

Rheological Behaviour of Stabilised Aqueous Alumina Dispersions in Presence of Hydroxyethyl Cellulose

Nikos Kiratzis* and Paul F. Luckham

Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London, UK, SW7 2BY

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Abstract

The flocculation behaviour of sterically stabilised aqueous α - Al_2O_3 dispersions in presence of hydroxyethyl cellulose (HEC) of various molecular weights has been studied by means of rheology. Steady state shear stress-shear rate measurements as well as oscillatory measurements suggest the existence of a critical flocculation polymer volume fraction (CFF) Φ_p^+ above which the rheological properties of the dispersions deviate from those observed when the dispersion contains no added polymer. The ceramic powder had an average diameter of $0.4\ \mu m$ and was stabilised in the dispersion by the polyelectrolyte ammonium polymethylmethacrylate. Both Φ_p (polymer volume fraction) and Φ_s (solids volume fraction) had a positive effect on the storage modulus G' . A Sisko type equation of the form $\eta = \eta_\infty + K\dot{\gamma}^{n-1}$ was found to closely fit the shear stress-shear rate data. The value of K , which can be seen as an effective yield stress of the suspension, was also found to increase with Φ_p and Φ_s . The exponent n was found to strongly depend on Φ_s and it was essentially insensitive to Φ_p above the critical flocculation fraction. This value decreased with increasing volume fraction. The polymer molecular weight was found to affect positively both G' and K although the effect on K was more pronounced. A depletion flocculation mechanism, whereby the HEC, which is non adsorbing on the alumina particles (Liang, W., Tadros, Th.F. and Luckham, P., *Rheological properties of concentrated sterically stabilized latex dispersions in the presence of hydroxyethyl cellulose*. *J. Colloid Interface Sci.*, 1993, **160**, 183–189), is depleted during a particle collision, giving rise to an osmotic

gradient, is suggested to explain the behaviour of the system. © 1997 Elsevier Science Limited. All rights reserved

Resumé

L'étude de la rhéologie de solutions aqueuses d'alumine- α (α - Al_2O_3) dispersées et 'stabilisées stériquement' a permis d'examiner leur comportement en flocculation en présence d'hydroxyethyl cellulose (HEC) de poids moléculaires variables. Les mesures des contraintes de cisaillement en fonction du gradient de cisaillement en écoulement à l'équilibre comme en mode d'oscillation montrent l'existence d'une fraction volumique critique de polymère (CFF) Φ_p^+ au delà de laquelle la flocculation apparaît: les propriétés rhéologiques des solutions dispersées changent par rapport à celles observées dans les solutions ne contenant pas de polymère. La poudre céramique utilisée a un diamètre moyen de $0.4\ \mu m$ et a été stabilisée en solutions dispersées par addition d'un polyelectrolyte de polyméthylméthacrylate d'ammonium. A la fois Φ_p (fraction volumique de polymère) et Φ_s (fraction volumique de solide) ont un effet positif sur le module élastique G' . La courbe montrant la contrainte de cisaillement en fonction du gradient de cisaillement est superposable à une courbe d'équation de Sisko de la forme $\eta = \eta_\infty + K\dot{\gamma}^{n-1}$. La valeur de K , qui pourrait correspondre à une contrainte seuil, augmente avec celles de Φ_p et Φ_s . L'exposant n dépend fortement de Φ_s et est pratiquement indépendant de Φ_p au delà de la fraction critique de flocculation. Cette valeur décroît avec l'augmentation de la fraction volumique de solide Φ_s . Le poids moléculaire du polymère a un effet positif à la fois sur G' et sur K bien que l'effet sur K soit plus prononcé. Le comportement du système peut être expliqué par un mécanisme de flocculation dû à la déplétion. L'HEC qui n'est pas

*To whom correspondence should be addressed.

absorbé à la surface des particules d'alumine (Liang, W., Tadros, Th.F. and Luckham, P., Rheological properties of concentrated sterically stabilized latex dispersions in the presence of hydroxyethyl cellulose. J. Colloid Interface Sci., 1993, 160, 183–189) est chassé lors des collisions entre particules ce qui donne lieu à un gradient osmotique.

