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The Rheology of Aqueous Alumina Suspensions in the Presence of Hydroxyethylcellulose as Binder

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Abstract

The rheological behaviour of aqueous colloidal alumina dispersions stabilised by the dispersant Darvan C, an ammonium salt of polymethacrylic acid, was investigated in presence of hydroxyethyl cellulose (HEC) at room temperature. Measurements were taken under both oscillatory and steady shear. It was found that the polymer induces flocculation of the particles probably due to a depletion mechanism. The flocculation process results in the creation of a particle network, which restricts particle movements and gives rise to a wide distribution of relaxation times. At high HEC concentrations, two sets of relaxation times can be distinguished, one at low and the other at high frequencies. At high solids content and high HEC concentrations, the response of the system becomes predominantly elastic at low frequencies. The behaviour is similar to an entangled network of high molecular weight uncross-linked polymer solution. Thus, HEC causes the formation of 'topological restraints' comprised of chains of particles that give rise to a wider distribution of relaxation times with significantly lower terminal relaxation times. In addition, similarly to a polymer solution, complete superposition occurs of the apparent and dynamic viscosity in accordance to the Cox–Merz rule. Taking into account the combined data, a Cross type of formulation was found to fit the behaviour of all dispersions that can be represented in terms of a single dimensionless parameter. The behaviour of the adjustable parameters of this empirical model suggests a diffusion controlled cluster–cluster aggregation process that induces a more closed packed particle arrangement at high shear rates.

Keywords: depletion flocculation, suspensions, Al_2O_3.

1 Introduction

The rheological behaviour of colloidal ceramic dispersions is of crucial importance to large-scale ceramic production industries. Liquid ceramic processing is still the main large-scale production method and understanding the mechanism of particle interactions is necessary for process optimisation and best design of the initial formulations.

Aqueous dispersing media are generally preferred due to environmental considerations and a dispersant and binder are ubiquitously used to enhance processibility. These additives affect the rheology of the dispersions and optimisation of their amounts in the initial formulation stage is always required for best results.

The liquid processing stage is followed by temperature controlled drying and sintering steps in order to obtain the final product. The general requirements are for the final ceramic body to have a high density (as close to theoretical as possible) and for the body to undergo minimum shrinkage during the thermal cycles to avoid internal stresses. Thus, a high initial solid content in the liquid stage is always desirable in addition to colloidal sized particles ($<1\,\mu$m). Dispersants are then used in order to prevent coagulation in this colloidal range due to the strong van der Waals forces present. The most effective form of stabilisation at present can be achieved through the use of polyelectrolytes. These are charged macromolecules that adsorb on

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*To whom correspondence should be addressed. Fax: +44-171-594-5604; e-mail: p.luckham01@ic.ac.uk the ceramic particle surface creating a repulsion between the surfaces partly due to the steric layer of the adsorbed macromolecule and partly due to the overlap of the electrical double layer that is formed around the now charged particle. The repulsion is sufficient to prevent van der Waals attraction forces becoming dominant. The role of the binder is essentially to increase the strength of the green body (i.e. the product prior to firing). The requirement here is to use the lowest possible amount of binder that can easily be removed later by burn out with minimum shrinkage.

In a recent publication,[1] results were presented on the flocculation behaviour of sterically stabilised aqueous α-Al_2O_3 dispersions in presence of hydroxyethyl cellulose (HEC) based on rheological measurements. Steady-state as well as oscillatory shear stress-shear rate experiments indicated the existence of a critical flocculation polymer volume fraction (CFF) $\Phi_P{}^+$, above which the rheological properties of the dispersions significantly deviate from those exhibited in the absence of polymer. Good initial dispersion of the ceramic particles, which had an average diameter of 0·4 μ, was ensured by using the polyelectrolyte ammonium polymethacrylate. It is well established that such polyelectrolytes adsorb on the particle surface creating a layer (steric stabilisation) which prevents the van der Waals forces becoming dominant while simultaneously induce electrostatic repulsion.

