 sample had a median particle diameter $d_{50} = 44$ μm, with a somewhat broader size distribution than the TiO_2 samples (~3% under 1 μm).

Table 1
Composition and particle size distribution data for TiO_2 samples **T1–T4**

TiO_2 sample	Other major components[a] (%, w/w)		Particle size data (μm)		
	Al_2O_3	SiO_2	d_{10}	d_{50}	d_{90}
T1	1	0	0.16	0.30	0.78
T2	3.5	0	0.17	0.31	0.64
T3	3.5	3	0.17	0.32	0.70
T4	2.5	7	0.17	0.39	1.73

[a] Composition is expressed as % (w/w) of bulk, although these components are known to be present as surface coatings.

Mixtures of SiO_2 and TiO_2 were dispersed in de-ionised water by gentle agitation on a bottle roller for at least 2 h before carrying out rheometry or FBRM measurements. Quantities of SiO_2 and TiO_2 were chosen so as to give a total volume fraction of suspended solids $\phi = 0.468$ for all slurries. Maximum packing fractions were determined by centrifugation, using a modified centrifuge tube with a glass stopper fitted with a capillary. This tube can be used as a density bottle to determine the density of a maximally-packed slurry. The slurry density can then be converted to a volume fraction according to the equation $\phi = (\rho_{sl} - \rho_l)/(\rho_s - \rho_l)$, where ρ_l, ρ_s and ρ_{sl} are the densities of the liquid phase, the solid phase, and the slurry respectively.

2.2. Rheometry

Rheological data was obtained using a Haake RV20 viscometer with concentric cylinder geometry. The sensor system comprised a profiled rotor with a slotted sleeve and rotating bowl apparatus designed for the study of coarse settling suspensions [11]. Rheograms were recorded at 20°C, with shear rate being uniformly increased and decreased over the range of 0 to 500 s^{-1}, with a total time period of 20 min for both the increasing and decreasing shear rate sweeps. A pH electrode was positioned in the rotating sample vessel to allow continuous monitoring, and pH was controlled by addition of a few drops of 5.0 M HCl or 5.0 M NaOH. Since the sample volume for a typical experiment was approximately 1.2 l, these additions did not affect the solids volume fraction of the suspension significantly.

2.3. Aggregate characterisation

Focussed beam reflectance measurement was carried out using an M200 field unit (Lasentec®, Redmond, Washington, USA), together with an M200L laboratory probe. The laboratory probe has a 12 mm diameter flat window set at the base of a probe body 318 mm long and 25 mm in diameter. The probe body is fitted to a larger casing which contains the electric motor for the scanning drive, and is connected to the controlling electronics in the field unit by a 10 m fibre optic cable. The probe was made of stainless steel and can be used at up to 120°C in strong acid or caustic solutions. For the measurements carried out in this study, the focal point of the laser was set to the window surface.

Slurries were mixed in the same rotating bowl apparatus as used for rheological tests, but with the M200L probe in place of the viscometer. The probe was placed eccentrically in the sample to ensure a steady flow of slurry past the probe window. Measurements were integrated over a 10 s interval, with the reported values and distributions representing the averages of 10 consecutive measurements (i.e. 100 s) at a time when the slurry pH was stable. The measured chord lengths were highly stable over this period, with variations typically less than ±0.5%.

Optical micrographs were recorded under transmitted light on an Olympus PMG 3 metallurgical microscope.

2.4. Zeta potentials

Surface (ζ) potentials were measured using a Matec ESA 800 electroacoustic analyser. Iso-electric points (IEP's) for the four TiO_2 samples were determined by titration with 0.5 M NaOH or 0.5 M HCl, in suspensions having a solids volume fraction of 0.01 in de-ionised water. Zeta potential values for silica were also determined at a volume fraction of 0.01, and were measured using the $-38\ \mu m$ fraction of the commercial material.

3. Results and discussion

Rheograms obtained for SiO_2 suspensions containing increasing amounts of TiO_2 (sample **T2**), at pH = 7.5 are shown in Fig. 2, and it can be seen that shear thinning behaviour is apparent with only 1% (w/w) TiO_2 present. Rheograms were measured in directions of both increasing and decreasing shear rate, and no hysteresis was observed in any of the slurries studied. Only curves measured in the direction of increasing shear rate are shown here. Slurries containing SiO_2 alone displayed Newtonian behaviour over the entire pH range, as would be expected for suspensions of coarse particles [12], but shear thinning behaviour was observed in SiO_2/TiO_2 mixed suspensions even with very small amounts of TiO_2 present. All silica/TiO_2 mixed slurries studied here exhibited characteristic Bingham plastic behaviour, and rheological data are presented in the form of extrapolated dynamic yield stresses and plastic viscosities determined from curves of the type represented in Fig. 2.

