Study of Interactions Between Polyelectrolyte Dispersants, Alumina and Latex Binders by Rheological Characterisation

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Abstract

The influence of varied polyelectrolyte concentrations in alumina suspensions with and without the addition of a latex binder has been studied using rheological measurements. Two types of latex binders (one anionic and another one nonionic) and a polyacrylic dispersant were used, and these systems have earlier been successfully used for tape casting of alumina. The stability of the suspensions was characterised using continuous shear measurements for viscosity data and oscillatory procedures for viscoelastic properties. Excess polyelectrolyte dispersant, even with a low molecular weight of about 5000, leads to increased viscosity and elasticity in highly loaded suspensions, volume fraction 0.55. The systems, however, are stable as no thixotropy effects were observed. The mechanism causing this phenomenon was found to be a combination of three mechanisms; (i) increased rigidity from the additional, charged particles which the polyelectrolyte at excess addition can be considered as, (ii) decreased electrostatic repulsion as a result of the increased ionic strength from the counterions of the polyelectrolyte, and (iii) increased viscosity of the liquid phase from free polymer. It was found that the optimum dispersant concentration in the mixed systems with latex added was higher than in the pure alumina system. It was also found that a correct dispersant level is critical as interactions were observed both for the anionic and the nonionic latex. Adsorption of the dispersant onto the latex-particles, both the anionic and nonionic ones, results in bridging flocculation at a low dispersant level. © 1998 Elsevier Science Limited. All rights reserved.

1 Background

Water-based binders are being more commonly used for tape casting of ceramic materials as a result of a strive to reduce the environmental impact, and latex binders have successfully been used as binders for tape casting for a number of systems.^{1–5} The main advantage of latex binders over water-soluble binders lies in the fact that they have a high polymeric content at reasonably low viscosity, which makes it possible to use slips with high solids loading and, thus, a short drying time. Suspensions for tape casting with solids loading well over 50 vol% can be prepared. At these high volume concentrations a high degree of stability is crucial to get a slip with good flow properties for tape casting. In ceramic suspensions for tape casting the dispersant is optimally adsorbed in a monolayer onto the ceramic particles, and there should be no interaction between the dispersant and the binder.^{6,7} If there is some interaction between binder and dispersant or if the binder competes with the dispersant in adsorbing onto the ceramic particle surface, this may lead to a destabilisation of the suspension, an inadequate performance of the slip for tape casting and inferior properties of the final material.

Latex binders can be sensitive to high ionic concentrations, especially to high concentrations of polyelectrolytes (e.g. polyacrylic acid), which are commonly used as dispersants for alumina. Most commercial aqueous latexes are stabilised by electrostatic repulsion and as such they are sensitive to changes in the ionic strength of the aqueous phase.⁸ The addition of concentrated electrolytes,

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especially electrolytes of a higher valence such as polyelectrolytes, may cause destabilisation and, as a consequence, result in latex flocculation.

Another concern at high solids loading is destabilisation due to excess polyelectrolyte dispersant. When the saturation limit for adsorbing the polyelectrolyte has been reached, further additions only serve to give excess polymer in solution.^{9,10} With excess polyelectrolyte the viscosity increases and with an increased molecular weight of the polymer the viscosity increases even more. This can partly be explained by the increased viscosity of the aqueous phase which is more pronounced with increased molecular weight. Another reason for the increased viscosity is a destabilisation mechanism called depletion flocculation.¹⁰ These effects are more severe at a higher solids volume concentration and for high molecular weight polyelectrolytes.

The objective of this work was to study these phenomena for a tape-casting composition of an alumina system with latex binders. In general it is possible to reach a higher volume concentration in aqueous systems than in organic systems. Efficient dispersants in combination with latexes with a high polymeric content and low viscosity makes it possible to use high volume concentration (> 50 vol%) in aqueous tape-casting systems. How robust are these systems to e.g. batch variations of powder and how critical is an optimum dispersant concentration? The questions are how the latex binder will be affected by the polyelectrolyte in the presence of alumina and how the stability of the whole system will be affected. Two different types of latex binders (one anionic and the other one nonionic) were studied together with a polyacrylic dispersant. Both binders and dispersant have earlier successfully been used for tape casting of alumina. The stability of the suspensions was characterised using rheological measurements.