Introduction

Ceramic dispersions are used in a variety of processes for the large scale production of a wide range of ceramics. Some of the widely used methods are slip casting, tape casting and tape calendaring. The dispersing media can be either aqueous or organic and a dispersant and binder, are always used to enhance processibility. The dispersions subsequently undergo drying and controlled sintering to obtain the final product.^{1,2} High final sinter densities and minimum shrinkage are always desirable and thus a high initial solid content of the ceramic dispersions (where typically the average particle size $< 1 \mu\text{m}$) is desired.^{3,4} Depending on the application, an optimum dispersion rheology is always required.^{5,6} Dispersing agents prevent coagulation caused by Van der Waals forces present in colloidal dispersions. One way in which ceramics may be stable towards aggregation is to adsorb a polymer to the surface of the particle, creating an adsorbed layer which extends to a distance large enough to prevent the Van der Waals attraction becoming dominant.^{7,8} Particle repulsion can also be achieved by electrostatic forces created by ions adsorbed on the particle surface. A combination of the above methods is possible by the use of polyelectrolytes as dispersing agents and this is the commonest form of stabilisation of ceramic particles.⁵

The role of the binder is to increase the strength of the green body (i.e. the product prior to firing). Ideally an as low as possible concentration of binder is desirable so that it may be removed easily during subsequent steps prior to sintering.^{2,3}

The purpose of the present communication is to examine the rheological behaviour of $\alpha\text{-Al}_2\text{O}_3$ sub micron dispersions in presence of hydroxyethyl cellulose as binder. The dispersion was stabilised with a commercial dispersant, Darvan C, which is a polyelectrolyte (ammonium polymethacrylate).

Experimental

Materials

The ceramic used in this study was a fine powder of $\alpha\text{-Al}_2\text{O}_3$ (99.9%) designated as AES-11 (Mandoval

Ltd., UK) with a particle size range between 0.1 and $1 \mu\text{m}$, a BET surface area of $9 \text{m}^2\text{g}^{-1}$, and fired density of 3.96g cm^{-3} . One polyelectrolyte, ammonium polymethacrylate (commercial name Darvan C, R.T Vanderbilt Company Inc.) was used. The quoted molecular weight was 10 000–16 000. The hydroxyethyl cellulose (HEC) polymers were the Natrosol 250 G,M,H, and HHX grades obtained from Hercules B.V. (Rijswijk, The Netherlands). Their molecular weights were 3×10^5 , 7×10^5 , 8.5×10^5 , and 10×10^5 , respectively. Distilled water was always used as the dispersing medium.

Procedure

For the preparation of the dispersion, first the dispersant was diluted in a known volume of water at concentrations corresponding to 1.3 wt% of dry powder. This amount was kept constant throughout the experiments and corresponds to a minimum dispersion viscosity according to a previous study.⁹ Dissolution of a known amount of HEC followed assisted by magnetic stirring. It never took more than one hour for complete dissolution of the polymer to occur. The ceramic powder was subsequently added to the solution and, after an initial shaking, the dispersion was ball milled for about 40 h before its introduction into the rheometer.

In an alternative procedure to the above, the dispersant and the powder were first ball-milled for 24 h after which HEC was added and ball milling continued for another 24 h. No difference on the rheology was found when the latter procedure was followed. In addition, preliminary runs using mechanical stirring as an alternative mixing method, verified that ball mill was more favourable in producing uniform dispersions for reproducible experiments.

Rheological measurements

Steady-state (shear stress-shear rate) and oscillatory measurements were carried out using a Bohlin VOR (Bohlin Reologie, Lund, Sweden) rheometer. The rheometer was interfaced with a computer for all measurements and the temperature was kept constant within 0.1°C at 25°C . A concentric cylinder geometry was used (system C25) with a moving cup of radius 27.5 mm and a fixed bob of radius 25 mm. The sample is in the annular gap between the two cylinders. Shear stress is transmitted from the outer cylinder, through the sample to the inner cylinder which is connected to a torque bar, the deflection of which is measured by a transducer. The instrument operates over the shear rate range of 10^{-3} – 10^3s^{-1} and over a frequency range of 0.001 to 20 Hz but in these measurements a range of 0.1 to 10 Hz was found adequate. In addition, three interchangeable torque bars were used to

allow for different sensitivities depending on the consistency of the sample.

In oscillatory shear, the rheometer moves the cup back and forth in a sinusoidal manner. The phase angle shift, δ , between stress and strain is computed from the time displacement of their corresponding waves Δt , as $\delta = \bar{\omega}\Delta t$, where $\bar{\omega}$ is the angular frequency given by $\bar{\omega} = 2\pi\nu$ and ν is the oscillation frequency in Hertz. Then, the following quantities are computed:

$$|G^*| = \tau_0/\gamma_0 \quad (1)$$

$$G' = |G^*| \cos \delta \quad (2)$$

$$G'' = |G^*| \sin \delta \quad (3)$$

$$|G^*| = G' + iG'' \quad (4)$$

where $I = (-1)^{0.5}$ and τ_0 and γ_0 are the stress and strain amplitudes, respectively.