The suspension pH has a significant effect on the rheology (Fig. 3). The yield stresses of SiO_2(90%)/TiO_2(10%) slurries of volume fraction $\phi = 0.468$ are plotted against pH for each of the four TiO_2 samples, and it is clear that the rheology is also greatly influenced by the surface properties of the fine particle component in the suspension. The largest yield stresses are observed for sample **T1**, with a surface coating containing Al_2O_3. Yield stresses generally decrease for samples **T2**–**T4**, with slurries containing **T4** exhibiting very low yield stresses above pH 7.

An important feature of the yield stress–pH curves (Fig. 3) is that each of the suspensions has its maximum yield stress at a pH close to the IEP of the TiO_2 particles. Fig. 4 shows the pH dependence of the zeta potential for the four TiO_2 samples and the SiO_2 in the range pH = 4 to pH = 12. The IEP's for the TiO_2 samples are 6.7, 7.6, 5.9 and 4.3 for samples **T1**, **T2**, **T3** and **T4** respectively, while the IEP for SiO_2 is below pH = 4 and the silica thus carries a negative surface charge over the full range of pH studied here.

It has been reported that in bimodal suspensions where the particle size ratio is large, the colloidal fraction is

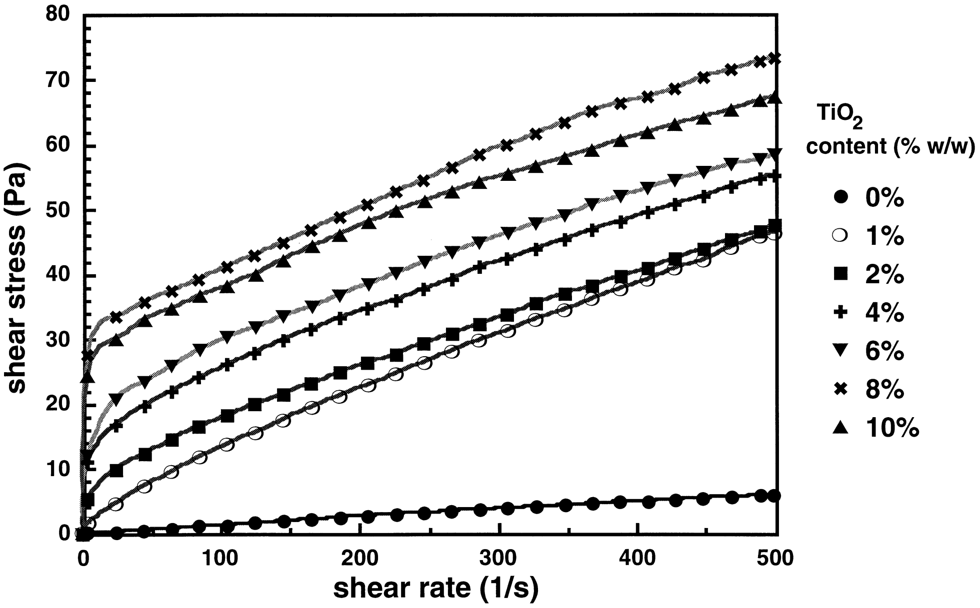


Fig. 2. Shear stress-shear rate curves for silica/TiO_2 suspensions showing the effect of increasing amounts of TiO_2 (sample **T2**). Total solids volume fraction = 0.468. pH = 7.5. Temperature = 20°C.