2 Experimental

2.1 Materials

A high-purity alumina, AKP 30 from Sumitomo Chemicals, with a mean particle size, d_{50} , 0.3– $0.4 \,\mu$ m and a specific surface area of 5–10 m² g⁻¹ was used. Information on the two latex binders and the polyelectrolyte dispersant is presented in Table 1.

The alumina slips of the tape-casting composition had a solids loading of 55 vol% before addition of the latex binder. The latex binder was added to the alumina slip to an amount of 7 wt%of polymer, which corresponds to 22 vol% of total solids volume. When the latex binder had been added, the total solids loading in the slip was

53.6 vol. Three different dispersant levels were chosen, 0.2, 0.3 and 0.5% as calculated on the alumina powder, solid dry weight basis. A dispersant level of 0.2% corresponds to suspensions at the optimum amount of dispersant with a monolayer coverage of the ceramic particles. The dispersant levels 0.3 and 0.5% suspensions with excessive amounts of dispersant corresponds to when some free polymer is present in the liquid phase.¹¹ Slips with and without latex were investigated using rheological measurements. Slips with alumina were prepared by ball milling for 16h at a speed of 70 rpm in 0.51 polypropylene jars filled with 500 g of Si₃N₄ milling balls. The batch sizes were 200 g of alumina in all cases. The pH of the suspensions was about 9.3 in all the slips. After milling, the alumina slips with no binder were evaluated with regard to their rheological properties. Slips with added latex binder were mixed and conditioned by magnetic stirring for 2-3 h before the rheological measurements took place. Some additional slips were made using planetary milling at 200 rpm, for 1 h with 500 g Si_3N_4 milling balls and 200 g of alumina.

2.2 Rheological measurements

The rheological characterisation was made both with a rheometer Haake RV20 with a testing unit CV100 and a controlled stress rheometer from Bohlin. (The measuring unit was a bob and cup model ME 30 for the Haake rheometer and C25 for the Bohlin rheometer.) The general flow behaviour was measured by a loop test in continuous shear, up sweep 0 to $100 \, \text{s}^{-1}$ for 5 min followed by a down sweep 100 to 0 s^{-1} . A stepwise, continuous shear measurement $(5s^{-1}$ for 3 min, recovery for 5 min, 20 s^{-1} for 3 min and finally a second recovery for 5 min) was used to check the time-dependent properties of the systems examined. Such an on/off procedure can provide useful information on the thixotropic responses of a sample, as the examination of the stress transient behaviour, resulting from the application of a constant shear rate, can reveal whether the structural recovery under rest conditions is appreciable or not. Some viscosimetry measurements were also made in continuous shear using a procedure reaching equilibrium values at constant shear rates from 0.4 to $323 \,\mathrm{s}^{-1}$ in 15 steps. To evaluate the viscoelastic properties of the slurries, two different types of measurements were used, mainly an oscillation strain sweep with start at 1% strain up to 10% strain in 10 logarithmic steps with the frequency set to 1 Hz, but a stress sweep measurement with a stress range from 0.1 to 10 Pa and a frequency of 1 Hz was also used for some measurements. The temperature was 25°C in all cases.

Table 1. Data on latexes and dispersants used in the study with trade names and some specifications