It was found that both Φ_P (the polymer volume fraction) and Φ_S (solids volume fraction) have a positive effect on the storage modulus G′. A Sisko type equation of the form $\eta = \eta_\infty + K_\gamma{}^{n-1}$ was found to closely fit the steady-state shear stress–shear rate data. The value of *K*, which can be seen as an effective yield stress of the suspension, followed a similar behaviour to the elastic modulus G' and increases with both Φ_P and Φ_S. The exponent *n* was found to strongly depend on Φ_S but it was essentially insensitive to Φ_P above the critical flocculation fraction.

The polymer molecular weight has a positive effect on both G' and *K* but the effect on *K* is more pronounced. As regards the flocculation mechanism, it was suggested that depletion flocculation is operative in the system, whereby HEC, which is non adsorbing on the alumina particles, is depleted during a particle collision, giving rise to an osmotic gradient which induces flocculation.

In the present communication more results are reported for the same system and emphasis is given on the relaxation characteristics of the dispersions as derived from both steady and sinusoidally varying shear deformations. The type of particle interactions is discussed and the oscillatory shear data are combined with the steady-state data to reveal the rheological behaviour in an extended shear rate range.

2 Experimental

The experimental procedure was the same as that described before[1] and a brief summary is given here. The ceramic α-Al_2O_3, obtained from Mandoval Ltd., UK (commercial name AES-11), consisted of particles with a diameter around 0·4 μ, had a BET surface area of $9\,m^2\,g^{-1}$ and a fired density of $3{\cdot}96\,g\,cm^{-3}$. The polyelectrolyte ammonium polymethacrylate (Darvan C) was obtained from R. T. Vanderbilt Company Inc. and was quoted with a molecular weight of 10–16,000.

Hydroxyethyl cellulose (HEC grade: 250 G with MW = 300,000) was obtained from Hercules B.V. (Rijswijk, The Netherlands).

The dispersant, Darvan C, was dissolved in a known volume of distilled water at concentrations corresponding to about 1.3% w/w of dry powder.[1] This amount was used for all the experimental runs and corresponds to a minimum dispersion viscosity in the absence of a binder.[2] Dissolution of a known amount of HEC followed assisted by magnetic stirring. The ceramic particles were subsequently added and the resulting dispersion was ball milled for about 40 h before introduction into the rheometer. In an alternative procedure the ceramic particles were firstly added to a dispersant aqueous solution and the dispersion was ball milled for about 24 h. A known amount of HEC was subsequently added in its dry form and ball milling continued for another 24 h before introduction into the rheometer. It was found that both preparation methods resulted in the same macroscopic rheological behaviour.

Steady-state and oscillatory shear stress–shear rate measurements were performed by means of a Bohlin VOR (Bohlin Instruments, Cirencester, UK) rheometer as described before.[1] For the oscillatory measurements a frequency range of 0·01 to 10 Hz was used. For the steady-state measurements a shear rate range of 0·1 to $10^3\,s^{-1}$ was used. In addition, a concentric cylinder geometry was employed and the temperature was kept at 25 ± 0·1°C. The viscoelastic parameters G^* (complex modulus), G' (elastic modulus) and G'' (loss modulus) were computed automatically. 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. In oscillatory measurements the behaviour is determined within the linear viscoelastic region, that is 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. It is found that at low strains, G' and G'' are independent of the amplitude of oscillation up to a critical strain γ_c. This is the linear viscoelastic region. At amplitudes above the critical strain γ_c, both G' and G'' are amplitude dependent with G' decreasing monotonically and, at high HEC concentrations, G'' going through a maximum. Frequency sweeps were performed at a fixed strain amplitude within the 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 stresses, as well as apparent viscosity, were computed.

3 Results and Discussion

3.1 Oscillatory shear data

The variation of both G' and G'' with frequency for several dispersions is shown in Fig. 1 for 34% solids and at different HEC concentrations. It can be seen that the form of the dependence of both G' and G'' changes with HEC concentration.