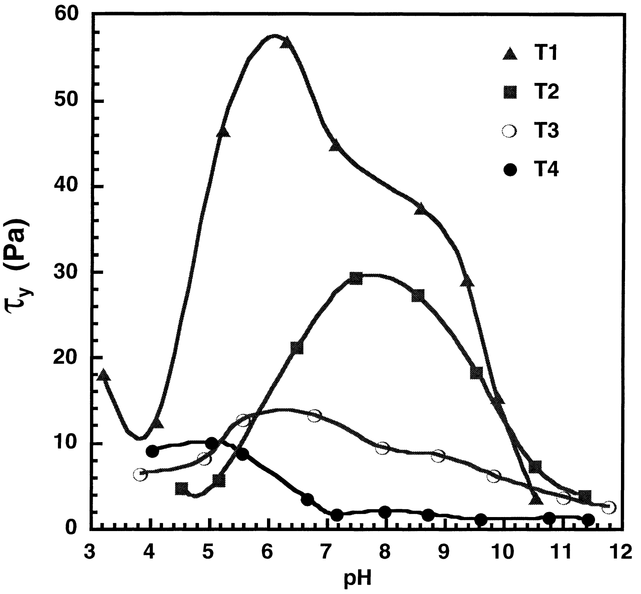


Fig. 3. Extrapolated yield stress (τ_y) vs pH behaviour for silica/TiO_2 suspensions prepared from four different TiO_2 samples (**T1**–**T4**). Total solids volume fraction = 0.468. TiO_2 component is 10% (w/w) of total solids. Temperature = 20°C.

primarily responsible for the non-Newtonian behaviour, while only hydrodynamic interaction takes place between the coarse particles [12]. Similar behaviour has been described in mixed aluminium hydroxycarbonate/magnesium carbonate suspensions [3] in which the pH sensitivity of rheological properties was analogous to that of aluminium hydroxycarbonate suspensions. The SiO_2/TiO_2 slurries studied here further demonstrate this principle, given that these mixed suspensions show yield stress vs pH behaviour which closely resembles that of pure titania even when the solid component contains 90% (w/w) silica.

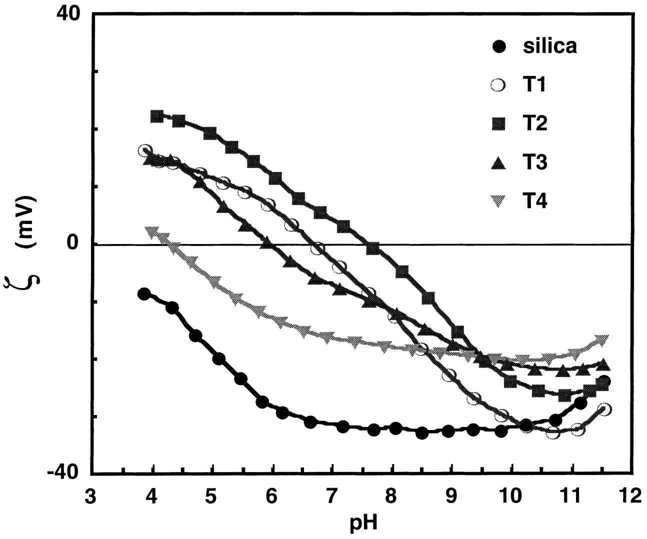


Fig. 4. Zeta potential (ζ) vs pH behaviour for four different TiO_2 samples (**T1**–**T4**) and silica.

Given the size difference between the two oxides, and their opposite surface charges, TiO_2 particles are expected to adsorb onto and coat the surface of the SiO_2 particles to produce suspensions in which surface properties of the SiO_2 particles are similar to those of the TiO_2 particles [1]. The maximum yield stress observed at the IEP will thus result from the formation of 3-dimensional interparticle aggregates or networks which can form readily in the absence of repulsive electrostatic forces between the colloidal TiO_2 particles.