Duramax B1035, Rohm and Haas, USA Mowilith DM765 S,Acrylic latex, T_g -40°C anionic surfactant, pH 7·5-8·7, disperse phase 55 wt%, low viscosity grade, shear thinning, 0·09 Pa s at 10 s ⁻¹ Acrylic-Styrene latex, T_g -16°C, nonionic surfactant, pH 8·5, 50 wt% disperse phase, high viscosity grade, shear thinning, 6·3 Pa s at 10 s ⁻¹ Polyacrylic acid modified with substituted alkyl groups, pH 7, counterion NH4, MW 5000, conductivity 63·2 mS cm ⁻¹	Trade name and producer	Data and specifications
	Duramax B1035, Rohm and Haas, USA Mowilith DM765 S, Hoechst-Perstorp, Sweden Duramax D3021, Rohm and Haas, USA	Acrylic latex, T_g -40°C anionic surfactant, pH 7·5-8·7, disperse phase 55 wt%, low viscosity grade, shear thinning, 0·09 Pa s at 10 s ⁻¹ Acrylic–Styrene latex, T_g -16°C, nonionic surfactant, pH 8·5, 50 wt% disperse phase, high viscosity grade, shear thinning, 6·3 Pa s at 10 s ⁻¹ Polyacrylic acid modified with substituted alkyl groups, pH 7, counterion NH ₄ , MW 5000, conductivity 63·2 mS cm ⁻¹

2.3 Packing behaviour

The state of dispersion of the slips is reflected in its packing behaviour,12 and a well stabilised suspension will pack more efficiently than a weakly flocculated suspension. In these studies, simple slipcasting experiments were made to give an indication of the packing behaviour of the alumina suspensions. Slip was poured into small cylindrical plastic moulds placed on a plate of plaster. The green samples were dried and prefired at a temperature of 900°C at which there is no shrinkage but some bonding between the alumina particles which give sufficient strength to the material to allow it to be handled. The density of the samples heated to 900°C was considered to be equal to the green density and was then measured by the water intrusion method (Archimedes' principle).

2.4 Influence of ionic concentration

To be able to establish the influence on the stability of the increased ionic strength caused by excess polyelectrolyte, $NaCl_{(aq)}$ was added to the alumina suspensions with 0.3 wt% dispersant. A highly concentrated salt solution (20 wt%) was added in small quantities to an alumina slip kept under vigorous stirring. The pH and solids loading were uninfluenced by the salt addition. The suspension was left to condition for 30 min before the conductivity and rheological measurements were made. This made it possible to estimate the contribution to the stability of the ionic strength.

2.5 Influence of free polymer

The observed increase in viscosity with excess polyelectrolyte was also studied by rheological measurements of suspensions with an addition of uncharged polymer or small electrostatically charged particles. The increase in viscosity from the increased viscosity of solution with free PE present was also measured. To an alumina suspension volume fraction 0.55 vol% with 0.3 wt% dispersant, 0.2 wt% of polyethylene glycol with a molecular weight of 7000–9000 was added and characterised by rheological measurements. The effect of non-adsorbed charged particles was tested adding silica sol and ion-exchanged water glass to a 50 vol% alumina suspension with 0.2% dispersant. As a reference, additional dispersant was added in the same volume concentrations as the sol and water glass.

3 Results

3.1 Rheological measurements

None of the alumina suspensions showed thixotropy as no appreciable time-dependent effects were observed either in the loop or in the stepwise tests. The interpretation would be that all the suspensions are stable and that there is no break-up or formation of aggregates in these suspensions. All the viscosity results presented are from the continuous shear measurements. All the compositions had shear thinning behaviour as can be seen from the continuous shear measurements of the suspensions containing alumina (Table 2). The viscosity level increased by about one magnitude with optimum amount of dispersant 0.2 wt% compared with 0.5 wt% dispersant, which represents excessive amount of dispersant.^{11,13} The optimum amount of dispersant, 0.2%, corresponds to an amount of dispersant giving a monolayer coverage on the alumina particles.⁶ At dispersant levels of 0.3% and 0.5%, there was excess free polyelectrolyte present in the solution. The viscosity curves were tested for fitting with different models. The generalised Casson model¹³ yielded the best result and the viscosity and yield stress values presented in Table 2 are calculated from this model:

Generalised Casson model
$$\eta = \frac{\left(\tau_0^{1/n} + (\eta_\infty \gamma)^{1/n}\right)^n}{\dot{\gamma}}$$

where τ_0 = yield stress, η_{∞} = limiting viscosity at high shear rate range, $\dot{\gamma}$ = shear rate, η = viscosity and n = exponent (0.5 in the original Casson model).

