Yield stress-Zeta Potential relationship of Oxide dispersions with Adsorbed Polyacrylate – Steric Effect and Zeta Potential at the Flocculated-Dispersed Transition State

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ABSTRACT

The yield stress-DLVO force relationship is obeyed by α -Al₂O₃ and alumina-coated TiO₂ dispersions with adsorbed polyacrylate only if the yield stress and its corresponding zeta potential data were collected in the positively charged region. In this region, the underlying surface positive charge density of the particles exceeds the negative charge density of the polyacrylate. At this state the adsorbed polyelectrolyte lies flat on the particle surface forming a steric layer of fixed thickness at a given polymer concentration. In the negative charge region, the steric layer thickness is not constant and hence yield stress-DLVO relationship is not obeyed. The (critical) zeta potential at the flocculated-dispersed transition state decreases with increasing polymer concentration. This result reflects a decreasing van der Waals force as the steric layer increases in thickness. A steric layer ensured that the surface or zeta potential is sufficiently low in the flocculated regime for the DLVO theory to remain valid. The ratio of the critical zeta potential square between alumina-coated TiO₂ and α -Al₂O₃ is an indication of their Hamaker constants ratio in water. The effect of alumina coating on the value of this ratio is presented and discussed.

Keywords: critical zeta potential, yield stress-DLVO relationship, polyacrylate, coated titania, alumina, flocculated-dispersed transition state

INTRODUCTION

There are a number of relationships between yield stress and particle pair DLVO interaction potential or forces and they all predict a linear relationship between yield stress and the square of the zeta potential [1,2]. A more recent relationship between yield stress and DLVO forces is given by [3]:

$$\tau_y \approx \frac{\phi^2}{a} \left(\frac{A_{121}}{12D_o^2} - \frac{C}{D_o} \zeta^2 \right) \quad (1)$$

where the first term is the van der Waals force and the second term the electrostatic force. A_{121} is the effective Hamaker constant of particle in water, $C = 2\pi\epsilon \ln[(1 - e^{-\kappa D_o})^{-1}]$, κ is the Debye-Huckel parameter or the inverse of the double layer thickness, ϵ is the permittivity of water, ϕ is the solid volume fraction of the dispersion, D_o is the minimum surface separation distance, a is the particle size and ζ is the zeta potential which is proportional to the surface potential. The term ϕ^2/a^2 is the number of particles per unit area [4] and is related to ϕ^2/a in Eq. (1) after the dependence on a for both the attractive and repulsive forces has been taken into account. Essentially the yield stress is the product of the number of particle bonds per unit area and the DLVO force interacting between a particle pair.

Equation (1) is only valid for surface or zeta potential of less than 25.6mV. A means of decreasing the zeta potential of the particulate fluid is to adsorb an ideal “hard wall” steric layer. This layer pushes the shear plane where the zeta potential is characterized, further out from the particle surface. Low molecular weight polyelectrolytes such as polyacrylate, are ideal for forming such barrier. Polyacrylates are often used as a dispersant in ceramic slip processing [5-7]. Hackley [8] measured the acid strength of polyacrylic acid (PAA) with different molecular weights using potentiometric titration. He reported a pKa value of 5.0 that is independent of molecular weight ranging from 5000 to 150000. However, the degree of ionization of 0.5 occurred at pH just over 6.0. Therefore at pH > 6.0 PAA is strongly negatively charged and will adsorb strongly on

any positively charge surface. Under a certain particle-polyelectrolyte charge condition, the adsorbed PAA may lie flat on the surface [7-9]. In the presence of a hard wall layer Eq. (1) becomes:

$$\tau_y \approx \frac{\phi^2}{a} \left(\frac{A_{121}}{12(D_o + 2\delta)^2} - \frac{C'}{(D_o + 2\delta)} \zeta^2 \right) \quad (2)$$

