Journal of the European Ceramic Society 20 (2000) 1555–1567

Coagulation of electrosterically dispersed concentrated alumina suspensions for paste production

J. Davies [1], J.G.P. Binner *,[2]

Division of Materials, School of Mechanical, Materials, Manufacturing Engineering and Management,
The University of Nottingham, Nottingham NG7 2RD, UK

Received 1 June 1999; received in revised form 15 December 1999; accepted 29 December 1999

Abstract

The effect of salt induced coagulation of concentrated alumina suspensions initially electrosterically dispersed with ammonium polyacrylate (NHPA) has been investigated. Addition of ammonium chloride caused enhanced adsorption of the NHPA onto the alumina surface. In terms of suspension characteristics minimum viscosity and minimum sediment height coincided with the attainment of complete surface coverage of the dispersing agent (3.7 mg g^{-1}). Coagulation resulted in a reduction in the degree of sample homogeneity in all samples. Coagulation of suspensions initially dispersed with NHPA levels below that needed for complete surface coverage under coagulated conditions (1.4 mg g^{-1}) produced viscous pastes with a yield stress suitable for processing by extrusion. At 70 wt% solids the green densities could not be distinguished from corresponding flocculated samples. Significantly, however, at 80 wt% solids a small degree of homogeneity was retained upon coagulation resulting in a higher green density than those prepared by a flocculated route. The approach of initial dispersion followed by coagulation is therefore of potential benefit in the processing of viscous, pastes such that higher degrees of homogeneity can be achieved compared to those prepared by a flocculated route. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Coagulation; Dispersion; Suspensions

1. Introduction

Suspensions are considered to be dispersed when the repulsive potential between the particles is of sufficient magnitude that the attractive van der Waals potentials are counterbalanced or exceeded. As a result the particles do not coalesce to form agglomerates, or flocs, but are forced as far apart as possible. Such systems are homogeneous, very fluid and upon consolidation the individual particles pack to a high density. However, the consolidation stage of the process can be very slow and the green body formed can be rather brittle and difficult to handle. These disadvantages can be overcome without undue sacrifice of the beneficial properties by the creation of a coagulated network,Velamakanni et al.[1] In this state the particles are attracted into a shallow hydration minimum to form a cohesive, non-touching, homogeneous network.

Coagulation can be achieved via the addition of a salt to a dispersed suspension. For electrosteric dispersion the electrostatic charges on the polyelectrolyte chains are shielded, allowing them to coil and act as uncharged polymers. Thus the salt reduces the solvent quality and hence enhances adsorption, Cesarano et al.[2] Upon suppression of the diffuse double layer, steric forces dictate the stability of the suspension. If the adsorbed layer is relatively thin, attraction may dominate due to van der Waals forces and the suspension will become more viscous Lyklema,[3] Williams et al.[4] However, the enhanced adsorption from solution may introduce a steric barrier to replace electrosteric stabilisation. Time dependent effects such as configurational changes to the adsorbed layer may further affect suspension stability.

In a previous paper, Davies and Binner[5] the role of ammonium polyacrylate, NHPA, was examined as an electrosteric dispersant for high solids content alumina suspensions at high pH. It was found to be effective yielding fluid, highly homogeneous, aqueous suspensions. The

---

* Corresponding author.
E-mail address: j.binner@lboro.ac.uk (J.G.P. Binner).
[1] Now with Blue Circle Industries plc, London, UK.
[2] Now with IPTME, Loughborough University, Leicestershire, UK

PII: S0955-2219(00)00013-3

most notable outcome of this work was the rather unusual feature of the presence of two viscosity minima, Fig. 1. These were believed to be a consequence of different adsorbed configurations for the NHPA. The first viscosity minimum was very unstable and decayed during drying, resulting in green bodies of relatively low density. It was believed to be associated with the NHPA being adsorbed in a tail type configuration. The second viscosity minimum was far more stable, producing more homogeneous green compacts with a much higher density. This second minimum was predicted to be associated with the NHPA being adsorbed in a very loose loop and tail configuration.