Values of viscosity and yield stress at a volume concentration of 0.536 were also estimated from earlier studies.^{11,13} For alumina slips with no binder the viscosity and the degree of shear thinning increased as an excess amount of dispersant was used, 0.4 and 0.5 wt%. At higher shear rates, the viscosity levels at the different dispersant levels

Alumina slip	Amount of dispersant ^a (wt%)	Viscosity from continuous shear, (Pas)			Yield Stress ^b
		$1 s^{-1}$	$10 s^{-1}$	$100 s^{-1}$	(Pa)
No binder	0·2 0·3	1.16 $1.92, (1.52)^c$	0.31 0.40, (0.33)	0.12 0.13, (0.11)	0.30 0.99, (0.88)
	0-4 0-5	5.66 11.9, (9.3)	0.83 1.60, (1.27)	0.19 0.30, (0.24)	4.41 12.23, (7.32)
Latex B1035, anionic	0·3 0·5	1·37 4·84	0·27 0·74	0.08 0.16	0.73 3.13
Latex DM765, nonionic	0·3 0·5	3·40 5·51	0·56 0·82	0·13 0·16	2·01 3·49

Table 2. Viscosity of alumina sips with and without addition of latex binder

^a Duramax D3021 dispersant in all cases except one.

^b Yield stress value from the generalised Casson model.

^c Values in brackets are estimations at a volume fraction of 0.536.

converged indicating that the hydrodynamic forces are more important than the interparticle forces. The viscosity curves of the pure alumina suspensions prepared by planetary milling are shown in Fig. 1.

When the latex binders were added to the alumina suspensions the viscosity levels of the mixed suspension were both higher and lower than the different alumina base suspensions depending on dispersant level and type of latex. When the nonionic latex was mixed with an optimally stabilised alumina slip, i.e. at 0.2% dispersant, this led to flocculation of the suspension (Fig. 2). At the 0.3%dispersant the viscosity of the mixed suspension was higher than the reference slip, whereas the mixed suspension with the nonionic latex had lower viscosity than the reference slip at the 0.5%dispersant. The anionic latex, on the other hand, gave slightly higher viscosity at 0.2% dispersant when mixed into the alumina slip, but resulted in lower viscosity at both 0.3 and 0.5% dispersant compared with the reference slips (Fig. 3).

The results from the strain sweeps in oscillatory measurements gave curves that were just at the end of the linear viscoelastic region at the lowest strain, 1%. In order to obtain values from the linear viscoelastic region a model was applied to the curves so that a value of the complex shear modulus in the linear viscoelastic region could be obtained by extrapolation. The following damping function was used to describe the strain dependence of the complex modulus:

$$G^* = G_0^* \frac{1 + \gamma^n}{1 + \alpha \gamma^n}$$

The parameter G_0^* is the value presented as the complex modulus in the linear viscoelastic region. From these measurements it is even more evident that the increased amount of dispersant strongly influenced the interparticle forces (Table 3). As can be seen the complex modulus in the linear viscoelastic region increased by more than one order of



Fig. 1. Viscosity of alumina suspensions with varied dispersant concentrations. Solids volume fraction 0.55. Suspensions prepared by planetary milling.



Fig. 2. Relative viscosity of alumina suspensions containing nonionic latex DM 765 at varied dispersant concentrations. Volume fraction of solids 0.536 of mixed suspension. Suspensions prepared by planetary milling.

magnitude when the amount of dispersant increased from 0.3 to 0.5% in the alumina suspension. The phase also indicates a stronger interaction with a more elastic contribution with an increased amount of dispersant. When binder was added to the slip with 0.3% dispersant, the same tendency as noticed from the viscosity measurements was seen. The anionic Duramax B1035 latex decreased the value of the complex modulus, whereas the nonionic Mowilith DM 765 latex increased the value of the complex modulus and the phase lag remained at about the same levels, 0.35 and 0.37, respectively. For an increased amount of dispersant the level of the complex modulus was shifted for the two latexes. The phase was also markedly increased for the slip with the nonionic latex, 0.72 compared to 0.32 in the case of anionic latex binder. In contrast to the results from the continuous shear measurements, these results show that there was more interparticle interaction in the system with anionic latex at high dispersant levels compared with the nonionic latex.



