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Rheological characterisation of ammonium polyacrylate dispersed, concentrated alumina suspensions

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Abstract

The effect of low-molecular weight ammonium polyacrylate (NHPA) dispersant on high solids content alumina suspensions has been rheologically characterised. The viscosity exhibited a strong dependence on the solid concentration, a relationship that could be accurately represented by the modified versions of Eilers and Chong equations from which the maximum packing fraction was found to be 0.655. When subjected to shear sweep investigations, the suspensions demonstrated shear-thinning and thixotropic behaviour as a result of changes to the suspension microstructure. Application of the Ostwald de Waele model successfully characterised the shear-dependent behaviour of the suspensions over a wide range of shear rates. The viscoelastic properties of the suspensions were found to be functions of both frequency and solids loading with the viscous component dominating over the elastic component under the conditions investigated.

Keywords: A. Suspensions; D. Al_2O_3; Rheology

1. Introduction

Colloidal powder processing is now a widely used method of producing high-integrity ceramic components; there is an abundance of literature outlining the principles involved [1–4]. However, when ceramic powders are added to a suspending medium such as water the presence of attractive van der Waals forces typically results in the particles aggregating to form clusters or flocs. These flocculated suspensions display a relatively high-suspension viscosity that can make processing difficult and, more importantly, the flocs can become flaws in the final microstructure leading to a reduction in the final component properties. It is, therefore, essential that these agglomerates are either prevented from forming or eliminated from the suspension prior to green body fabrication. Such agglomerate-free systems are termed dispersed and tend to be relatively fluid and homogeneous. When dried they yield high-density compacts.

Dispersed systems can be achieved by controlling the surface charge of the powders in solution, for example, by the adsorption of charged polymers referred to as polyelectrolytes. A previous study has examined the role of ammonium polyacrylate (NHPA) in dispersing concentrated alumina suspensions [5]. NHPA of molecular weight 3500 was found to be an effective dispersant for a Bayer processed alumina (A16SG) that had a point of zero charge (PZC) of pH 8.0, yielding suspensions with a pH of 9.5. Minimum suspension viscosity was observed at two different NHPA concentrations for each solids loading examined between 37.2 and 57.1 vol.% (70 and 84 wt.%) alumina. They were believed to be a consequence of different adsorbed conformations of the NHPA. The first viscosity minimum occurred at 1.4 ± 0.1 mg g^{-1} NHPA and was independent of solids loading up to 55.3 vol.%. Measured sedimentation data and calculated maximum packing density values supported the view that complete dispersion was achieved at this concentration whilst incomplete adsorption and relatively low green density dried compacts opposed it.

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Table 1
Outline of the rheological measurement configurations used

Measuring configuration	Rheometer			
	V-88		CS-10	
	Designation	Sample volume (ml)	Designation	Sample volume (ml)
Concentric cylinder	C 30	17	N/A	N/A
Cone and plate	CP 5/30	0.5	CP4/40	0.9
Parallel plate	PP 15	0.2	PP 40	1.2

Based on the results, it was suggested that the first viscosity minimum corresponded to an unstable dispersed phase with the NHPA adsorbed in a dangling tail conformation. Whilst the minimum was present in suspensions of up to 55.3 vol.% alumina, it did not correspond to maximum surface coverage by the NHPA and dispersion appeared to be lost on drying. In contrast, the second viscosity minimum was suggested to correspond to maximum adsorption, occurring at a concentration of 2.7 ± 0.2 mg g^{-1} NHPA at 37.2 vol.% and increasing with increasing solids content up to 4.3 ± 0.2 mg g^{-1} at 57.1 vol.% alumina. It was concluded that this second minimum, comprising NHPA adsorbed in a proposed loose loop and tail conformation, was the most stable dispersed state, yielding the most favourable properties expected for a dispersed suspension. The current work seeks to extend the investigation by examining the consequences of the ammonium polyacrylate additions on the rheology of the suspensions in more detail.