where δ is the thickness of the steric layer and will depend upon the degree of surface coverage. $C' = 2\pi\epsilon \ln(1 - e^{-\kappa(D_o + 2\delta)})$. Steric interaction is very short range and so it does not affect the linear relationship between yield stress and square of zeta potential, as predicted by Eq. (2). The steric layer increases the minimum separation distance between the interacting particles in the flocculated state by 2δ . The greater minimum separation distance reduces the van der Waals force, which is at maximum strength. This maximum van der Waals force is equal and opposite of the repulsive force at the flocculated-dispersed transition state. The zeta potential at this transition state is therefore a measure of this maximum van der Waals force. This transition potential is known as the critical zeta potential [10].

At the flocculated-dispersed transition state, the yield stress is zero and Eq. (2) is reduced to

$$\zeta_{critical} = \sqrt{\frac{A_{121}}{12(D_o + 2\delta)C'}}. \quad (3)$$

At a fixed ionic strength, the critical zeta potential is proportional to the square root of the Hamaker constant of the solid in water with both C' and the minimum surface separation distance between interacting particles, $(D_o + 2\delta)$, being constant. Farrokhpay et al. [11] studied the effect of polymers on the surface separation distance between interacting particles and showed that polymers forming a steric barrier on titania can indeed increase this distance. According to Eq. (3), critical zeta potential should be independent of particle size and concentration. This was indeed true [12-14].

In this study we will determine whether Eq. (2) is obeyed by particle dispersions containing adsorbed polyelectrolytes, i.e. whether a linear relationship exists between yield stress and the square of zeta potential, and the conditions under which this is obeyed. If obeyed then the critical zeta potential can be easily determined. How this parameter varies with surface coverage and the nature of oxide dispersions are important information that helps us understand the surface forces operating and the particle-particle interactions in greater details.

The oxides used in this study are an α -Al₂O₃ and a range alumina-coated TiO₂. These coated TiO₂ powders are used in the manufacturing of plastics, paints, inks and can coatings. Investigations on the rheological behaviour of TiO₂ dispersions are numerous [15-17]. More recently, the influence of aluminum doping on titania pigment structural and dispersion properties was briefly reported [18]. Farrokhpay et al. [11] also investigated the influence of polymer functional group architecture on titania pigment dispersion. These polymers were a polyacrylic acid, a polyacrylamide and two modified polyacrylamide copolymers. Plots of yield stress versus the square of zeta potential for each polymer at a given concentration were presented showing a linear relationship. However, upon analysis of these yields stress-zeta potential data it was found that one of the critical zeta potential values was much larger than that with no adsorbed polymer. Also the zeta potential and yield stress data collected were much less extensive and this may have led the authors to miss some of the new observations reported in this study.

Materials and Method

The α -Al₂O₃ used in the study was supplied by Sumitomo Chemical Company. It has a BET surface area of 6.4 m²/g, a particle size of 0.41 μ m and a density of 3900 kg/m³. The pure rutile titania was from Unilab with a BET surface area of 9.6 m²/g and density of 4200 kg/m³.

The samples of rutile TiO₂ coated with alumina (CR50, CR58 and CR60) were obtained from ISK Singapore Pte Ltd. These rutile TiO₂ were produced by the Chloride process

and thus they have a much lower amount of adsorbed sulphate impurities as compared to the Sulphate process. The properties of the TiO_2 as reported by ISK are listed in Table 1.

The particle sizes of the ISK oxides were characterised using an SEM. As the particles are irregular in shape, the sizes of the particles are approximated with the SEM using the best fitting sphere over a random sample of the particles. The BET surface area was measured with a Micrometric Tristar 3000 porosimeter.

The polyelectrolyte, sodium salt of polyacrylic acid (PAA-Na) of molecular weight, M_w , 2103 Da was used. This polymer has an M_w/M_n value of 1.23, an indication of a relatively narrow M_w distribution. It has on average has 22 repeating units.