Fig. 3. Relative viscosity of alumina suspensions containing anionic latex B1035 at varied dispersant concentrations. Volume fraction of solids 0.55 of mixed suspensions. Suspensions prepared by planetary milling.

Table 3. Viscoelastic properties from oscillation strain sweep

Alumina slip	Amount of dispersant (wt%)	Complex modulus, G_0^* (Pa)	Phase lag, δ (rad)	G ₀ * ratio*
No binder	0.2	5.0	0.76	_
	0.3	34	0.43	
	0.4	187	0.22	
	0.5	405	0.32	
Latex B1035,	0.3	31	0.35	0.92
anionic	0.5	428	0.32	1.06
Latex DM765,	0.3	101	0.37	3.01
nonionic	0.5	160	0.72	0.4

3.2 Packing behaviour

Figure 4 shows the green densities of the slip-cast samples. The results from the oscillatory measurements were confirmed by these results. The highest green density was obtained for the slip that had the lowest elastic shear modulus, which indicates that this was the most stable slip. The green density continuously decreased as excessive amount of dispersant was used. With the addition of the latex binder the green density was dramatically decreased. The green density dropped from a value of more than 66% in relative density with no latex addition to a green density of 56% in relative density when latex had been added to the composition. The latex addition dilutes the system, which explains why the effective density of the alumina was lowered. The obtained green density with added latex binder is probably related to the packing of the ceramic and latex particles and to the onset of the coalescence of the latex particles when the continuous liquid phase has decreased to a critical value. It can also be noted that the slip with 0.5% dispersant reached a higher green density with the nonionic latex compared with the anionic latex, as the polyelectrolyte addition did not affect the particle interaction to the same extent as was observed in the oscillatory measurements.

3.3 Influence of ionic concentration

When salt was added to an alumina slip the viscosity increased as a result of the increased ionic strength, which lowered the electrostatic repulsion. Figure 5 shows how the viscosity of an alumina slip with 0.3 wt% dispersant increased with the salt additions almost to the viscosity level of the slip with the 0.5 wt% dispersant. The tendency was the same for the values from the stress sweep measurements (Table 4). In addition to the viscoelastic



Fig. 4. Relative green density of slip-cast alumina samples.



Fig. 5. Viscosity of alumina slips at varied ionic concentrations. Alumina slips without NaCl, $-\blacksquare$ - with 0.3 wt% dispersant, ionic strength 86.5 mM, -●- with 0.5 wt% dispersant, ionic strength 144.1 mM. Alumina slips with 0.3 wt% dispersant and addition of NaCl and ionic strengths; $-\Box$ -121.4 mM, $-\diamondsuit$ - 135.6 mM, $-\bigcirc$ - 153.8 mM and -△- 191.8 mM.

quantification, the values of yield stress modelled from continuous shear measurements were also considered.

The increase in shear modulus by increased ionic strength from the baseline value at 0.3% dispersant to the same level as with 0.5 wt% dispersant is approximately 28% of the total. The decrease in electrostatic repulsion from increased ionic strength is therefore responsible for a minor part of the reduced stability, whereas the rest can be attributed to other mechanisms.

The increase in viscosity of the water solution from free polyelectrolyte resulted in relative viscosities of 1.05 and 1.15 corresponding to the dispersant levels 0.3 and 0.5% in an alumina suspension of volume fraction 0.55, assuming 0.2%dispersant being adsorbed and the rest free in solution. Figure 6 shows the relative viscosity of the suspensions with addition of PEG, sol, water glass or additional dispersant. With the addition of the uncharged polymer, the viscosity did not increase whereas the viscosity increased in all three cases of the charged particles.



Fig. 6. Relative viscosity of suspensions with added uncharged polymer, PEG, or charged particles; silica sol, ion exchanged water glass and excess dispersant polyelectrolyte.