2. Experimental

2.1. Sample preparation

Preparation of the initial dispersed suspensions followed the procedure developed by Davies and Binner [5]. Prior to sample preparation, all polypropylene beakers were thoroughly rinsed with de-ionised water in order to ensure the complete removal of residual ions. The beakers were then dried and stored in a refrigerator overnight. Appropriate quantities of deionised water (±0.01 g) and Dispex A40[2] (±0.003 g) were mixed in a beaker until the dispersant was uniformly distributed. Since Dispex A40 is an aqueous solution, the actual quantity of ammonium polyacrylate (NHPA) utilised corresponded to only 37.6 wt.% of the amount of dispersant added. In order to account for this and allow fair comparison between suspensions of different solids loading, the quantity of NHPA utilised was recorded in terms of the mass added per gram of alumina powder, denoted mg g^{-1} hereafter. Furthermore, all associated water was allowed for during the batching process calculations. A-16SG alumina[3] ±(0.01 g) was then carefully blended with this mixture until an homogenous suspension resulted. The alumina content of a suspension is expressed as a weight percentage of the total dispersed sample weight, values from 37.2 to 57.1 vol.% were produced. The slurries were covered to avoid contamination and left to stand at room temperature for 1 h to allow adsorption of the dispersant onto the alumina.

In order to breakdown any soft agglomerates, the mixture was then subjected to ultrasonic agitation produced by a Kerry[4] ultrasound unit for 90 s. The vibrational output was at a frequency of 20 kHz and a power level of 150 W. In order to reduce subsequent water evaporation, the samples were covered with Nescofilm[5] and cooled in a refrigerator for 1 h. The dispersed suspensions were stirred and then placed in a 60 ± 10 mmHg vacuum for 1 h in order to remove as much of the entrapped air as possible. Finally the suspensions were re-sealed and allowed to equilibrate in a refrigerator for 24 h.

3. Rheological measurements

The rheological behaviour of the dispersed suspensions was measured using two rotational Bohlin[6] Instruments:

- *V88*: A constant strain type viscometer capable of continuous shear flow characterisation. The viscometer was interfaced to a PC running version 3 of the Bohlin V-88 controlling software.
- *CS-10*: An advanced constant stress rheometer capable of continuous shear and viscoelastic characterisation. The instrument was linked to a PC via version 4.85 of the CS-10 software. This software possesses a control loop allowing the stress to be regulated in order to provide operation in constant strain mode.

Table 1 provides details of the measuring geometries used and sample volumes required for the rheological characterisation.

The suspensions were subjected to the two forms of shear deformation, continuous and oscillatory, and within these to a range of different rheological conditions.

3.1. Continuous shear deformation

This flow pattern was most suited to analysing the behaviour of a material when subjected to shear during processing. The analysis techniques included:

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[2] Allied Colloids, Bradford, UK.

[3] Alcoa Manufacturing (GB) Ltd., Worcester, UK; specific surface area ~9 m^2 g^{-1}.

[4] Kerry Ultrasonics Ltd., Hitchin, Hertfordshire, UK.

[5] Nescofilm™, Nippon Shoji Kaisha Ltd., Osaka, Japan.

[6] Bohlin Instruments (UK), Cirencester, Gloucestershire, UK.

- Constant shear evaluation—at a rate of 109 s^{-1} to match the work of Davies and Binner [5].
- Shear sweep loop evaluation—at between 18 and 1100 s^{-1} in an incremental stepwise manner, first increasing and then decreasing. The samples were allowed to relax for 2 min before measurements began in order to counteract the shearing effects of placing the sample on the instrument. Measurements were performed under non-equilibrium conditions to highlight time dependent effects, i.e., only a short delay before measurement was used for each step in shear rate to allow the sample to approach, but not attain, steady-state conditions. Since it is generally found that longer delay times are required at lower shear rates, the delay time was set to be inversely proportional to the shear rate using the function provided by the software. Values for a thixotropic index (TI) were obtained using the equation $\mathrm{TI} = 100 \times [(\sigma_{\mathrm{inc}} - \sigma_{\mathrm{dec}})/\sigma_{\mathrm{inc}}]$, where the increasing and decreasing shear stress values were obtained at a shear rate of 109 s^{-1}.

3.2. Oscillatory shear deformation

The information provided by continuous shear only described the materials' flow characteristics and hence, in order to study the viscoelasticity, small amplitude oscillatory rheometry was utilised using the CS-10 rheometer. Once again, samples were allowed to relax for 2 min prior to rheological testing. To establish the level of shear deformation that could be applied without exceeding the linear viscoelastic response (LVR) region, the complex modulus, G^*, was monitored as a function of applied stress for five frequencies in the range 0.1–10 Hz for an 52 vol.%, 1.4 mg g^{-1} suspension. An acceptable strain was found to be 0.01 (1%), in line with the results of other authors for ceramic suspensions [6,11]. Therefore, all oscillatory rheological testing was performed at a strain of 0.01. For continuous oscillatory testing, a frequency of 1 Hz was used for all measurements in accordance with the ASTM D 4473 standard and at a constant temperature of 25 °C.