These quantities are known as the complex (G^*), elastic (G') and loss (G'') modulus. The elastic modulus is an indication of the energy stored elastically in the system after a shear perturbation while the loss modulus is a measure of the energy lost as heat against friction.¹⁰ In oscillatory measurements the behaviour is determined within the linear viscoelastic region, i.e. the region within which the above parameters (G^* , G' , G'') are independent of the applied strain. Thus, in all experiments, the linear viscoelastic region was first established by fixing the frequency at 1 Hz and measuring the parameters as a function of strain amplitude. Then, at a fixed strain amplitude, measurements with respect to frequency were performed. No difficulty was encountered in most of the runs in establishing the linear viscoelastic region except at the highest solid fraction examined (53 vol%) where it was difficult to establish a linear region. Care was always taken to perform the experiments below the resonance frequency of the torque bar used.

In the steady-state measurements, a constant shear rate was applied and the corresponding shear stress, as well as apparent viscosity, determined. The shear rate range was 0.1 to 1160 s^{-1} .

A Sisco model¹⁰ was applied successfully to all these data which follow a shear thinning type behaviour:

$$\eta = \eta_\infty + K\dot{\gamma}^{n-1} \quad (5)$$

where η is the apparent viscosity and η_∞ is the viscosity at high shear rates. There was always

observed a limiting viscosity in all dispersions. The parameter K is an indication of the non-Newtonian nature of the dispersion; $K = 0$ for a Newtonian fluid and it is equivalent to the yield stress for a Bingham type fluid.

Results

Oscillatory measurements

The effect of frequency of oscillation on the elastic and loss moduli at solids volume fraction of 34% at various concentrations of HEC of MW = 300 000 is shown in Fig. 1. In the absence of any HEC, all the moduli are close to zero with the loss modulus being greater than the elastic modulus. These data are consistent with the dispersion being well dispersed. As the amount of HEC added to the alumina dispersion is increased, both G' and G'' increase and G' becomes greater than G'' . This is consistent with the interactions between the particles becoming greater and is usually seen in suspensions undergoing flocculation.¹¹ To examine this effect further, we plot in Fig. 2 the elastic modulus at 1 Hz as a function of HEC concentration. A linear relation is followed for all solid

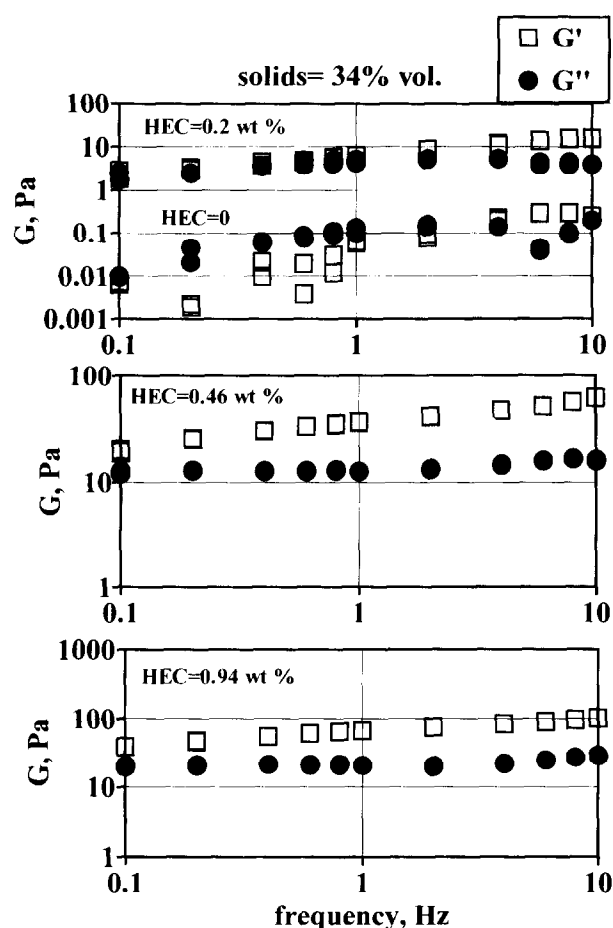


Fig. 1. Effect of frequency of oscillatory shear on elastic and loss moduli at various HEC concentrations (wt%, medium weight basis) (MW = 300 000).