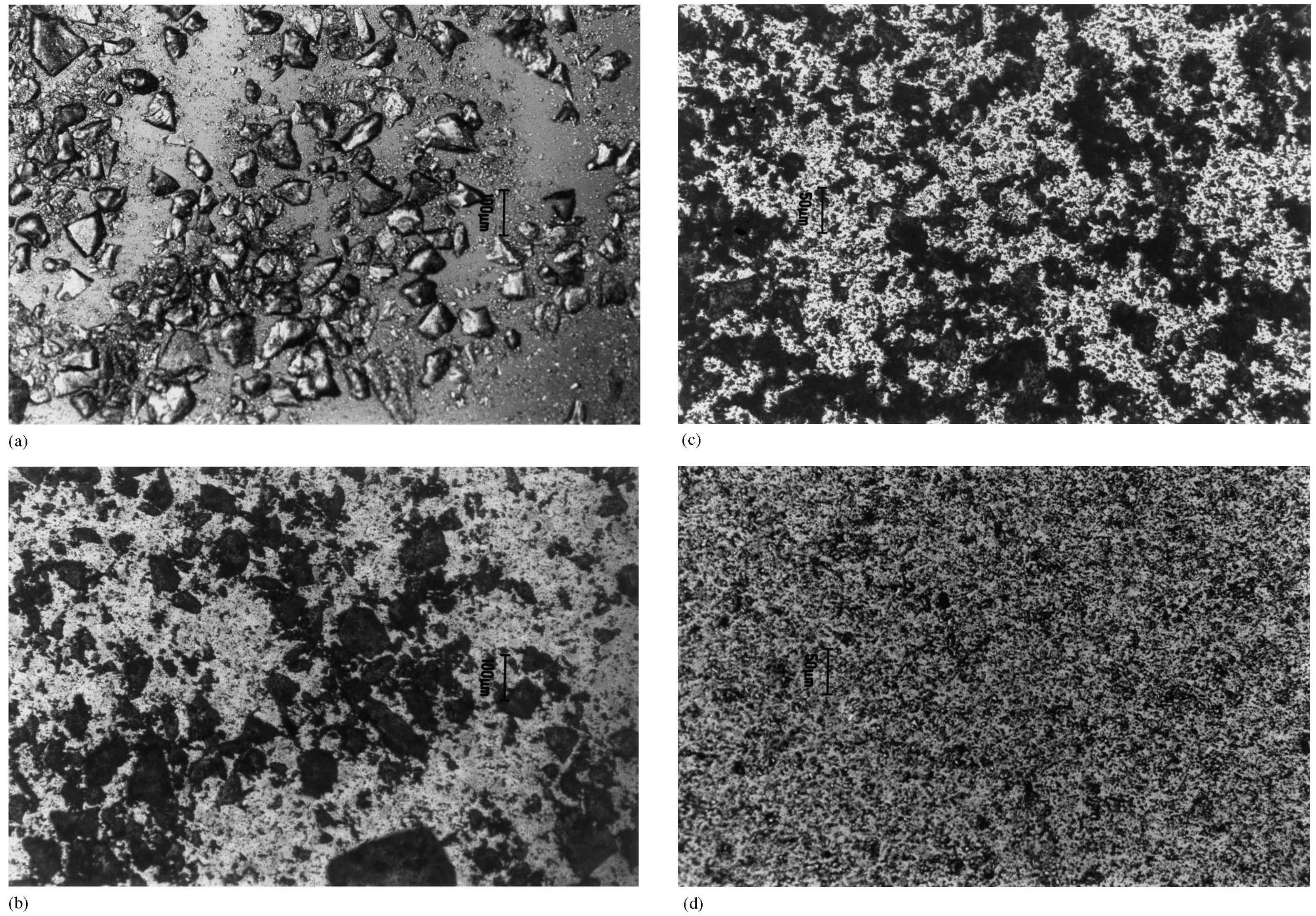


Fig. 5. Optical micrographs of SiO_2 and mixed SiO_2/TiO_2 suspensions at a concentration of 5% (w/w) solids. (a) SiO_2 suspension, pH 7, magnification 100× (b) SiO_2/TiO_2 9:1 suspension, pH 7, magnification 100× (c) SiO_2/TiO_2 9:1 suspension, pH 7, magnification 200× (d) SiO_2/TiO_2 9:1 suspension, pH 4, magnification 200×.

Optical microscopy of SiO_2 and mixed SiO_2/TiO_2 suspensions provides some visual evidence of such behaviour, as illustrated by the micrographs shown in Fig. 5. By comparison of the micrographs (a) and (b) in Fig. 5 it can be seen that in the presence of TiO_2 and at pH 7, the normally transparent SiO_2 particles are rendered more opaque as the fine TiO_2 particles coat their surface. Evidence of the pH dependence of aggregation in the SiO_2/TiO_2 mixtures is provided by a comparison of micrographs (c) and (d) in Fig. 5. These are images of SiO_2/TiO_2 mixed suspensions of the same composition at pH 7 and 4 respectively, showing an aggregated network of particles in the suspension at pH 7, while at pH 4 the particles are uniformly distributed throughout the sample and show little indication of any aggregate formation.