- Time-dependent viscoelasticity (time sweep)—the effect of time on the viscoelastic properties was investigated for samples subjected to a continuous oscillation at a frequency of 1 Hz, the strain being kept constant at 0.01 by the autostress function. A maximum of five stress adjustments were used in order to regulate the strain at the desired amplitude and the acceptability factor was set at ±5% of the target strain. The applied stress and the resulting oscillatory strain were automatically measured and analysed to yield G^*, G', G'' and δ.
- Frequency-dependent viscoelasticity (frequency sweep)—often called mechanical spectroscopy because it provides a unique 'fingerprint' of the material, the strain was similarly held at a constant value of 0.01 using the autostress function with identical stress estimation and acceptance criteria to the time sweep measurements.

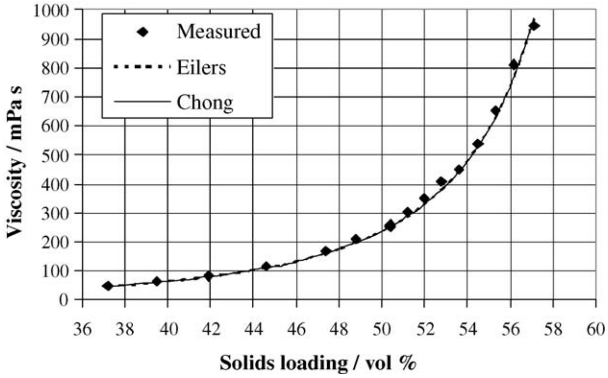

Fig. 1. Influence of the solid volume fraction on the relative equilibrium viscosity of suspensions dispersed using 1.4 mg g^{-1} NHPA at a reference shear rate of 109 s^{-1}. Both the Eilers and Chong equations fit the data precisely.

4. Results

4.1. Constant shear rheology

4.1.1. Solids loading

The effect of solids concentration on the relative viscosity[7], η_r, for suspensions dispersed using 1.41 mg g^{-1} NHPA dispersant is shown in Fig. 1, together with theoretical curves generated from the modified Eilers and Chong equations [7]. The latter can be, respectively, defined as:

$$\eta_r = 1 + \left[\frac{C_{\mathrm{EE}}\phi\phi_{\max}}{\phi_{\max} - \phi}\right]^2 \text{which can be rearranged to}$$

$$\frac{1}{\eta_r^{1/2} - 1} = \frac{1}{C_{\mathrm{EE}}}\frac{1}{\phi} - \frac{1}{C_{\mathrm{EE}}\phi_{\max}} \qquad (1)$$

and

$$\eta_r = \left[\frac{C_{\mathrm{EC}}(\phi/\phi_{\max})}{1 - (\phi/\phi_{\max})} + 1\right]^2 \text{which rearranges to}$$

$$\frac{1}{\eta_r^{1/2} - 1} = \frac{\phi_{\max}}{C_{\mathrm{EC}}}\frac{1}{\phi} - \frac{1}{C_{\mathrm{EC}}} \qquad (2)$$

where C_{EE} and C_{EC} are the disposable constants as defined by Edrisinghe [7] and ϕ is the packing fraction. It can be seen from the figure that both approaches display remarkably good agreement with each other and the experimentally measured values. When the data was transformed into a linear expression, correlation coefficients >0.998 were obtained. Table 2 shows that identical maximum packing fraction, $\phi_{\max}$, values of 0.655, i.e., 65.5 vol.% (~88 wt.%), are indicated by the two approaches. This value also shows

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[7] The influence of solid volume fraction on the suspension viscosity for suspensions is usually represented in terms of the relative viscosity, whereby $\eta_r = \eta/\eta_s$ where η and η_s are the viscosity of the suspension and dispersant phases, respectively. In this case, it is assumed that the dilute NHPA solution has a viscosity, η_s, identical to water at ambient temperatures, i.e., 1.0 mPa s. Therefore, providing the suspension viscosity is also measured in mPa s, then $\eta_r = \eta$.