For the yield stress measurements, the dispersions were prepared by sonicating the oxide powder in water with a sonic probe. The pH of the dispersions was made alkaline with 4M NaOH. The concentrations of the TiO_2 dispersions were all prepared at 50 wt%. About 70 g dispersion was prepared each time. A solution of PAA-Na at 4wt% was added dropwise to the dispersion to the required concentration. NaCl was added to adjust the conductivity to about 5mS/cm. The prepared dispersion was allowed to rest for about an 1hr. Solutions of 1M to 5M HCl were then used to reduce the pH of the dispersions. The Brookfield DV-II+ viscometer was adapted to perform vane yield stress measurements [19] on the samples. Vanes with four blades and a height to diameter ratio of two were used. In the yield stress measurement the vane was rotated at a slow constant speed ranging from 0.2 to 0.4 rpm. The viscometer has a spring constant at maximum (100%) deflection of 0.0007187 N.m.

For zeta potential measurement, a 5.0 wt% dispersion was prepared. Again, the conductivity was adjusted to 5 mS/cm with NaCl and the 4 wt% polyelectrolyte, PAA-Na, was added dropwise to the solution before sonicating. The zeta potentials of the dispersions were measured with the Colloidal Dynamics ZetaProbe. The ZetaProbe autotitrates the sample to a lower pH using 1M HCl and the zeta potential is recorded in a step-wise decrease.

RESULTS AND DISCUSSION

Zeta Potential

The effect of PAA-Na concentration on the zeta potential of a 5wt% α -Al₂O₃ dispersion is shown in Fig. 1(a). Without the addition of PAA-Na, the isoelectric point (IEP) was found to be at a pH of 9.3. The pH of zero zeta potential is shifted to the left with increasing concentration of polyelectrolyte. At a concentration of 0.4%dwb (g polyelectrolyte/100g oxide), this pH is as low as 3.1.

The adsorption of a negatively charged polyelectrolyte like PAA-Na onto a positively charged particle like α -Al₂O₃ is due to electrostatic attraction between unlike charged groups. At low additive concentration of polyelectrolyte, the total negative charge of PAA-Na is small. So the amount of positive surface charge on the particles needed to accommodate all these negative polyelectrolyte charge is equivalently small. A small downward shift in pH from the IEP is sufficient to generate enough surface positive charge to neutralize all the polyelectrolyte charge. This explains the small shift in pH of zero zeta potential at low polyelectrolyte concentrations. At a higher polyelectrolyte concentration, a larger decrease in pH is needed for the particles to acquire sufficient charge to neutralise the polyelectrolyte charge. As a result the pH of zero zeta potential is at a much lower pH.

For the dispersion containing the highest polyelectrolyte concentration of 0.4%dwb, it can be seen that at pH>6, the magnitude of zeta potential is more than 70mV. At this concentration, the charge from the adsorbed polyelectrolyte is more than sufficient to counterbalance the surface positive charge of the particle. Under such a condition, it is possible for a polyelectrolyte molecule to bridge particles, i.e. it adsorbed onto two or more particles at the same time. If the polyelectrolyte is of low molecular weight, particle bridging is less likely to occur. It adsorbed to form loops or dangling segments and tails on a particle surface. The excess charges from the adsorbed polyelectrolyte lead to the high negative zeta potential.

The effect of PAA-Na on zeta potential of CR 50, CR 58 and CR 60 and rutile TiO₂ dispersions is generally similar to that observed with α -Al₂O₃ dispersion. In all cases the pH of zero zeta potential is shifted to a lower pH. At any pH in the negative charge regime, the magnitude of the zeta potential is larger at higher PAA-Na concentration. See Fig. 1(b) and (c) for its influence on the zeta potential of CR50 and CR58 dispersions.