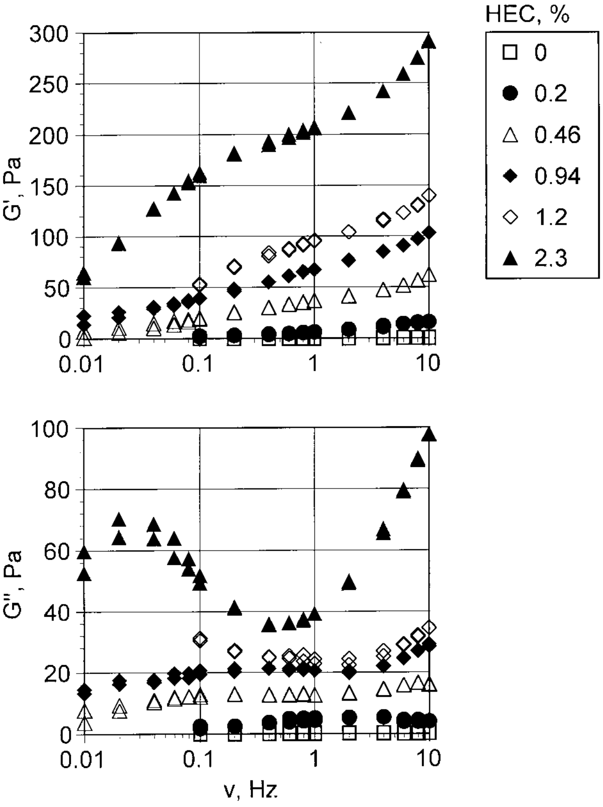

Fig. 1. Effect of frequency of oscillatory shear on the elastic (G') (top) and loss (G'') (bottom) moduli of dispersions at 34 vol% solids with the HEC weight fraction as a parameter.

G' increases monotonically with frequency at all HEC concentrations examined but the form of the dependence changes with HEC concentration. At 0·2% HEC, G' exceeds by more than an order a magnitude its value in the absence of HEC. As the HEC content increases even further, inflection points start becoming evident in the G' curve. At 0·2% HEC no inflection exists but at 0·46% a weak inflection point appears at about 1 Hz. These become progressively more intense as the HEC concentration increases.

Similarly to G', G'' increases by more than an order of magnitude as the HEC concentration rises from 0 to 0·2%. The form of the dependence also changes. At 0·2%, a slight maximum is evident with respect to frequency at about 3 Hz. As the HEC concentration exceeds a value of 0·2%, minima start appearing in the G'' curve. These minima correspond to the same frequency as the inflection points in the G' curve. Thus, a slight minimum is evident at 0·46% HEC at about 1 Hz. As the HEC concentration increases to 2·3% these minima become progressively more distinct.

In addition, these minima seem to shift to lower frequencies as the HEC concentration increases. It could be suggested that at 0·2% HEC the minimum occurs at frequencies higher than 10 Hz which is outside the measurement range of the Bohlin viscometer.

Figure 2 shows the corresponding strain sweep measurements for the dispersions of Fig. 1. These represent the variation of G' (top) and G'' (bottom) with strain amplitude in a sinusoidal type of deformation at constant frequency of 1 Hz. The strain amplitude is expressed as percentage of the maximum applied strain, which was about 0·20 rad.

It can be seen that a linear range can be established for all HEC concentrations. The critical strain γ_c, is defined as the strain above which no linear viscoelastic behaviour is observed and both G' and G'' become amplitude dependent. It is more difficult to establish the linear range at 0 and 0·2% HEC where essentially no elastic behaviour is observed and G' and G'' are both very small. Above the onset of flocculation[1] (i.e. at HEC concentrations higher than 0·2%), both G' and G'' increase as the HEC content increases. Notice that G' decreases monotonically above the critical strain γ_c. The same behaviour is followed by G'' up to 0·46% HEC. At higher HEC concentrations, however, (i.e. $\geq$0·94%) maxima start becoming evident in the G'' curve.