4 Discussion

It is clear from the results that there was more interparticle interaction in the alumina slips as the dispersant level increased, as evidenced by increased viscosity, an increased degree of shear thinning and an increased shear modulus. There was no sign of thixotropy in any of the pure alumina systems and they are therefore believed to be stable, i.e. there is no formation or break-up of aggregates. Another fact, which speaks in favour of the suspensions being stable although the viscosity increased is the fact that the volume fraction of solids was very high, 0.55 for the alumina slips. If flocculation had been the case in these slips, this would have resulted in a more drastic increase in viscosity level. What is then causing the increased viscosity and elasticity when excess polyelectrolyte is present?

Cesarano and Aksay¹⁰ studied a similar system and suggested that the destabilisation due to excess polyelectrolyte be caused by a depletion flocculation mechanism. Depletion flocculation is a destabilisation mechanism that may occur when free polymer is present in a sufficiently high concentration.^{14,15} When the distance between two colloidal

 Table 4. Ionic strength, conductivity and viscoelastic properties from stress sweep and yield stress for alumina suspensions with and without additions of NaCl

Alumina slip	Conductivity (a) $25^{\circ}C$, (mS cm ⁻¹)	Ionic strength $(mM)^a$	$G^a(Pa)$	Phase lag (rad)	Yield stress (Pa)
0.3% disp	1.87	86.5	38	0.24	0.99
0.5% disp	3.22	144.1	732	0.09	12.23
0.3% disp, NaCl	2.90	121.4	102	0.16	2.25
0.3% disp, NaCl	3.35	135.6	148	0.12	2.98
0.3% disp, NaCl	3.97	153.8	288	0.10	5.01
0.3% disp, NaCl	5.05	191.8	438	0.14	9.12

^a Estimate of ionic strength with only the counterion of the polyelectrolyte taken into account.

particles is less than the mean size of the free polymer part the polymer chains are excluded from the space between the particles. If the polymer chains are to enter the space between the particles they have to change conformation. If the conformation of the polymer changes from its conformation in the bulk solution, the total free energy of the system increases, assuming that the solvent is a good solvent for the polymer. When the particles have come sufficiently close to each other and excluded the polymer chains, a closer approach therefore occurs spontaneously. This is thermodynamically favoured and results in depletion flocculation if the minimum in the potential energy is sufficiently large. The amount of polymer necessary to induce flocculation decreases with increasing molecular weight. Processing with lower molecular weight polyelectrolytes (i.e. MW 1000 to 10 000) is therefore recommended as this will give a more robust system.10

The particle separation distance in the alumina slips with a volume fraction of 0.55 was estimated to be approximately 21 nm assuming random close packing, 0.64, and monosized particles of $0.4 \,\mu m$ diameter. The size of the polyelectrolyte dispersant, D3021, with a MW of 5000 has an approximate unperturbed radius of gyration of 3.2 nm.16 The adsorbed polymer layer also contributes to a larger effective volume concentration in the suspension and a smaller separation distance. If we assume that the 0.2 wt% addition of dispersant corresponds to all dispersant being adsorbed and at concentrations of 0.3 and 0.5% dispersant the rest is free in solution, the attractive energy per unit area due to depletion can be estimated from the above information using the following relationship:¹⁶

$$W(D \to 0) \cong -\rho R_{\rm g} k T$$

where ρ is the number of free polymeric particles in the solution, (m⁻³), R_g the radius of gyration, k, Boltzmann's constant and T the temperature.

With the above assumptions and a volume fraction of 0.55 the attractive energy is 7.7×10^{-6} J m⁻² and 23×10^{-6} J m⁻² for the 0.3 and 0.5% dispersants, respectively. Both these values are very low and depletion flocculation is therefore not believed to be causing these effects. The experiment with added uncharged polymer, PEG, showed that the viscosity was uninfluenced by this addition, which indicates that depletion flocculation is not the mechanism responsible for the observed viscosity increase as does the fact that no thixotropy was observed.