Table 2
Summary of Eilers, Chong and Kosmac line fitting parameters for suspensions containing 1.4 mg g^{-1} dispersant

Parameter	Fitting equation	
	Eilers	Chong
Disposable constant	6.949	4.550
Maximum volume fraction (ϕ_{max})	0.655	0.655
A''	6.382	6.388
n''	2.511	2.509

Table 3
Variation of ϕ_{max} obtained using the modified Mooney approach in conjunction with various non-linear extrapolation techniques

Extrapolation technique	ϕ_{max}	Correlation coefficient
Logarithmic	1.005	0.998
Polynomial (order = 2)	1.056	0.999
Polynomial (order = 3)	0.952	0.999
Polynomial (order = 4)	0.952	0.999
Polynomial (order = 5)	0.690	0.994

reasonable agreement with the maximum solids loading that is achievable in practice, typically ~59 vol.%, before the suspension exhibits a high-viscosity, quasi-solid consistency that is too great to allow processing.

Kosmac and Novak [8] have stated that good agreement between relative viscosity and the solid volume concentration can be obtained using the following three-parameter model:

$$\eta_r = A''\left[1 - \frac{\phi}{\phi_{max}}\right]^{-n''} \tag{3}$$

Taking logarithms establishes the linear relationship:

$$\ln \eta_r = \ln A'' - n'' \ln\left(1 - \frac{\phi}{\phi_{max}}\right) \tag{4}$$

Utilising the ϕ_{max} values obtained using the Eilers and Chong approach allows the parameters A'' and n'' to be established (Table 2). The difference in values between the two approaches arises from the manipulation of the gradient and intercept values required to obtain the maximum packing volume fractions and the disposable constant.

A modified Mooney equation was also evaluated:

$$\eta_r = \exp\left[\frac{C_{EM}\phi}{1-(\phi/\phi_{max})}\right] \text{which rearranges to}$$

$$\frac{1}{\ln \eta_r} = \frac{1}{C_{EM}}\frac{1}{\phi} - \frac{1}{C_{EM}\phi_{max}} \tag{5}$$

where C_{EM} is the disposable constant. Unfortunately, when the experimental data was plotted deviations from linearity were apparent, consequently ϕ_{max} and C_{EM} could not be determined using a linear line fitting technique, and therefore, non-linear approaches were required. The technique that was utilised was to determine by extrapolation which value of ϕ corresponded to $\ln(\eta_r)^{-1} = 0$, since this latter expression corresponds to a suspension of infinite viscosity, i.e., ϕ_{max}. Table 3 depicts the range of values that were obtained when a variety of extrapolation techniques were employed.

4.1.2. Shear sweep loop behaviour

The flow behaviour of 37 and 52 vol.% 1.4 mg g^{-1} suspensions, when subjected to a shear sweep loop test, is given in Fig. 2. It may be observed that the suspensions displayed shear thinning and thixotropic behaviour. The degree of thixotropy is expressed by the values given in Table 4.

The shear flow behaviour of the suspensions represented by the increasing shear portion of the flow curves was examined using the empirical Ostwald de Waele power law model:

$$\eta = c\dot{\gamma}^{n-1} \text{ which can be rearranged to}$$

$$\ln \eta = \ln c + (n-1)\ln \dot{\gamma} \tag{6}$$

It can be seen from Fig. 3 that the above expression shows good agreement with the experimentally determined points for both suspensions over a range of shear rates. A summary of the Ostwald de Waele parameters is also given in the figure.

4.2. Oscillatory shear rheology

Fig. 4 shows the frequency dependence of the viscoelastic properties for 37 and 52 vol.%, 1.4 mg g^{-1} suspensions. Whilst both G' and G'' increase with increasing frequency, G' increases at a faster rate such that the curves converge.