Figure 1 reveals that as the HEC content increases, the dispersions start exhibiting a wider distribution of relaxation times which progressively become separated into two sets. This is indicated

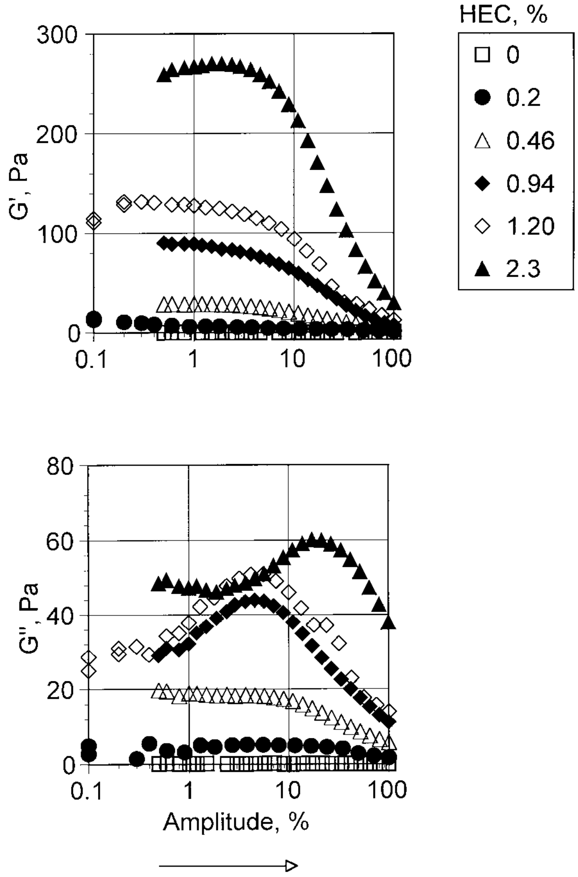

Fig. 2. Effect of strain amplitude on the elastic (G') (top) and loss (G'') (bottom) moduli of dispersions at 34 vol% solids with the HEC weight fraction as a parameter (frequency = 1 Hz).

by the minima in G'', which correspond to inflection points in G'. These minima are more distinct at the highest HEC content, i.e. 2.3%.

The above behaviour is analogous to that observed in uncross-linked polymer solutions as their molecular weight increases.[3] It is well established that, above a critical molecular weight, the behaviour of viscoelastic functions in polymer solutions indicates a strong coupling between neighbouring polymeric molecules which seem to be localised at widely separated points along the molecular chain. This is the basis for the well-known entanglement theory used by Ferry[3] in explaining the viscoelastic behaviour of solutions of high molecular weight uncross-linked polymers. At this critical molecular weight, the zero shear viscosity dependence on molecular weight changes from 1 to a 3·5 power law. In a more general sense and avoiding the term entanglement, it can be said that above this critical molecular weight, the solution exhibits a viscoelastic behaviour that indicates the existence of physical 'topological restraints' that delay significantly the long-range configurational rearrangements of the molecule. Consequently, these long-range motions (characterised by the slowest relaxation times) are shown in an experiment involving dynamic perturbation at much lower frequencies than they would have been observed in the absence of these constraints.

The formation of this restraint network results in the viscoelastic properties featuring two sets of relaxation times with different magnitudes, the overlap of which give rise to a plateau zone in the G'-frequency curve and a minimum in the corresponding G'' curve. The above behaviour has been observed in a wide variety of polymer systems.[3] The nature of the coupling is still speculative, although it conforms more closely to topological rather than intermolecular forces as has been observed both in polar and nonpolar polymers.