While optical microscopy can provide a useful visualisation of aggregate formation in dilute suspensions, the behaviour observed at low solids concentration may not necessarily be a true reflection of the aggregate structure in a concentrated, flowing suspension. FBRM provides a means of following the trends in aggregate size under identical conditions to those used for rheological measurements, and hence allows changes in rheology to be linked directly with changes in particle aggregation. In Fig. 6 changes in the average chord lengths are shown as a function of pH for the four suspensions represented in Fig. 3. The changes in yield stress values with pH are also shown for the sake of comparison, revealing that in each case, the pH corresponding to the maximum average chord length is close to that at which the maximum yield stress is observed. While the magnitude of the maximum yield stress in these mixed suspensions is clearly dependent on the nature of the surface coating on the TiO_2 component, it is interesting that the average chord length varies over much the same range for each of the four suspensions shown in Fig. 6. (Note that the scale of the

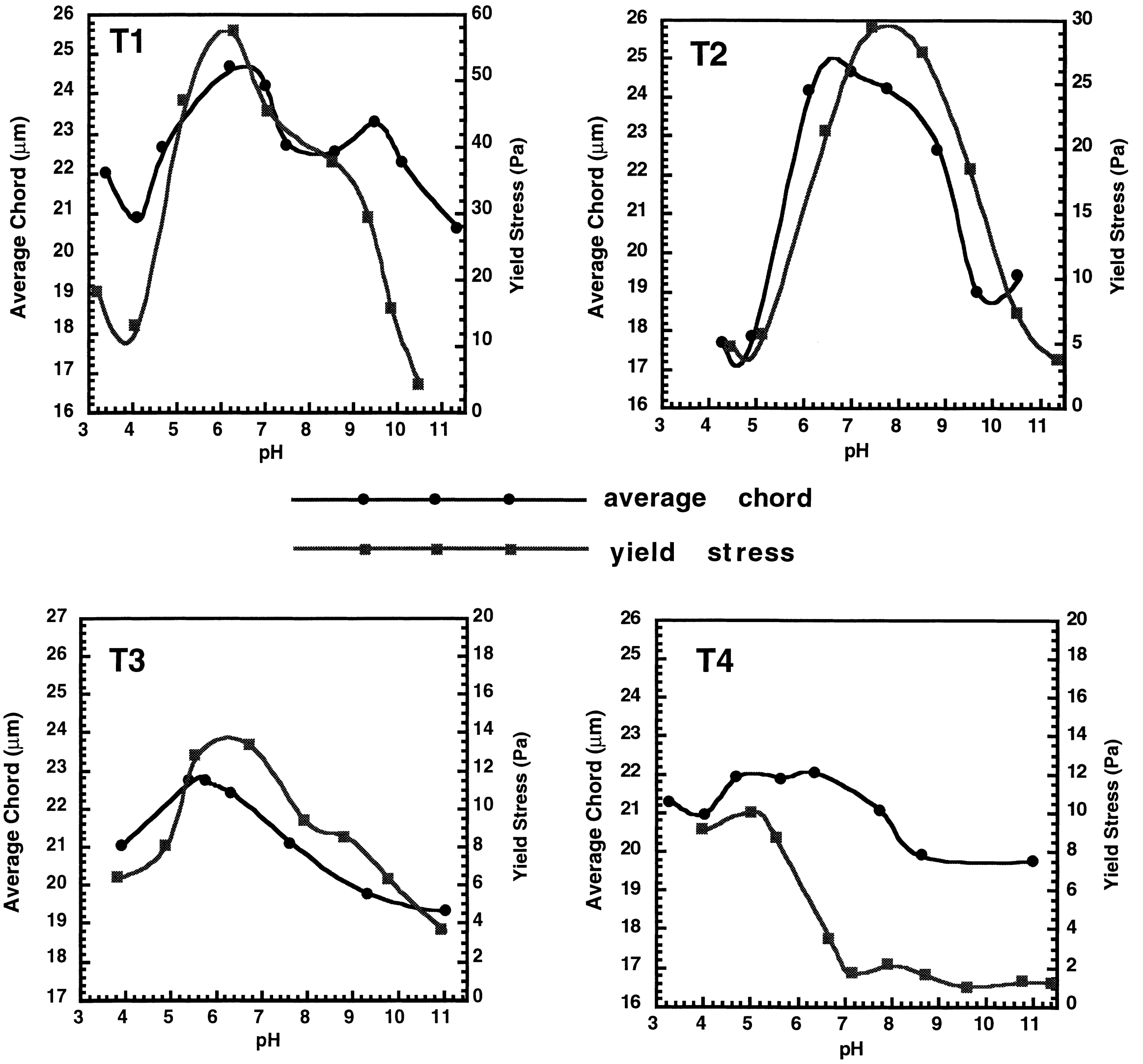
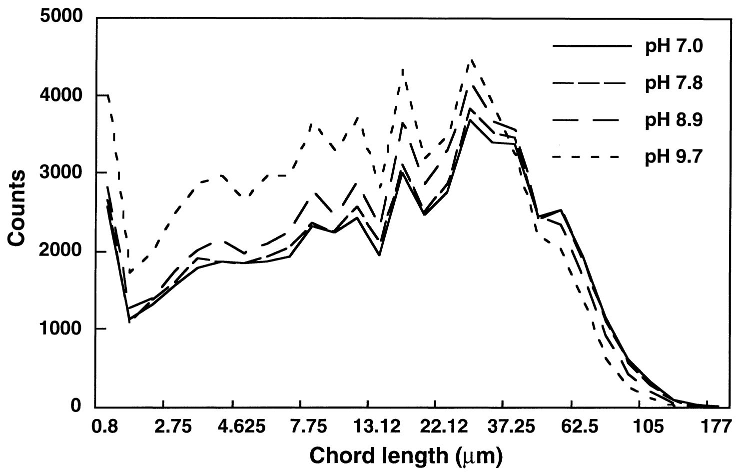
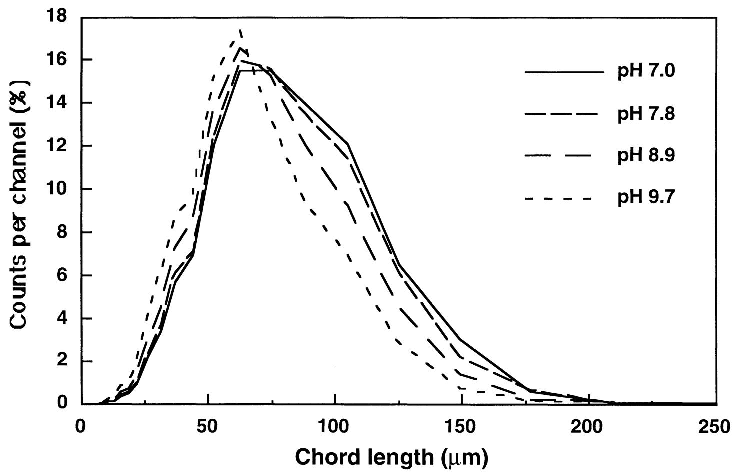