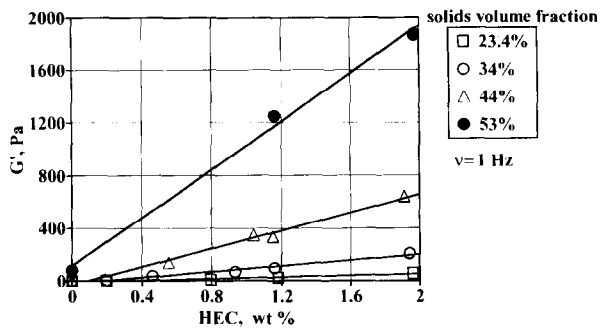


Fig. 2. Effect of polymer concentration on elastic modulus at various solids volume fractions at $\nu = 1$ Hz (MW = 300 000).

fractions up to about 2% HEC. Moreover, it would appear as though a critical amount of HEC need be added before any increase in G' is observed. The HEC concentration where G' starts increasing corresponds to the HEC concentration required to flocculate the suspension. Thus, we may define the critical flocculation fraction (CFF) Φ_p^+ as the polymer concentration above which G' exceeds the base value at HEC = 0. It can be seen from Table 1 that Φ_p^+ varies from 0.1 to 0.3% for the different solids volume fractions.

In Table 1, Φ_p^+ is estimated from the x-axis intercepts of the straight lines obtained for G' in Fig. 2 with the exemption of the highest solids fraction (53 vol%) in which Φ_p^+ is taken as the concentration required to exceed the base value observed at HEC = 0. The values of the last column of this table are estimated from the steady-state measurements as described in the following section.

The effect of molecular weight of HEC on the storage and loss moduli at a fixed solids and HEC concentrations are shown in Fig. 3. It can be seen that the storage modulus is not significantly affected up to a MW of 850 000. Above this molecular weight it starts increasing by about a factor of 2 at MW = 1 000 000. If we assume that the storage modulus G' is a measure of the number of elastic bonds of the flocculated system, this behaviour would suggest that this number remains essentially constant from MW = 300 000 to 850 000 and starts increasing significantly above MW = 850 000. On the other hand, the molecular weight does not

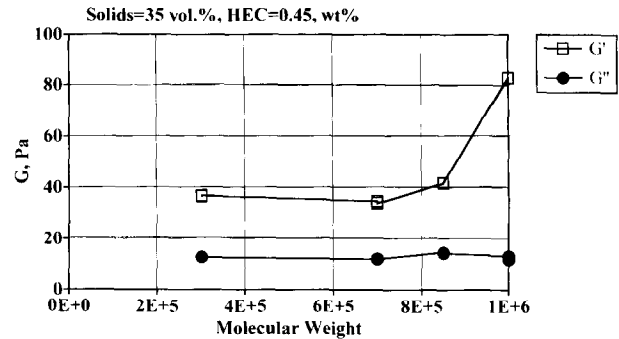


Fig. 3. Effect of polymer molecular weight on elastic and loss moduli at constant solids volume fraction ($\phi_s = 34\%$) and constant polymer concentration ($\phi_p = 0.45$ wt%, medium weight basis).

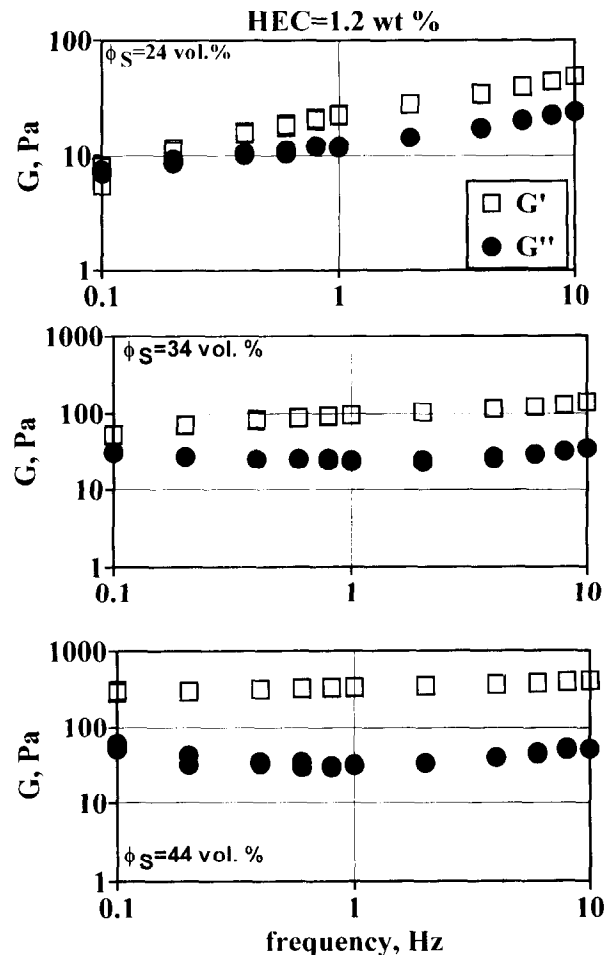


Fig. 4. Effect of frequency of oscillatory shear on the elastic and loss moduli at various solids volume fractions (MW = 300 000).