The constraints most probably take the form of looping of chains around each other in their long-range contour.[3]

The dispersions in the presence of HEC exhibit similar behaviour to that described above for polymer solutions. As the HEC concentration increases, a wider distribution of relaxation times is observed which progressively are separated in two sets, one in the low and the other in the high frequency range. HEC induces particle flocculation that in turn gives rise to the formation of chains of particles that impose topological restraints in their motion. Thus, flocculation inhibits significantly the particle long-range motions. This gives rise to much longer terminal relaxation times than those which would have been observed in the absence of these constraints. The number of these constraints increase as the HEC concentration increases and the dispersion becomes more flocculated. This increase in the number of restraints is the result of more particle chains and more connections between individual chains being formed as the HEC concentration increases. These additional topological restraints in turn are responsible for even slower relaxation processes that shift the terminal relaxation times to a lower frequency range. This eventually results in the dispersions exhibiting two widely separated sets of relaxation times in a similar fashion to an entangled polymer solution. This is shown clearly in Fig. 1 for the highest HEC concentration (i.e. 2·3%).

3.2 Steady-shear viscosity

In further examining the rheological behaviour of the above dispersions, we present in this section the steady-state shear rate- shear stress measurements that correspond to the suspensions of Fig. 1. In our previous publication[1] we reported that a non-Newtonian behaviour is followed for most of the dispersions and the data can be adequately described by a Sisko type model for shear thinning behaviour.

A frequency dependent viscosity can be defined as

$$|\eta^*| = \frac{\sqrt{G' + G''}}{\omega} \tag{1}$$

and it has been used in representing viscoelastic behaviour. In polymer solutions the function $|\eta^*|(\omega)$ closely resembles the steady-state apparent viscosity–shear rate function $\eta(\gamma)$. This is known as the Cox–Merz rule frequently employed in polymer solution rheology. At low frequencies or shear rates this resemblance is more pronounced since the molecular motions underlying both types of deformation are similar. At higher frequencies or shear rates, however, there are deviations due to the different mechanisms responsible for periodic and steady flow deformations.[3]

Figure 3 shows the variation of steady-state viscosity as a function of shear rate for the same dispersions in Figs 1 and 2. Superimposed with filled symbols are the corresponding values of the Cox–Merz viscosity as given by eqn (1). In this case, since in the present dispersions linearity is observed within a certain strain amplitude range, this dynamic viscosity is plotted as a function of the product $(\omega\gamma_c)$ where ω is the radian frequency and γ_c is the critical strain amplitude below which linearity holds for each dispersion. γ_c is expressed as % of the maximum applied amplitude which was 0·2 rad. The values of γ_c were easily estimated from amplitude sweeps similar to that depicted in Fig. 2. Above the critical flocculation concentration (i.e. $\Phi_P > 0{\cdot}2\%$) γ_c was generally in the range 1–2%.

Complete superposition is evident for all the dispersions represented in Fig. 3 for 34% solids except for HEC = 0. This is probably due to the large error involved in the G' and G'' measurements which in this case are both close to zero. In fact, one can resolve from these curves the zero shear viscosity. Doraiswamy *et al.*[4] showed that complete superposition between the complex dynamic and steady shear viscosity exists for strains equal or higher than the critical value γ_c which means, at the onset or within the non-linear viscoelastic region. These authors derived a theoretical correlation analogous to the Cox–Merz rule for concentrated suspensions exhibiting a yield stress. Good agreement with experiment was obtained for concentrated silicon suspensions in polyethylene.

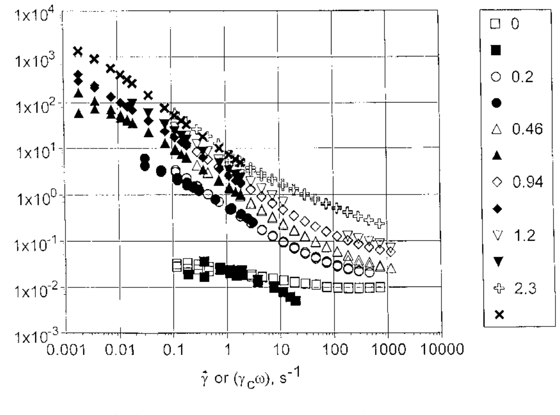

Fig. 3. Effect of shear rate or effective shear rate ($\ddot{\omega}\ \gamma_c$) on the steady-state or Cox–Merz viscosity [eqn (1) in the text], respectively, at 34 vol% solids with the HEC weight fraction as a parameter. Open symbols: steady; closed symbols: Cox–Merz viscosity.