Fig. 2 shows the effect of PAA-Na surface coverage (mg polyelectrolyte per m² of oxides) on the pH of zero zeta potential. With no additives, the IEP of α -Al₂O₃ is at pH 9.3 while the IEP of rutile TiO₂ is at pH 6.0. The IEP of alumina-coated titania; CR50, CR58 and CR60 is at pH 7.7, 8.8 and 8.0 respectively. It is not surprising to find the IEP of the alumina-coated titania to lie in between the IEP of pure α -alumina and pure rutile titania. CR58 has a higher IEP as compared to CR50 and CR60. This is because CR58 contains a higher amount of alumina which has a higher IEP [18]. The data in Fig. 2 also show that for all oxides, the pH of zero potential decreases with increasing polyelectrolyte concentration. At high polyelectrolyte concentration, the pH of zero zeta potential approaches a value of 2.0, the IEP of carboxylate group dominated particle surface [20].

The plot of the difference between the isoelectric point and the pH of zero zeta potential versus surface coverage of polyacrylate for all oxides is shown in Fig. 3. The surface coverage of polyelectrolyte was calculated with the assumption of complete or 100% adsorption. This assumption is often true for polyelectrolyte adsorption at the pH of zero zeta potential [7]. It is a linear-log plot and the relationship is normally linear [7]. The slope of the plots is a measure of the acid strength of the functional groups of the polyelectrolyte. The stronger the acid group the steeper is the slope [21]. However the result in Fig. 3 appears to show two different slopes for the same polyelectrolyte. The slope appears to show a dependence upon the nature of the oxide dispersions. CR50 and CR60 both with 95wt% TiO₂ and the same isoelectric point displayed approximately the same slope. However CR58 with a lower TiO₂ content of 93% and α -Al₂O₃ and again with approximately the same isoelectric point, displayed the same slope that is steeper.

Like the isoelectric point result, the slope may be a good indication of the surface composition or degree of coating of the oxides. The result suggests that CR58 has similar surface properties to α -Al₂O₃. This is only possible if CR58 is completely coated with alumina.

Yield Stress

The effects of PAA-Na concentration on the yield stress-pH behaviour of 50wt% α -Al₂O₃, CR50 and CR58 dispersions are shown in Fig. 4(a), (b) and (c) respectively. In the absence of polyelectrolyte, the maximum yield stress of the α -Al₂O₃ dispersion with a conductivity of 5mS/cm, is 135 Pa located at pH 9.3. In contrast, the maximum yield stress of CR50 dispersion is 40 Pa at pH 8.1, whilst CR58 dispersion displayed a maximum yield stress of 34 Pa at pH 8.3. CR60 dispersion displayed a higher maximum yield stress of 75 Pa at pH 7.8 .

The particle size of CR60 is smaller than CR50 and CR58, thus a larger yield stress is expected for CR60. Surprisingly, α -Al₂O₃ with larger median particle size, displayed the highest maximum yield stress. In significant amount, it is the very fine size fractions that control the rheology or yield stress of the dispersions [22]. It is possible that while the mean particle size of α -Al₂O₃ is larger, it might have a larger fraction of fine particles. Note that the size distributions of alumina-coated TiO₂ and α -Al₂O₃ were determined by different techniques. The particle size distribution of α -Al₂O₃ was determined via the laser diffraction method while the SEM optical method was employed for the alumina-coated TiO₂.

The maximum yield stress for all oxides was located at their respective isoelectric point. This result is predicted by the DLVO theory. At this point, the electrostatic repulsive force is absent and only the van der Waal attractive force is present. So the net attractive force interacting between particles is at maximum strength. The flocculated network structure must also be at maximum strength and this is reflected by the maximum yield strength.