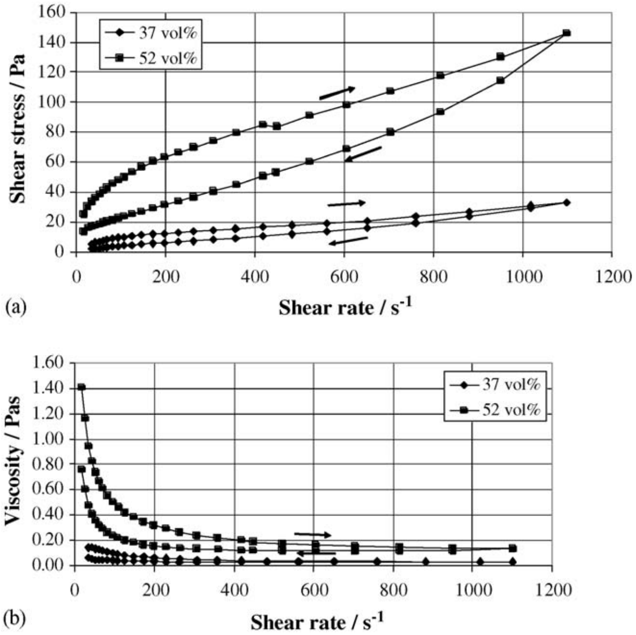

Fig. 2. Rheological flow curves for 37 and 52 vol.%, 1.4 mg g^{-1} dispersed suspensions. (a) Shear stress vs. shear rate, (b) viscosity vs. shear rate. The increasing and decreasing portions of the shear sweep cycle are represented by the appropriate arrows.

Table 4
Thixotropic index for 37 and 52 vol.% 1.4 mg g^{-1} suspensions

Solids content (vol.%)	Thixotropic index (TI) (%)
37	56
52	53

However, within the range investigated no crossover point is observed, and thus, the viscous component always dominated the elastic component.

5. Discussion

5.1. Constant shear rheology

5.1.1. Solids loading

It is important to utilise the maximum particle concentration in colloidal processing. A high-volume fraction of solids reduces drying shrinkages and helps maintain uniform particle packing, both of which are significant in achieving near-net shape forming. However, as illustrated by Fig. 1, at high-solids contents a variation in volume loading of just ~1%, which can result from an erroneous batching procedure or loss of small amounts of suspending phase through adsorption, reaction or evaporation, can exert a pronounced influence on the viscosity.

For polyacrylate-dispersed alumina suspensions, two contributory factors account for the observed solid concentration dependence of viscosity. Firstly, as the solids content increases the hydrodynamic interactions occurring between the particles in the suspension increases. The volume fraction $1 - \phi_{\max}$ represents the quantity of liquid required to completely fill the voids between the closely packed particles. Consequently, this fraction of liquid is permanently immobilised within all suspensions. However, the fraction $\phi_{\max} - \phi$ represents the free volume fraction of liquid phase above the required minimum amount. It is this free volume fraction which represents the portion of liquid that contributes to the shear flow of the body [7,9]. Increasing the solids content, ϕ, closer towards $\phi_{\max}$, thus leads to a decrease in the free volume fraction of liquid. As ϕ approaches $\phi_{\max}$ the rheology of the body rapidly changes from a viscous fluid to a quasi-solid [9]. When the solids loading exceeds $\phi_{\max}$, the batch material has a stiff, powdery consistency.

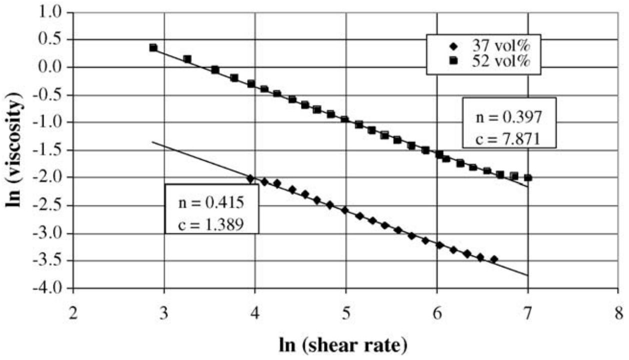

Fig. 3. Analysis of the shear flow curves for 37 and 52 vol.%, 1.4 mg g^{-1} dispersed suspensions using the Ostwald de Waele model, $\eta = c\dot{\gamma}^{n-1}$. Symbols represent the experimental data points, solid lines indicate the theoretical values from the model. Values for c and n in the model equation are shown on the plot.