Table 1. The critical flocculation fraction of polymer at various solids fraction of alumina as estimated from steady state (K) and oscillatory shear measurements (G')

Powder Concentration ϕ_s , (vol%)	Φ_p^+ (G') (wt%)	Φ_p^+ (K) (wt%)
23.4	0.29	0.4
34	0.16	0.18
44	0.10	0.10
54	0.12	0.13

affect the loss modulus G'' which indicates that the energy lost in friction between the flocs is not affected by molecular weight of the polymer.

The effect of frequency on the elastic and loss moduli at constant polymer concentration is shown in Fig. 4 for different solids fractions. Again as in Fig. 1, increasing the volume fraction has a positive effect on both G' and G'' with their difference becoming greater at higher volume fractions. Note that in this case $G' > G''$ even at 23% solids due to

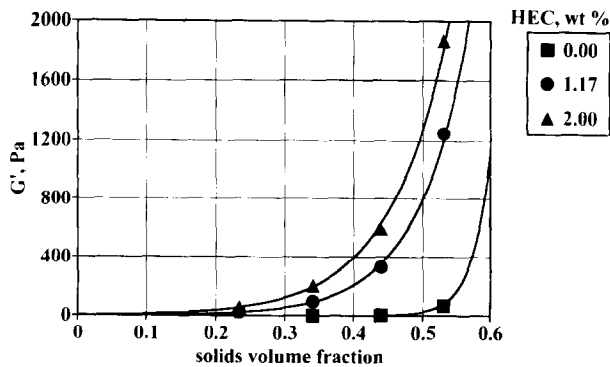


Fig. 5. Effect of solids volume fraction on elastic modulus at various polymer concentrations (MW = 300 000).

the presence of HEC which is aggregating the dispersion. The effect of solid fraction on the elastic modulus is shown more clearly in Fig. 5. G' follows an exponential increase with solid volume fraction for all HEC concentrations. This exponential relation is also followed when no HEC is present. The effect of HEC is to shift the G' versus Φ_S curve to lower volume fractions. This is likely to be due to the flocculated particles occupying a larger effective volume than the true volume.

Steady state shear stress-shear rate measurements

In absence of HEC, the effect of shear rate on the relative viscosity of the ceramic dispersion is shown in Fig. 6 for several volume fractions of alumina. The relative viscosity is defined as the ratio of the dispersion viscosity to the viscosity of the medium. Dispersions at volume fractions below about 24% behave essentially as Newtonian fluids. For higher solids concentrations of alumina, it can be seen that a shear thinning behaviour is followed for small shear rates and eventually a high shear limiting viscosity is always reached. These data are consistent with the particles being very well dispersed.

When HEC is added to the stabilised dispersion, flocculation takes place but the system again follows shear thinning behaviour as it can be seen from Fig. 7. Results in this figure are for a constant

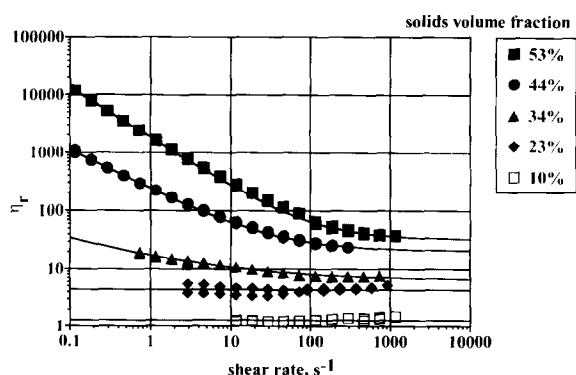


Fig. 6. Effect of shear rate on apparent viscosity at various solids volume fractions in absence of HEC.