The increased ionic strength, as shown by the experiments with added salt, partly contributes to

the increased viscosity. Free polymer in the solution also contributes to the increased viscosity observed, but only to a small degree, as shown by the viscosity measurements of PE solutions and calculations of relative viscosities. Both these effects only partly explain the observed viscosity increase.

Yet, another explanation to the observed increased viscosity and elasticity at high dispersant levels would be that the increased number of small charged dispersant particles increases the electrostatic repulsion in the system. This could lead to a more rigid structure between the particles at equilibrium state, which would result in increased elastic behaviour as observed in the systems, without causing destabilisation. Indeed this was what was observed in the experiments with added sol and water glass. When using the 0.5% dispersant, both the pure alumina suspension and the suspension with anionic latex had a dramatically increased shear modulus compared with the optimum amount of dispersant. The suspension with nonionic latex however had a lower shear modulus and a larger phase lag. One explanation, which would support the above theory is the fact that, in the case of the nonionic latex, PE is adsorbed on the latex decreasing the amount of free PE in the solution. The observed flocculation of the mixed system with nonionic latex at 0.2% dispersant supports this explanation. This would also explain the lower modulus and the uninfluenced particle packing in the mixed system with nonionic latex.

The ionic strength has a significant effect and this highlights the importance of working under optimum conditions for these tape-casting compositions, as other ionic species, such as soluble sintering additives in more complex systems, can also influence the stability, especially at high solids loading. A difference at high polyelectrolyte concentration in suspensions with anionic or nonionic latex was observed with the anionic latex being more susceptible to destabilisation. Results from oscillatory strain measurements indicated that the mixed suspension with anionic latex at 0.5% dispersant is less stable than the pure alumina system, especially in view of the lower volume concentration, 0.536 compared to 0.55 for the pure alumina system. This study also showed that it is necessary to use both continuous shear and oscillatory measurements to get a better understanding of the interactions in the system. As an example, it can be mentioned that the viscosity levels of the alumina systems with anionic latex were lower than those with the anionic latex at 0.5 wt% dispersant. The opposite was seen for the value of the complex modulus, which is correlated to the packing behaviour.

In the mixed systems with both alumina and latex it was found that the optimum dispersant concentration was 0.3% instead of 0.2% as was found for the alumina system. It is believed that the strong interaction leading to flocculation in the system with nonionic latex at 0.2% dispersant was caused by bridging flocculation. This could occur if some dispersant molecules desorb from the alumina particles leading to insufficient amount for full stability and instead adsorb onto the latex particles. This could also be the case in the mixed system with anionic latex at 0.2% dispersant, which showed a higher viscosity level compared with the alumina slip. The destabilisation was much less pronounced here, which probably is due to the fact that the latex particles already have a large negative charge and therefore less PE adsorbs. However, further studies including adsorption behaviour and zeta-potential measurements of the latexes are necessary to fully explain these observed phenomena.

5 Conclusions

Interactions between stabilised alumina particles, free polyelectrolyte dispersant and latex binders (both the anionic and nonionic, stabilised latexes) were observed and found to be largely dependent on the dispersant concentration. It was found that an excess PE concentration with regard to the alumina was necessary to achieve stable mixed suspensions for both the anionic and the nonionic latexes. The reason for this is believed to be adsorption of dispersant onto the latex particles. More dispersant was adsorbed onto the nonionic latex compared with the anionic latex. The optimum dispersant level must be studied separately for the pure alumina system and the mixed systems with both alumina and latex. A slight excess of dispersant also seems to be beneficial in giving lower viscosity at high shear rates which could be a way to reduce dilatancy. Excess polyelectrolyte dispersant, even with a low molecular weight of about 5000, causes increased viscosity in highly loaded suspensions which is believed to be due to three different mechanisms. First and foremost, the effect is believed to be due to more repulsive forces as the number of charged particles increase with excess free PE, and secondly a decreased electrostatic repulsion from increased ionic strength and, finally, an increase in the viscosity of the liquid phase from free polymer. The electrostatic effects dominated at the studied conditions.

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