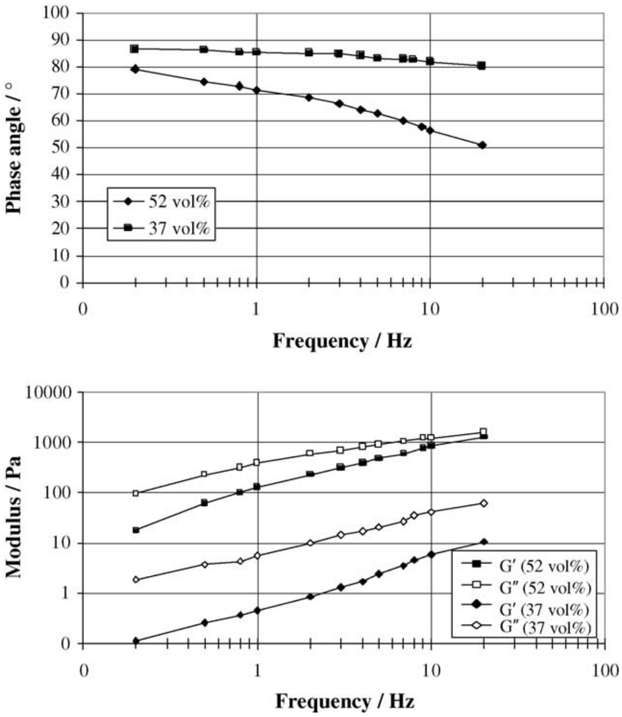

Fig. 4. Frequency dependence of the viscoelastic properties for 37 and 52 vol.%, 1.4 mg g^{-1} dispersed suspensions. (a) Phase angle, (b) storage and loss modulii.

This consideration in isolation only accounts for those systems that can be described by the hard sphere idealisation. However when colloidal processing techniques are employed, other interparticle interactions, repulsive or attractive, must also be evaluated. A colloidally stable suspension is characterised by repulsive interparticle potentials, which in this study are electrosteric in nature (although the profile of the curve in Fig. 1 is virtually identical to that obtained by Nienburg who investigated electrostatically dispersed A-16SG suspensions at low pH [10]). The repulsive forces cause the particles to adopt positions as far apart from each other as possible in order to minimise repulsive interactions with all the neighbouring particles. Upon increasing the solids loading of the suspension, the mean distance between the particles containing surface adsorbed polyacrylate decreases. Consequently, an increase in the repulsive interaction transpires, increasing the resistance to flow and hence the viscosity. At the maximum packing volume the adsorbed polymeric layers interlock preventing the suspension from flowing [11].

As indicated earlier, it was found that the trends associated with the modified Eilers and Chong approaches were in good agreement with the experimentally determined values (Fig. 2). The suggested maximum packing efficiency of the dispersed system, $\phi_{\max}$ corresponded to 65.5 vol.%, a value in reasonable agreement with what can be achieved in practice, ~59 vol.%. However, the modified Mooney approach was less satisfactory for the suspensions utilised in this study. Table 3 indicates that $\phi_{\max}$ is critically influenced by the extrapolation technique adopted to determine it, ranging from invalid values above 1 to numbers similar to those obtained using the modified Eilers and Chong approaches. In all cases, the correlation coefficient was above 0.993 indicating an apparent good fit. As a result of the large observed variations in $\phi_{\max}$, the modified Mooney approach displays serious deficiencies.

It has been shown by Edirisinghe [7] that at high shear rates the disposable constant, C_{EE}, produced by the modified Eilers approach corresponds to:

$$C_{\mathrm{EE}} = \frac{[\eta]}{2} \tag{7}$$

where $[\eta]$ = intrinsic viscosity. Accordingly, the intrinsic viscosity associated with the dispersed suspension can be readily calculated as 13.9. In order to analyse this assertion the intrinsic viscosity was recalculated in accordance with the expression used in its definition [12]:

$$[\eta] = \lim(\phi \to 0)\left[\frac{(\eta/\eta_{\mathrm{s}}) - 1}{\phi}\right] \tag{8}$$

Unfortunately, plotting $[\eta_{\mathrm{r}} - 1/\phi]$ as a function of ϕ produces a non-linear profile such that accurate extrapolation back to zero is difficult. A more fruitful approach was provided by adapting Eq. (3), such that:

$$\left(\frac{\eta_{\mathrm{r}} - 1}{\phi}\right) = A'''\left[1 - \frac{\phi}{\phi'_{\max}}\right]^{-n'''} \tag{9}$$

Taking logarithms establishes a linear relationship, shown in Fig. 5, and results in Kosmac line fitting parameters of $A''' = 14.1$ and $n''' = 2.9$. Substituting these values into Eq. (9) and utilising the zero concentration requirement for the intrinsic viscosity, Eq. (8), yields an intrinsic viscosity of 14.1. This is within experimental error of the value of 13.9 determined using the modified Eilers approach. Furthermore, the close agreement between both these intrinsic viscosity values suggests that the shear rate of 109 s^{-1} is sufficiently high to satisfy the stipulation of high shear conditions expressed by Edirisinghe [7].