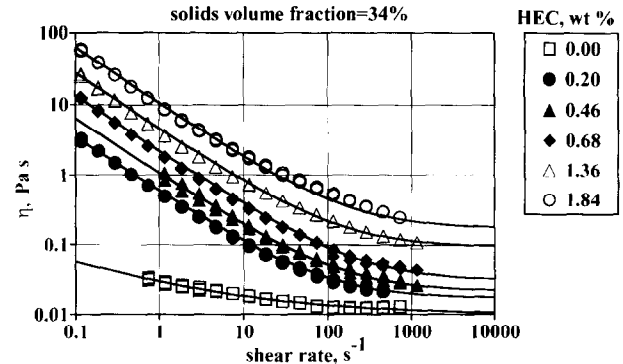


Fig. 7. Effect of shear rate on apparent viscosity at $\phi_S = 34\%$ and various polymer concentrations (MW = 300 000).

solids volume fraction at 34% and with HEC ranging from 0 to 1.84%. The lines in both Figs 6 and 7 correspond the best fits to a Sisco type of empirical eqn (5). This type of behaviour was followed closely for all the viscosity-shear rate curves. The parameters of the above equation n and K are generally functions of Φ_S (solid volume fraction) and Φ_P (polymer concentration in weight per volume of suspending medium) and can be used to represent the behaviour of this system in a concise manner. The procedure which was followed for fitting the above parameters was performed by a Deltagraph spreadsheeting software (Deltapoint Inc., California, USA). This is based on minimisation of the parameter $\chi^2 = [(f(x_i) - y_i)/y_i]^2$ for each individual point.

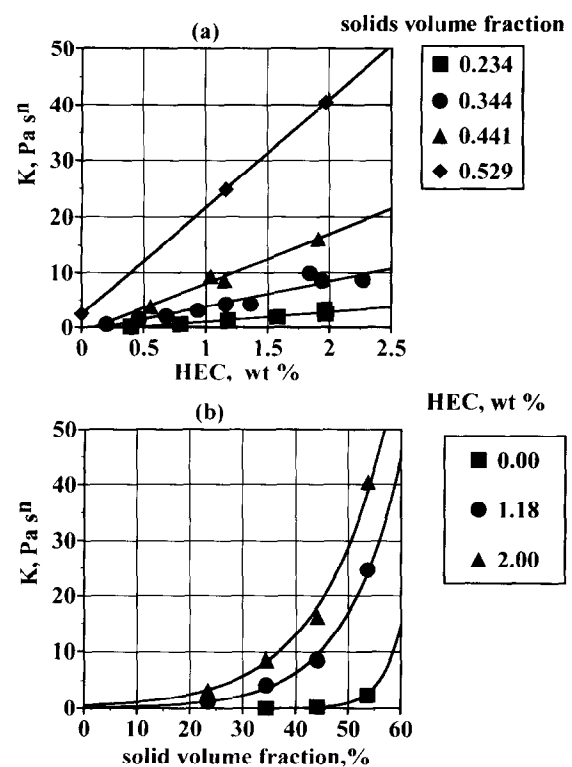


Fig. 8. (a) Effect of polymer concentration on the parameter K at various solids volume fractions. (b) Effect of solids volume fraction on the parameter K at various polymer concentrations (MW = 300 000).

Figure 8 shows the variation of the parameter K with respect to Φ_P [8(a)] and Φ_S [8(b)]. It can be seen that K follows a linear dependence on HEC in a similar fashion to G' . This indicates a critical flocculation point for each volume fraction which agrees quite well with the corresponding one found from the elastic modulus as can be seen from Table 1. The value of K can be seen as analogous to yield stress in a Bingham type of behaviour. Thus, a value of $K = 0$ should indicate a Newtonian behaviour.

Again since the high solids volume fractions exhibit a non zero value of K even in absence of HEC, it was decided to define Φ_P^+ as the point at which the zero HEC K value is exceeded. Figure 8(b) shows that K follows an exponential dependence on the solid volume fraction in a similar manner to G' .

The effect of HEC and solids volume fractions on the second parameter n of the Sisko model is shown in Fig. 9(a) and (b), respectively. The value of n does not essentially change with Φ_P for the range of HEC concentrations examined. This goes down to $\Phi_P = 0.2$ wt% for a solids volume fraction of $\Phi_S = 34\%$. No data were taken in the region designated by the broken lines. This graph suggests that above the CFF at each solids volume fraction no significant variation of n with Φ_P should be expected. To explore this further we plot in Fig. 9(b) the variation of n with Φ_S . It can be seen