Fig. 6. Average chord length vs pH behaviour and extrapolated yield stress (τ_y) vs pH behaviour for silica/TiO_2 suspensions prepared from four different TiO_2 samples (**T1**–**T4**). Total solids volume fraction = 0.468. TiO_2 component is 10% (w/w) of total solids. Temperature = 20%.



(a) Unweighted chord length distribution



(b) Volume-weighted chord length distribution

Fig. 7. Chord length distributions for a silica/TiO_2 (sample **T2**) suspension at selected pH values demonstrating the breakup of aggregates as pH is increased. (**a**) Unweighted chord length distributions. (**b**) Volume weighted chord length distributions.

average chord length axis is identical for each of the graphs shown in Fig. 6.)

The graphs in Fig. 6 demonstrate that FBRM can provide valuable information on trends in aggregate size which correlate well with trends in rheological behaviour. An advantage of using the unweighted chord lengths from FBRM is that the measurement responds to the number of particles in the range of channels, rather than their volume. Although the slurries studied here contain only 10% (w/w) TiO_2, the TiO_2 particles make up more than 99.9% of the total *number* of particles, so it is expected that the chord length data will be dominated by the fine TiO_2 component of the suspension. Changes in the chord length distribution are shown in Fig. 7(a) for selected pH values of a SiO_2/TiO_2 suspension containing **T2** as the TiO_2 component. As the pH is increased above 7, aggregates break up, and this is detected as an increase in the number of chords counted in the channels at the fine end of the distribution. The decrease in the number of counts in the longer chord length channels is not as dramatic, but still significant considering the inherently skewed form of chord length distributions.