Like the zeta potential, the yield stress curve is shifted progressively to a lower pH as the amount of PAA-Na used increase. Also, the maximum yield stress is located at the pH of zero zeta potential at any concentration of PAA-Na. In addition, the maximum yield stress is generally smaller as the amount of PAA-Na added increase. The polyelectrolyte adsorbed to form a steric layer on the particles. The effective thickness of this layer increases with increasing amount of polyelectrolyte adsorbed. This has the effect of increasing the minimum separation distance between the interacting particles. As a result, the van der Waals attractive force weakened progressively and hence the decrease in the maximum yield stress with polyelectrolyte concentration.

For CR58 at 0.08% dwb PAA-Na, the maximum yield stress actually increased slightly as seen in Fig. 4(c). In fact, the decrease in the maximum yield stress for the other oxides, is also not significant at the same concentration of PAA-Na. This is probably due to charged patch attraction occurring between the positively charged particle surface and the negatively charged polyelectrolyte formed on an adjacent particle. Charge patch attraction usually occurs at low surface coverage of polyelectrolyte [21]. This attraction is not much stronger than the van der Waals force of attraction [23].

The variation in the maximum yield stress with surface coverage of PAA-Na is shown in Fig. 5 for all four oxide dispersions. In all cases, the maximum yield stress displayed a trend that decreases with increasing surface coverage. At low polyelectrolyte concentrations, the decrease is very small and sometimes the trend shows a small rise. As explained earlier, this is likely due to some degree of charge patch attraction. At higher polyelectrolyte concentration the maximum yield stress is significantly smaller. Here, steric effects have become very pronounced.

Yield stress-zeta potential relationship and critical zeta potential

The yield stress and zeta potential square data for α -Al₂O₃ dispersion at a conductivity of 5mS/cm displayed a considerable degree of scatter from the best-fit linear relationship. However when the data pairs collected in the negative charge or positive charge region

were correlated separately, an excellent linear relationship for each charge regime was obtained. See Fig. 6 and note that the deviation of the data from the best-fitted line is very small. The two linear relationships are very different. The value of the intercept at zero yield stress differs quite considerably. It is 3000 mV^2 in the negative charge regime while it is only 1800 mV^2 in the positive charge regime. This gives a critical zeta potential of magnitude 55 mV in the negative regime and 42 mV in the positive regime. The slope of the plot in the negative charge regime is also gentler as compared to that in the other charge regime. This means that either the van der Waals attractive force is much stronger or there is a presence of an additional attractive force in the negative charged regime. This phenomenon certainly needs to be clarified with a separate study. It should be noted that the isoelectric point of $\alpha\text{-Al}_2\text{O}_3$ dispersion and pH of maximum yield stress differed slightly in pH values. It is just not possible to obtain identical pH value. The pairing of the yield stress and zeta potential must be at the same surface chemistry condition, i.e. $(\text{pH} - \text{pH of maximum yield stress})$ must be equal to $(\text{pH} - \text{IEP})$. Scales et al [2] made $\text{pH}_{\tau_{\text{max}}} = \text{IEP}$ before pairing the yield stress with zeta potential.

In the presence of adsorbed polyacrylate, the yield stress-zeta potential square relationship is not linear in the negatively charged regime. See Figs. 7(a) and (b) for the plots of yield stress versus square of zeta potential for $\alpha\text{-Al}_2\text{O}_3$ and alumina-coated TiO_2 CR58 dispersions in the presence of polyacrylate. In the negative charge regime and at pH below the oxide IEP, the negative charge density of the adsorbed polyacrylate greatly exceeds the positive charge density of the particles. In this region, the adsorbed polyacrylate molecules do not lie flat on the particle surface. The adsorbed molecules will assume a conformation with dangling segments and tails. Under this condition, it is not possible to maintain an adsorbed layer with constant thickness. With a slight decrease in pH, more positive charges developed on the particle surfaces. At this state, the adsorbed molecule will assume a conformation with less dangling segments and tails. The effective thickness of the adsorbed layer is therefore thinner. In summary, in the net negative charge regime, the thickness of the steric layer will vary with the concentration of underlying surface positive charge. With a non-constant steric layer thickness, the

separation distance, i.e., $(D_o + 2\delta)$, between the interacting particles will also vary and hence the breakdown of the linear relationship.