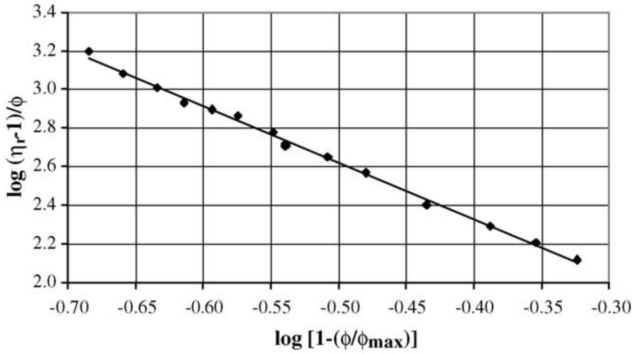

Fig. 5. Adapted form of the Kosmac equation used to determine the intrinsic viscosity. Symbols represent the experimental data points, the solid line indicates the theoretical values from the model.

It is interesting to note that when Edirisinghe and co-workers [7,9] utilised the unmodified Chong, Eilers and Mooney equations to characterise A-16SG alumina/polypropylene blends for injection moulding they found that the Mooney equation again failed to fit the experimental data at high solids concentrations (although Rajala [13], who utilised the modified version of the equation to model clay slips, found better agreement). Both the Eilers and Chong equations showed better agreement with the experimentally determined data points. A slightly higher packing density was suggested when the modified Eilers approach was used. Upon application of the equations to other shear rates and other alumina powders, Edirisinghe found $\phi_{\max}$ to be virtually independent of shear rate, but critically dependent on the particle morphology with powders possessing large median sizes, broad size distribution and an equiaxed shape exhibiting larger values. In addition they demonstrated that the disposable constant, C_{EE}, was found to be highly dependent on the shear rate and powder characteristics, with higher shear rates, finer median sizes and broader particle size distributions exhibiting lower values.

Comparison with the values obtained by Edirisinghe indicates that in the current study $\phi_{\max}$ was found to be notably lower even though the same grade of alumina powder was utilised. The difference between the two situations is believed to be attributable to the extra colloidal stabilisation term provided by the highly charged, surface-adsorbed polyelectrolyte present in this study. The repulsive interaction generated by this extra factor will inhibit flow relative to the hard sphere situation, resulting in higher viscosities for a particular combination of solids concentration and suspending medium. This consequently reduced the solids concentration required to achieve maximum packing.

This work indicates that the optimal condition required for dispersion represents a balance between maintaining the flow properties for effective dispersion and suspension processing whilst utilising a minimum quantity of the liquid phase. A viscosity of 2 Pa s was found to represent the upper limit whereby suspensions could be acceptably poured. As a result, a 52 vol.% dispersed suspension displayed the optimum compromise between these two opposing factors.

5.1.2. Shear sweep loop behaviour

The flow behaviour of the 37 and 52 vol.%, 1.4 mg g^{-1} suspensions were given in Fig. 2, the most apparent characteristics being the existence of shear-thinning and thixotropic behaviours. These features are common to virtually all highly concentrated dispersed suspensions [14], although it is interesting to note that the magnitude of the difference in the actual shear stress values between the two portions of the sweep cycle at 109 s^{-1} is considerably larger for the more concentrated suspension (Fig. 2a). Nevertheless, the relative effect as expressed by the thixotropic index indicates that the suspensions possess a similar relative degree of thixotropy.

The flow behaviour of the dispersed suspensions was further characterised using the Ostwald de Waele function (Fig. 3). The figure shows good agreement, for both solids loadings, between the experimentally determined points and the line of best-fit results over the majority of the shear range investigated. The Ostwald de Waele line fitting parameters were also summarised in the figure, it can be seen that the constant, n, known as the flow behaviour index, is substantially below 1, describing the pronounced shear-thinning exhibited. Furthermore, this constant is similar in both cases, confirming that the suspensions display a similar relative degree of shear-thinning. The value c, known as the consistency, reflects the larger viscosities associated with suspensions of high-solid concentration.