The decrease in the aggregate size can be more clearly seen if the raw chord length data are treated with a volume-based weighting algorithm to provide distributions which approximate better to conventional size distributions. Modified distributions of this type are shown in Fig. 7(b). In these distributions the reduction in the number of counts in channels at the large end of the distribution as pH is increased is more evident, as is the decrease in the peak value to shorter chord lengths. It should be noted that volume-weighting will emphasise larger chord lengths, and therefore for non-spherical particles the distributions obtained will always

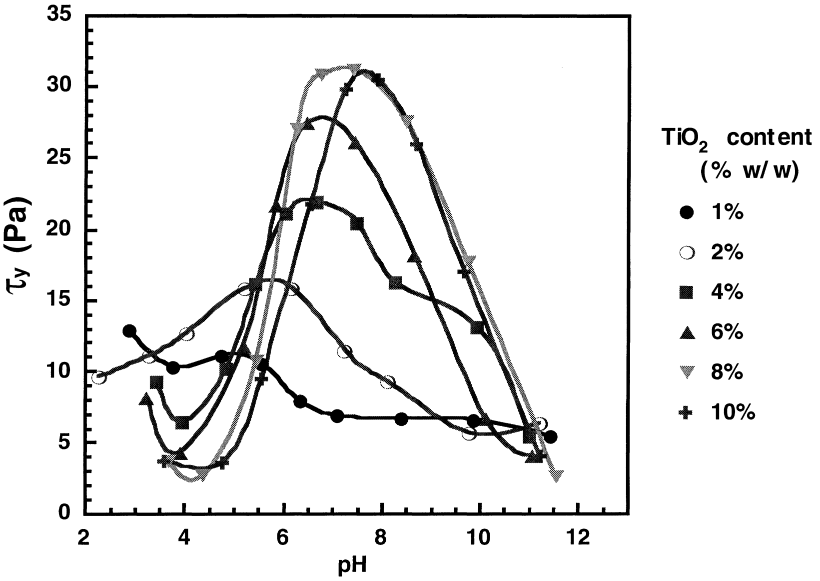


Fig. 8. Extrapolated yield stress (τ_y) vs pH behaviour for silica/TiO_2 slurries showing the effect of increasing amounts of TiO_2 (sample **T2**). Total solids volume fraction = 0.468. Temperature = 20°C.

be larger than those generated by conventional sizing techniques.

The results described above demonstrate that, for bimodal suspensions of the type described here, the yield stress is a parameter largely influenced by the nature of the fine particle fraction in the suspension. This point is further illustrated in Fig. 8, which shows the changes in yield stress with pH as increasing amounts of TiO_2 (sample **T2**) are incorporated into a coarse SiO_2 slurry. The magnitude of the yield stress maximum increases as the amount of TiO_2 is increased, and the pH at which the maximum is observed increases from ~pH 5 with 1% (w/w) TiO_2 to ~pH 8 at 10% (w/w) TiO_2. Assuming that both the SiO_2 and TiO_2 particles are spherical, and that their diameters are 44 μm and 0.32 μm respectively, we can estimate that complete coating of the SiO_2 surface with TiO_2 requires a volume ratio (volume TiO_2/volume SiO_2) of at least 0.027. This corresponds to a composition by weight of between 4% (w/w) and 5% (w/w), we expect that at this composition the IEP of a mixed SiO_2/TiO_2 slurry should have a value close to that of a suspension of TiO_2 alone. The shift in the pH at which the maximum yield stress is observed (Fig. 8) reflects the change in the IEP as the TiO_2 particles coat the surface of the SiO_2 particles, and the position of the yield stress maximum changes very little after the TiO_2 content of the slurry exceeds 4% (w/w). However, subsequent increases in the actual magnitude of the maximum yield stress at higher TiO_2 concentrations may be a result of the increased proportion of fine particles in the suspension.