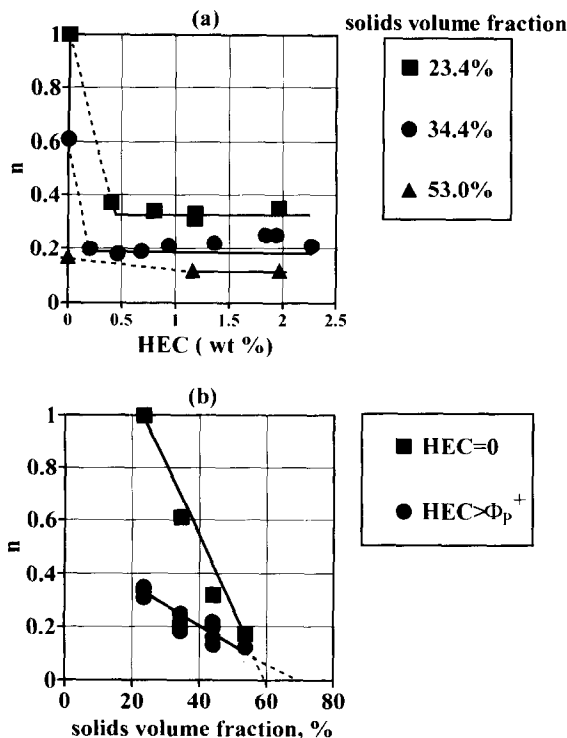


Fig. 9. (a) Effect of polymer concentration on the parameter n at various solids volume fractions. (b) Effect of solids volume fraction on the parameter n in absence and in presence of HEC at concentrations higher than its critical flocculation fraction (MW = 300 000).

that a linear behaviour is followed with the slope being different in absence of HEC. If we extend these lines to $n = 0$ we obtain a volume fraction of about 0.6 in absence of HEC and 0.74 in presence of HEC and $\Phi_P > \Phi_P^+$. A value of $n = 0$ essentially indicates a clear Bingham type of behaviour with the K value in this case representing the Bingham yield stress. On the other hand, a value of $n = 1$ is indicative of Newtonian behaviour.

Figure 10 shows the behaviour of the constant K as a function of molecular weight of the HEC. A nearly linear increase is observed with MW. If we see the value of K as an effective yield stress which is related to the strength of the bonds between the flocs, then it is suggested that this strength increases with molecular weight.

Discussion

It is clear then, that the effect of the addition of HEC is to aggregate the particles. The question is how is this aggregation brought about? In a recent study by Liang *et al.*,¹² it was shown that addition of HEC to a dispersion of polystyrene latex particles also brought about flocculation of the dispersion. In that study rheology was used to detect the onset of flocculation and was monitored by changes in the elastic modulus and yield values in much the same way as we have used rheological methods here. Furthermore, it was observed that a critical concentration of polymer of around 0.3% was required to induce flocculation of these systems. It would seem likely, therefore, that a similar flocculation mechanism is operating in both cases.

Polymers in a good solvent may flocculate particles in two ways. One mechanism is bridging flocculation where at low concentrations of polymer the macromolecule can adsorb simultaneously to two particles and hence bridge between the particles. Such a mechanism is very unlikely to be occurring here because hydroxyethylcellulose does not adsorb to alumina since an adsorbed layer of

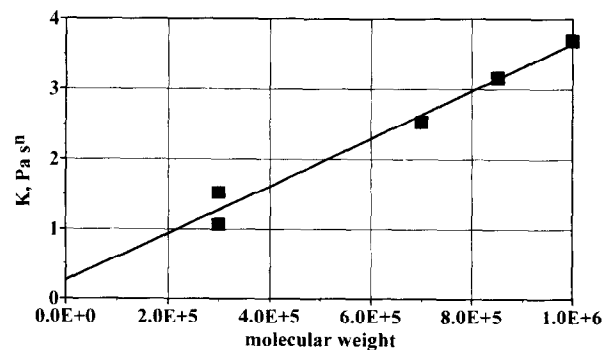


Fig. 10. Effect of MW on the parameter K at $\phi_S = 34$ vol% and $\phi_P = 0.45$ wt% (medium weight basis) (data correspond to those of Fig. 3).