The results of Fig. 3 constitute another example of the application of the Cox–Merz analogy in a colloidal dispersion in accordance with the analysis of the above authors.

The behaviour depicted in Fig. 3 was followed by all dispersions at all solids contents (i.e. 24–53%). These data have been fitted to a Sisko type empirical model as described before.[1] Combining the information of the oscillatory as well as the steady-state shear data we can generalise the model to a Cross type[5] equation as:

$$\frac{\eta - \eta_\infty}{\eta_o - \eta_\infty} = \frac{1}{[1 + (\mathbf{K}_c\dot{\gamma})^m]} \tag{2}$$

where η_o and η_∞ are the asymptotic values for the viscosity at low and high shear rates respectively and K_c is a constant. While, however, η_∞ can always be estimated from the data, η_o can only be estimated for the less concentrated suspensions. The above equation can be rearranged as:

$$\eta_o - \eta_\infty = \eta - \eta_\infty + (\eta - \eta_\infty)\mathbf{K}_c^m\dot{\gamma}^m \tag{2'}$$

or

$$\eta_o - \eta = (\eta - \eta_\infty)\mathbf{K}_c^m\dot{\gamma}^m \tag{2''}$$

which finally yields

$$\frac{\eta_o - \eta}{(\eta - \eta_\infty)\mathbf{K}_c^m} = \dot{\gamma}^m \tag{3}$$

For the more concentrated dispersions this becomes:

$$\frac{\eta_o}{(\eta - \eta_\infty)\mathbf{K}_c^m} = \dot{\gamma}^m \tag{4}$$

which is actually equivalent to the Sisko equation:

$$\eta = \eta_\infty + \frac{\eta_o}{(\mathbf{K}_c\dot{\gamma})^m} \tag{5}$$

or

$$\eta = \eta_\infty + \frac{\mathbf{K}}{\dot{\gamma}^m} \tag{5'}$$

with

$$K = \frac{\eta_o}{\mathbf{K}_c^m} \tag{6}$$

Thus, eqn (6) connects the parameter K defined before[1] with the more general parameter K_c in eqn (5). Figure 4 shows the behaviour in terms of the above equations for all the rheological data in the presence of HEC. It can be seen that all the data can be represented in the form of power law depicted in eqn (3). Table 1 shows the best values of the exponent m.

It can be seen that the exponent, m, lies within the range of 0·7–0·9. Notice that m is essentially constant above 34% solids at about 0·85. This value is very close to that reported for a polymer solution of high degree of entanglement.[3] Following the analogy with polymer solutions outlined above, this means that above 34% solids, and in presence of HEC, the dispersion particles experience the highest degree of restriction in their movement. The lower value of m, at the lowest solids content, could mean that a complete particle network has not yet been formed and some Newtonian behaviour still persists as some of the dispersion volume is not occupied by aggregates. This results in a lower value of m. Note that $m = 0$ essentially indicates Newtonian behaviour as it is evident from eqn (5).

The lines drawn in Fig. 4 indicate the limiting slopes of Table 1. At very low shear rates, it is evident, that the parameter plotted in the Y-axis should essentially achieve the value of zero as $\eta \to \eta_o$ for all dispersions.