The main purpose of the present research was to investigate the coagulation of the electrosterically dispersed suspensions described above using the salt ammonium chloride. The specific objective was to achieve a viscous, pseudoplastic paste possessing a yield point suitable for plastic forming by extrusion. The hypothesis behind the research was that initial dispersion would create homogeneity within the sample that would not be completely lost upon coagulation if the suspension contained a sufficiently high concentration of alumina. Sample homogeneity is essential if the defects that lead to reduced strength in the final sintered component are to be minimised.

To avoid any confusion in terminology the following definitions are used throughout this paper:

Flocculated:	a suspension with no dispersant added such that an attractive network exists in which van der Waals potentials dominate, resulting in touching, agglomerated particles;
Dispersed:	a suspension with sufficient dispersant added to create a fluid, homogeneous suspension in which repulsive potentials dominate, resulting in individual, non-touching particles;
Coagulated:	an initially dispersed suspension to which salt has been added so that an attractive potential dominates and a network of individual, non-touching particles is created.

2. Experimental

2.1. Suspension preparation

Appropriate quantities of distilled water, weighed to ± 0.02 g, and Dispex A40[3] [a 37.6 ± 0.5 wt% solution of ammonium polyacrylate (NHPA) of molecular weight 3500], weighed to ± 0.003 g, were mixed until the dispersant was uniformly distributed. The water associated with the dispersant solution was accounted for in the calculations. A16SG alumina powder[4], weighed to ± 0.02 g, was added to the mixture and the blend stirred until an homogeneous slurry formed. This was then left for 1 h to allow adsorption of the dispersant onto the alumina.

The suspension was subjected to ultrasonic agitation produced by a[5] ultrasound unit using 150 W at 20 kHz. Following previous work,[5] all samples prepared below 80 wt% alumina were subjected to an ultrasonic agitation time of 60 s, whilst those made at 80 wt% and above were exposed for 45 s. To prevent water evaporation the beakers were sealed and left for one hour to cool and attain equilibrium. Finally, the samples were held at a reduced pressure of 60 mm mercury for 1 h as a de-airing stage.

To coagulate the dispersions, the salt ammonium chloride, NH_4Cl, was mixed into the dispersed suspensions in the range 0.01–2.00 M. The final homogenised samples was then de-aired for a second time at a reduced pressure of 60 mm mercury for 1 h to remove as much entrapped air as possible. In a small number of separate experiments, the salt was added to the polyelectrolyte solution prior to the addition of alumina powder. The process of adding NH_4Cl not only caused an increase in the ionic strength, but also caused a pH decrease. In some experiments this pH shift was nullified by adding ~3 ml of concentrated NH_4OH to maintain a pH of 9.5, the pH of the originally dispersed suspensions, simultaneously with the 1.2 M NH_4Cl addition. To avoid dilution effects when comparing the viscosities to standard coagulated bodies, the latter were prepared with 3 ml less water so that a 70 wt% suspension resulted on addition of the NH_4OH.

For comparison flocculated bodies were also prepared by mixing appropriate quantities of alumina powder and distilled water to give the desired solids content and then adjusting to pH 8.0, the measured PZC of the A16SG alumina.[5] In several experiments salt was also added. Where viscosity permitted, ultrasonic agitation was used as described above.

2.2. Rheological measurements

The flow behaviour of the suspensions was monitored using a Bohlin Visco 88 viscometer[6] to measure shear stress and viscosity as a function of shear rate. Three types of measuring system were used depending on the fluidity of the sample. A concentric cylinder (C30) was used for low viscosities (10–500 mPa s), a cone and plate (CP5/30) for intermediate values (500–8000 mPa s) and a parallel plate (PP15) for very viscous bodies (8000–18,000 mPa s).

---

[3] Allied Colloids, Bradford, UK.

[4] Alcoa Manufacturing (GB) Ltd, Worcester, UK.

[5] Kerry Ultrasonics Ltd., Hitchin, UK.