Small amounts of TiO_2 induce a marked increase in the plastic viscosity of the mixed suspensions in comparison to suspensions of SiO_2 alone. As the TiO_2 content in the slurries is increased in the range 1 to 10% (w/w), the plastic viscosity becomes increasingly sensitive to pH and, with TiO_2 content above ~4% (w/w), the plastic viscosity vs pH behaviour follows a similar trend to the yield stress vs pH curves, although maximum viscosities are observed at values slightly above the IEP. This behaviour is consistent with the expectation that in slurries containing less than 4% (w/w) TiO_2, the fine TiO_2 particles will be adsorbed on the SiO_2 surface, giving an aggregate composition which, in terms of hydrodynamic interactions, does not differ greatly from the uncoated SiO_2 particles. However, when there is a quantity of 'excess' TiO_2 in the suspension, TiO_2 aggregates and mixed SiO_2/TiO_2 aggregates can form, which entrain some of the water in the system and thus increase the apparent volume fraction of the suspension, leading to an increase in the measured viscosity.

At a given pH, viscosity changes appear to scale in accordance with changes in the vacancy fraction of the suspension. Table 2 shows the change in viscosity of a SiO_2/TiO_2 suspension of volume fraction 0.468 at a pH of 7.5 as the TiO_2 content of the suspension is increased. When the overall particle size distribution of a bimodal suspension is altered by increasing the number of fine particles, as is the case here, the maximum packing fraction

Table 2
Maximum packing fractions, vacancy fractions and plastic viscosities for silica/T_6TO_2 suspensions at pH = 7.6

% w/w TiO_2	ϕ_{max}	$1-(\phi/\phi_{max})$ ($\phi = 0.468$)	η (mPa s^{-1})
0	0.523	0.105	11.0
1	0.548	0.146	79.5
2	0.551	0.151	72.4
4	0.565	0.172	70.8
6	0.577	0.189	68.4
8	0.580	0.193	70.3
10	0.582	0.196	64.9

(ϕ_m) will increase, since the fine particles are able to pack within the gaps between the larger particles [13]. The increase in ϕ_m was confirmed by measurement of the slurry density in centrifuged samples of suspensions containing increasing amounts of TiO_2 (Table 2). Thus, although the overall solids volume fraction in the suspensions remained constant, the decrease in viscosity as the TiO_2 content is increased from 1% to 10% can be attributed to the increase in ϕ_m as the number of fine particles in the suspension is increased.

4. Summary

The results described here demonstrate the significance of the surface properties of the fine particle component in determining the aggregation characteristics of a suspension. Although the suspensions contain 10% (w/w) or less TiO_2, their rheological behaviour is similar to that of pure TiO_2 suspensions [14] in that the yield stress vs pH curves follow a generally parabolic form, with a maximum at the pH value corresponding to the IEP.

When the TiO_2 content of the slurries is less than about 4% (w/w) of the suspended solids, the bulk of this TiO_2 will be adsorbed on the surface of the much larger SiO_2 particles. However, as the TiO_2 content is increased further, the SiO_2 particles become completely coated, and the extra TiO_2 is able to form aggregates which bind the coated SiO_2 particles together. When the interparticle distance is very small (as it is once the TiO_2 is adsorbed onto the SiO_2 surface) the attractive Van der Waals forces will dominate over the electrostatic interactions, [1] so the nature of the SiO_2/TiO_2 interaction changes very little with pH. Thus, the trends in yield stress–pH behaviour for these suspensions are a reflection of the electrostatic interactions between TiO_2 surfaces, as is the case for colloidal suspensions.

The FBRM measurements described here show that the changes in yield stress with pH can be attributed to the formation of larger aggregates and networks of particles as the surface charge on the TiO_2 particles approaches the iso-electric point. In mixed suspensions containing 90% (w/w) SiO_2 and 10% (w/w) TiO_2, the maximum values of the yield stress were observed at pH values corresponding to the IEP of the particular TiO_2 sample, and likewise the maximum average chord length measured by FBRM was observed at this pH. These results demonstrate the value of FBRM in characterising particles and aggregates in systems where an understanding of the behaviour of the fine particle component is very important. Size distributions based on the number of particles are more sensitive to fine particles than distributions based on volume, so the formation and break-up of aggregates of fine particles, which might not greatly affect volume based size distributions, will have a large influence on distributions based on particle number.

While the addition of a small amount of TiO_2 produces a marked increase in plastic viscosity relative to a pure SiO_2 suspension, the subsequent changes in plastic viscosity as more TiO_2 is added appear to be due to the corresponding change in the particle size distribution of the suspended solids. The plastic viscosity of the mixed suspensions studied here does show some variations with pH, but the variations are not large, and practically negligible when the TiO_2 content of the suspension is below 4% (w/w) of the total suspended solids.

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