Finally, Fig. 5 shows the effect of HEC content (top) and solids volume fraction (bottom) on the parameter K given in eqn (6). As it has been mentioned before, this parameter can be seen as an effective yield stress representing the strength of the bonds in the floc. We have shown[1] that K varies according to:

$$K \infty \left(\Phi_P - \Phi_P^{+}\right) \tag{7}$$

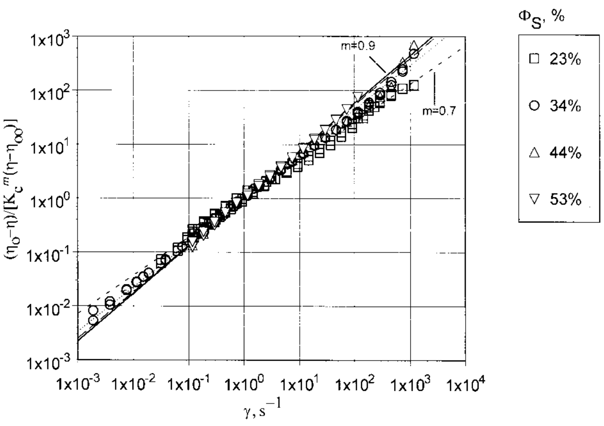

Fig. 4. Effect of shear rate on the parameter $(\eta_o - \eta)/[K_c{}^m(\eta - \eta_\infty)]$ in the Cross equation [eqn (3) in the text] for all the dispersions in presence of HEC with the solids volume fraction as a parameter and values of the non-Newtonian parameter m indicated.

where Φ_P^{+} ~0·1% represents the critical polymer volume fraction above which flocculation starts taking place and the rheological properties change significantly.

Since in absence of HEC, the dispersion also exhibits an effective yield stress $K_{(\text{at HEC}=0)}$, eqn (7) can be rewritten in order to separate the effect of HEC, as

$$K_R = \left[K - K_{(\text{at HEC}=0)}\right] \infty \left(\Phi_P - \Phi_P^{+}\right) \tag{8}$$

Table 1. Variation of the exponent m in the Cross type fitting eqn (3)

Solid fraction (%)	*23*	*34*	*44*	*49*	*52*	*53*
m	0·70	0·82	0·85	0·82	0·86	0·88

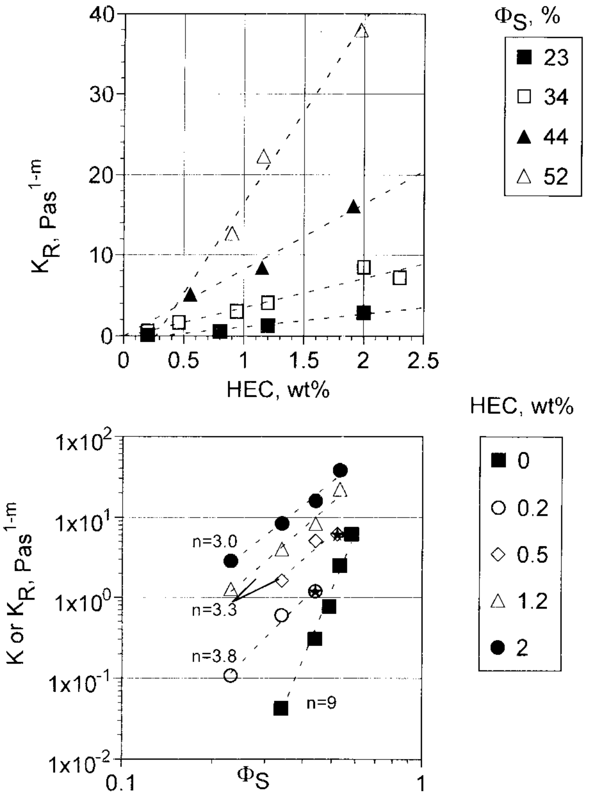

Fig. 5. Top: effect of HEC weight fraction on the parameter K_R [eqn (8) in the text] at various solids volume fractions. Bottom: effect of solids volume fraction on the parameter K (in absence of HEC) or K_R (in presence of HEC) [eqn (9) in the text] at various HEC weight fractions with best slopes indicated. The star symbols indicate points estimated by extrapolation from the top part.