Fig. 8(a) shows the plots of yield stress versus zeta potential square obtained in the positively charged regime for unwashed α -Al₂O₃ dispersions with 0.08, 0.16 and 0.4%dwb of PAA-Na. At each polyacrylate concentration, an excellent linear relationship was obtained. Using only zeta potential data with value less than 25.6mV, the limit of validity of the DLVO theory, a linear relationship is still obtained. In fact all the data for 0.4dwb% PAA-Na were below 25 mV. The intercept at zero yield stress was observed to decrease with increasing polymer concentration. The intercept gives a critical zeta potential of 44, 36 and 23mV for 0.08, 0.16 and 0.4%dwb PAA-Na respectively. In the positively charged regime, the underlying positive charge of the particles exceeds the total negative charge of the adsorbed polymer. The adsorbed polymer must therefore lie flat on the particle surface as it can anchor all its charged groups on the particle surface. In this regime, the effective thickness of the adsorbed or steric layer does not vary with pH. Essentially this layer behaves like a “hard-wall” steric barrier. At higher polyacrylate concentration, the adsorbed layer gets thicker as it becomes more developed with increasing surface coverage. This weakened the strength of the van der Waals force as the minimum separation distance increases. As a result the maximum yield stress and critical zeta potential are smaller in magnitude. Note that steric interaction is very short range of the order of a nanometer and is zero once the adsorbed layers of the interacting particles are not in contact.

Figs. 8(b) and (c) show the plot of yield stress against square of zeta potential for alumina coated titania CR50 and CR58 respectively in the positively charged regime. In all cases a linear relationship is obtained. Table 2 lists the critical zeta potential of the oxide dispersions at different concentration of PAA-Na. For all oxides, the critical zeta potential with no polyelectrolyte additive is much larger than that with PAA-Na. The trend shows a decreasing critical zeta potential value with increasing polymer concentration for all oxide dispersions. Sometime if the bad data are not ignored, we observed the trend to increase upward. For example, for CR58 at 0.4%dwb PAA-Na, if

the last data point in Fig. 8(c) is not ignored we obtained a critical zeta potential value of 36mV, which is higher than 33mV obtained for 0.16%dwb additive. Ignoring this last point, a critical zeta potential value of 27mV was obtained.

The critical zeta potential obtained for the three alumina-coated titania; CR50, CR58 and CR60), is 49, 46 and 38mV respectively. CR50, CR58 and CR60 contained 95, 93 and 95% TiO₂ respectively and have an IEP of 7.8, 8.8 and 8.0. CR58 with 93% TiO₂ has an IEP very close to that of α -alumina of 9.3. Both CR50 and CR60 with the same amount of TiO₂ of 95% have the same IEP. The similarity in IEP suggests that CR58 is completely coated with alumina but not CR50 and CR60. The critical zeta potential did not show any trend in relation with the TiO₂ content. Both CR50 and CR60 have the same TiO₂ content and yet their critical zeta potentials are quite different; 49mV and 38mV. With the critical zeta potential of α -Al₂O₃ ranging from 42mV to 55 mV, the only conclusion that can be drawn is that all four oxides have similar critical zeta potential value. The critical zeta potential data with adsorbed polymer may reveal otherwise.

The critical zeta potential of α -Al₂O₃ and rutile titania without additive was found to be 40 and 49mV respectively [14]. The value for α -Al₂O₃ obtained in the positive charge region is very close, 42mV. The Hamaker constant of α -Al₂O₃ in water is ~ 40zJ and that for rutile TiO₂ is ~60zJ (1zJ=10⁻²¹J). Rutile TiO₂ with alumina coating should have a Hamaker constant of value in between 40 to 60zJ. The critical zeta potential obtained in this study suggests that the Hamaker constant of alumina-coated TiO₂ is very similar to that α -Al₂O₃. Now we examined whether the critical zeta potential obtained at the same coverage of PAA-Na supports such finding. The relationship between critical zeta potential and PAA-Na surface coverage of α -Al₂O₃, CR50, CR58 and CR60 dispersions can be calculated from the data listed in Table 2.