5.2. Oscillatory shear rheology

The frequency dependence of the viscoelastic properties, G' and G'', for the ceramic suspensions prepared with solids contents of 37 and 52 vol.% was presented in Fig. 4. The data shows close agreement to that previously reported in the literature, for example the studies by Barclay [6] and Zupancic [11] who, respectively, studied electrosterically and electrostatically stabilised aqueous alumina suspensions. It can be seen that G'' is always much greater than G', indicating that the viscous properties of the suspension dominate the elastic properties. Although the cross over and subsequent plateauing of the viscoelastic parameters was not directly observed with the conditions utilised in this study, the overall trend of a suspension approaching $\phi_{\max}$ is apparent for the higher solids content suspension. Furthermore, the relatively low absolute value of G'' compliments the findings obtained under constant shear conditions that signified the fluid, well-dispersed nature of the suspension.

It can also be seen that at the solid volume fractions utilised in the present work, G' and G'' were found to increase with frequency, indicative of fluid dominated behaviour. This observation may be rationalised by considering the characteristic timescale of the experiment, τ_0 and the relaxation time of the specimen, τ_{relax}. τ_o may be defined according to:

$$\tau_0 = \omega^{-1} \text{ where } \omega = 2\pi f \tag{10}$$

where f is the test frequency. For suspensions tested at a low frequency, the prolonged associated characteristic timescale of the experiment, τ_0, will be longer than the relaxation time of the suspension, allowing the perturbed structure to relax during oscillation. This results in a viscous response ($G'' > G'$) since the suspension dissipates most of the energy. With increasing frequency, τ_0 approaches τ_{relax}, resulting in an increased contribution from the elastic component and hence the storage of energy. At the highest frequencies, τ_0 decreases below τ_{relax}, such that the perturbed structure is unable to relax and the suspension exhibits an elastic response whereby $G' > G''$ and both become independent of frequency.

The onset of elasticity can be explained by considering the suspension microstructure. The repulsive interparticle forces cause the formation of a highly ordered rest structure, termed a pseudo-lattice. Upon oscillation, the particles are forced to move; however, motion is impeded by the like-charges that surround adjacent coated particles. The storage modulus gives an estimation of the magnitude of this interparticle repulsion [15]. For suspensions of low concentration, the repulsive force and low concentration allows the particles to become well separated in the medium. In these suspensions the interparticle interactions between the particles are small, such that the viscous response is much larger relative to the elastic contribution. For the highly concentrated 52 vol.%, 1.4 mg g^{-1} suspensions, the close proximity between particles intensifies the magnitude of the repulsive interparticle potential [16].

6. Conclusions

Upon shearing at a constant rate of 109 s^{-1}, the viscosity of aqueous based suspensions dispersed using 1.4 mg g^{-1} NHPA exhibited a strong dependence on the solid concentration, ϕ. Although this observation applies to all suspensions as a result of hydrodynamic interactions, the presence of the additional repulsive interaction further inhibits flow. In a given suspending medium, this results in higher suspension viscosities at a given solids concentration, higher intrinsic viscosities and lower maximum packing volume fractions, $\phi_{\max}$. Furthermore, it was found the relationship between solid concentration and viscosity could be accurately represented by the modified versions of Eilers and Chong equations, from which $\phi_{\max}$, was found to be 0.655.

When subjected to shear sweep investigations, the suspensions demonstrated shear-thinning and thixotropic behaviour as a result of changes to the suspension microstructure. Upon the application of shear the ‘rest’ structure that forms because the particles are forced to take up positions as far apart from each other as possible is progressively broken. Since the particles possess charged surfaces of the same polarity the driving force for reformation is low, and therefore, highly time dependent. Application of the Ostwald de Waele model successfully characterised the shear-dependent behaviour of the suspensions over a wide range of shear rates.

The viscoelastic properties of the suspensions were found to be functions of both frequency and solids loading. The application of oscillatory deformation again forces the particles to move; however, motion is resisted by repulsive interactions arising from adjacent particles possessing like charges. For suspensions tested at low frequency the characteristic timescale of the experiment is longer than the time required for the perturbation to relax, such that the suspension exhibits a viscous response. With increasing frequency the characteristic timescale of the experiment reduces, which therefore does not allow the perturbed structure to completely relax, resulting in the elastic contribution becoming more prominent. In addition, as the solid loading of the suspension increases the reduced separation between particles intensifies the magnitude of the repulsive inter-particle potential, and hence, suspension elasticity.

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