Darvan C is already present on the particles. The polyelectrolyte concentration used here (1.3 wt% dry powder basis) is close to a minimum suspension viscosity at the natural pH in absence of binder.⁹ Hence, in the absence of binder, the particles are as fully dispersed as they can be. Under these conditions the amount of polyelectrolyte remaining in solution is very low because of the high-affinity type of adsorption of Darvan C on the alumina particles.¹³⁻¹⁵ In addition, the polyelectrolyte chains assume a relatively flat configuration covering a large amount of surface area.^{13,14}

The second mechanism, which is the one proposed to occur for the polystyrene particles,^{11,12} is that of depletion flocculation. In depletion flocculation the polymer does not adsorb on the particles but is rather repelled from the surface of the particle. This leaves a region close to the surface of the particle which is depleted in polymer. When two such particles approach each other such that these depletion layers overlap, there will be a concentration gradient between the gap, where there is a depleted amount of polymer and the bulk solution. This will give rise to an osmotic pressure difference between the gap and the bulk. To overcome this osmotic pressure difference, solvent will flow out of the gap between the particles (low osmotic pressure region) to the bulk (high osmotic pressure region). This will occur if the particles move together, hence flocculation. Such a mechanism is expected to increase as the bulk polymer concentration is increased as we observe here and to increase with increasing molecular weight of the polymer, which is again indicated by the rheology data, the K values, reported in this paper. Thus, it appears as though this depletion mechanism is the way by which the alumina particles aggregate. Thus in this particular case where we are using HEC as the binder for alumina, it appears as though the binder acts by binding the ceramic particles together by inducing a weak attractive interaction between the particles and that this is brought about by a depletion mechanism. Moreover, since polymeric binders dominate in ceramic processing, it is likely that this mechanism occurs in other particulate binder systems.

We now need to ask ourselves whether the binder adds any beneficial properties to the ceramic dispersion other than of increasing the strength of the green body. The rheological data presented here suggest that this is probably so. This is probably best illustrated in Fig. 11 where $\eta_r^{-1/2}$ is plotted as a function of volume fraction of particles. We may define as being the maximum packing fraction of particles as the point where $\eta_r^{-1/2} = 0$, i.e. $\eta_r \rightarrow \infty$. In the absence of HEC, this is around 0.6, which is typical of many stable particulate systems, but in

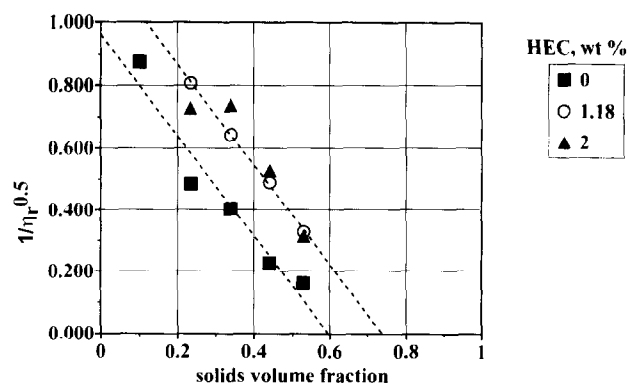


Fig. 11. Effect of solids volume fraction on $\eta_r^{-1/2}$ at various HEC concentrations (MW = 300 000).

presence of HEC, $\eta_r^{-1/2} = 0$ at $\phi_S = 0.74$. This is a consequence of the weak attractive interactions induced by the HEC essentially consolidating the particles such that a more uniform packing of particles may be obtained. This is very beneficial in ceramic processing where a maximum solid fraction is desirable for shrinkage minimisation during sintering. It is interesting to observe that these values are the same as those estimated from the plots of n versus ϕ_S (Fig. 9). Note, however, that these data are obtained at high shear. At low shear, where the moduli data were obtained, it was noted (Fig. 5) that the flocculated structure (i.e. in the presence of HEC) had a larger effective volume fraction than the stable suspensions. Thus, we must conclude that this particle consolidation is brought about by the applied shear.

Conclusions

The flocculation behaviour of stabilised colloidal alumina dispersions in presence of hydroxyethyl cellulose was studied by means of rheology. Measurements under oscillatory as well as steady shear revealed the existence of a critical flocculation polymer volume fraction above which the rheological behaviour of the suspension deviates significantly from that in absence of polymer. This type of behaviour is similar to that observed in polystyrene colloidal dispersions and suggests a similar flocculation mechanism. Thus, the depletion flocculation mechanism seems to be operative in this case. According to this mechanism, the polymer does not adsorb on the particles but rather is repelled from its surface, leaving a depleted region close to the surface. This situation gives rise to an osmotic pressure gradient which is overcome by the movement of solvent in the opposite direction, and thus, causing flocculation of the particles. In addition, it was found that, in the presence of polymer, although higher effective

volume fractions are observed at low shear, a more uniform packing can be achieved at high shear giving rise to a higher maximum solids fraction. This is very beneficial in ceramic processing where higher solids concentrations are desirable for minimisation of shrinkage during subsequent thermal treatment. A more elaborate examination of the particle interactions is in preparation.

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