At a constant surface coverage of 0.25mg/m², the critical zeta potential of α -Al₂O₃, CR50, CR58 and CR60 was found to be 36, 29, 27 and 33 mV respectively. CR58 and α -Al₂O₃ displayed the largest different in critical zeta potential value despite other property data such as IEP, suggested that they should be very similar. The reason for the

discrepancy here is not clear. However, it is likely that the experimental error involved in the critical zeta potential determination is relatively high. So all four critical zeta potential values could be just similar and fall within the experiment error.

CONCLUSION

1. The yield stress – DLVO force relationship is obeyed by oxide dispersions with adsorbed polyacrylate layer provided that the yield stress and zeta potential data are collected in the positively charged region. In this region, the adsorbed polymer lies flat on the particle as the underlying surface positive charge density exceeds the negative charge density of the polymer.
2. In the negative charged regime, the yield stress does not decrease linearly with the square of zeta potential for oxide dispersions with adsorbed polyacrylate. This is explained in terms of a non-constant thickness of the adsorbed layer as the negative charge density of adsorbed polymer exceeds the underlying surface positive charge density. The adsorbed polymers will take up a range of conformations such as the formation of loops and dangling tails.
3. The critical zeta potential at the flocculated-dispersed transition state decreases with increasing PAA-Na concentration. The decreasing critical zeta potential reflects a weaker van der Waals attraction due to an increasing separation distance between interacting particles as the adsorbed layer thickness increases.

Nomenclature

a	particle size (m)
D_o	minimum surface to surface distance between particles without adsorbed additive in the flocculated state (m)
M_w	weight average molecular weight
M_n	number average molecular weight
A_{121}	Hamaker constant of particles in water, (J)

δ	thickness of adsorbed layer (m)
ϕ	volume fraction of particle (-)
ε	permittivity of the medium
ζ	zeta potential (V)
κ	inverse of debye length (m)
τ_y	yield stress (Pa)

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Fig. 2: The effect of polyelectrolyte (PAA-Na) concentration on pH of zero zeta potential of 5 wt% dispersions of α -Al₂O₃, CR50, CR58, CR60 and rutile TiO₂ at a conductivity of 5mS.

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Fig. 8: Effects of PAA-Na on the yield stress-zeta potential square relationship in the net positive charge region for a range of oxide dispersions; a) α -Al₂O₃ , b)CR 50 and c)CR58. Both the yield stress and zeta potential data were measured at an ionic strength of ~ 5mS/cm.

Table 1

TiO ₂ classification	TiO ₂ %	Main modifier	Ave particle size (μm)	Specific gravity	Specific surface area (m ² /g)
CR50	95	Al	0.25	4.2	14
CR58	93	Al	0.28	4.2	16
CR60	95	Al	0.21	4.2	10

Table 2

		Critical Zeta Potential (mV)		
	Al ₂ O ₃	CR50	CR58	CR60
No additives	42-55	48.8	46.2	38
0.08%dwb	44	39	36.8	39.5
0.16%dwb	36	29	33.2	34
0.4%dwb	23	30	27.2	32

Fig 1(a)/OBC

Fig 1(b)/OBC

Fig 1(c)/OBC.

Fig.2/OBC

Fig. 3/OBC

Fig 4a/OBC:

Fig 4b/OBC

Fig4c/OBC

Fig5/OBC

Fig. 6/OBC

Fig 7a/OBC

Fig 7b/OBC

Fig 8a/OBC

Fig.8b/OBC

Fig. 8c/OBC