This parameter is plotted at the top part of Fig. 5 as a function of the HEC weight fraction. It can be seen that a linear relation is followed with all lines crossing the *X*-axis at $\Phi_P^+ = 0{\cdot}1 - 0{\cdot}2$, the critical flocculation point.[1]

This linear dependence of the effective yield stress on the polymer volume fraction is typical of systems exhibiting a depletion flocculation mechanism.[6] Thus, the bond strength between the particles increases linearly with HEC content and there is a critical HEC concentration above which flocculation takes place. The critical flocculation concentration is defined as that concentration above which the rheological properties of the suspension deviate significantly from those observed in absence of polymer. According to this flocculation mechanism, HEC does not adsorb on the particle surface but rather is repelled from its surface, leaving a depleted region close to the surface. This, in turn, produces an osmotic pressure gradient that is overcome by the movement of solvent out of the polymer depleted region, thus, causing particle flocculation. This is achieved only above a certain concentration of non-adsorbing polymer as it has been shown theoretically.[7]

In the bottom part of Fig. 5, K (in absence of HEC) or K_R (in presence of HEC) are plotted with respect to solids volume fraction. A power law is followed in all cases with the power exponent decreasing from about 9 in absence of HEC to 3 in the highly flocculated suspension of HEC = 2%; thus:

$$K \quad \text{or} \quad K_R \propto \Phi_S^n \tag{9}$$

This indicates a transition from a stable state with a high value of the exponent n (i.e. $HEC = 0$ and $n = 9$) to an unstable flocculated state with values of n of the order of 3.6 ± 0.6. In absence of HEC the type of dependence reported here is typical of other sterically stabilised systems such as polystyrene.[8] These systems, in fact, behave very closely to hard sphere systems.

On the other hand, when the system is in a flocculated state, the value of $n = 3{\cdot}6 \pm 0{\cdot}6$ is consistent with the predicted values by Brown[9] for a diffusion-limited cluster–cluster aggregation process where the clusters comprising the network are fractal. This is also shown[10] from rheological measurements on aggregated colloidal silica and polystyrene dispersions. In this regard, we note that Bergstrom et al.[11] also observed a power law dependency of the compressive yield stress on solids fraction with $n = 3{\cdot}2 \pm 0{\cdot}4$ for flocculated alumina dispersions. These authors also suggest the possibility of a fractal particle network.

4 Conclusions

The rheological behaviour of sterically stabilised colloidal alumina dispersions was studied in presence of hydroxyethyl cellulose. Experiments were performed under oscillatory as well as steady shear. Both types of experiments suggest that a depletion flocculation mechanism is operative in presence of HEC molecules. According to this mechanism, HEC molecules do not adsorb on the particle surface but induce flocculation after forming an osmotic pressure gradient between the bulk of the solution and the interparticle space. This is created due to the large size of the HEC molecule and only occurs above a critical polymer concentration. The relaxation behaviour of the dispersions is similar to that observed in high molecular weight uncross-linked polymer solutions. This behaviour suggests that HEC promotes the formation of a particle chain network that is topologically constrained and significantly restricts particle movement. This gives rise to a wider distribution of relaxation times than that observed in the absence of HEC. As the amount of HEC increases, two distinct sets of relaxation times become evident in the dispersion, one at low and the other at high frequencies. Terminal relaxation times (i.e. corresponding to those processes with the longest relaxation times) shift to very low values as the amount of HEC increases.

The dispersions also follow the Cox–Merz analogy widely observed in polymer solutions according to which the dynamic and steady shear viscosity data superimpose after appropriate modification of their respective arguments. All rheological data can be fitted to a single Cross type[5] rheological equation. An examination of the behaviour of the fitted parameters of this equation can reveal some information on the flocculation process in presence of HEC. Thus, the flocculation seems to follow a diffusion controlled cluster–cluster aggregation mode, with the clusters comprising a fractal network.

Acknowledgements

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