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

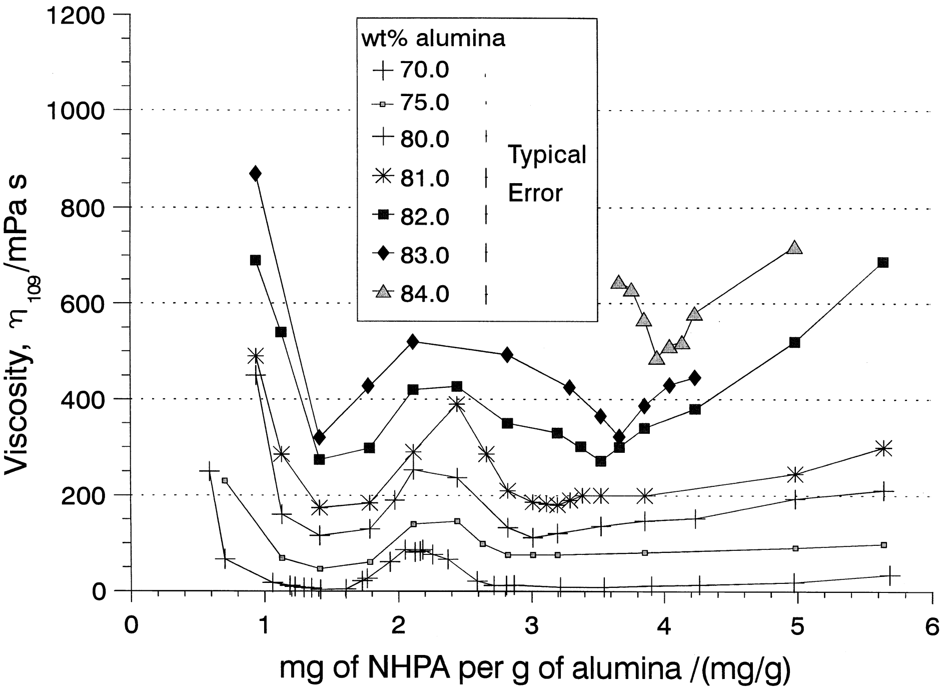

Fig. 1. Viscosity plotted as a function of both NHPA concentration and wt% alumina at pH 9.5.

After an equilibration time of 5 min in the sample holder, the rheological characteristics where measured as a shear sweep cycle across 18 to 1200 s^{-1}. The sample was then left for 5 min to equilibrate again after which time the viscosity was recorded at a constant shear rate of 109 s^{-1} for 3 min or until the viscosity became independent of time.

Sample yield stress, τ_y, was calculated from the rheological data using the Casson equation,[6] Eq. (1) below, a graph of $\tau^{1/2}$ versus $\gamma^{1/2}$ producing a linear relationship. Linear regression yielded the yield stress as the square root of the intercept.

$$\tau^{1/2} = \tau_y^{1/2} + \eta_\infty^{1/2}\gamma^{1/2} \tag{1}$$

The pseudoplastic constant of fully coagulated samples was calculated using the power law equation, Eq. (2) below,[7] a graph of log $(\tau - \tau_y)$ versus log γ producing a linear relationship. Linear regression was used to calculate the gradient and therefore the pseudoplastic constant.

$$\tau - \tau_y = c\gamma^n \tag{2}$$

A thixotropic index, *TI*, was measured simply as the percentage difference in shear stress measured during the increased shear sweep, τ_i, compared to the decreasing shear conditions, τ_d, at the shear rate of 109 s^{-1}.

$$TI = \frac{\tau_i - \tau_d}{\tau_i} \times 100 \tag{3}$$

2.3. Sedimentation experiments

The sedimentation behaviour of the suspensions was monitored over time, the final sediment heights being used as a measure of the ability of the samples to pack to a high density. The smaller the final volume, the higher the packing ability. All samples were based on 30 wt% alumina in order to achieve a satisfactory sediment height and placed in 10 ml sealed graduated test tubes. The sediment height was monitored as a function of time until a steady height was obtained. Approximately 3 months was sufficient for dispersed samples, 1 month for coagulated and flocculated bodies.

2.4. Adsorption experiments

The amount of NHPA adsorbed onto the alumina powder from solution was calculated from the amount of polymer remaining in solution using first derivative titration techniques making use of the acid/base functionally of the carboxylic acid groups on the polyacrylate chain. Full details of the procedure have been reported elsewhere.[5] A typical titration curve is given in Fig. 2. A calibration curve correlating the quantity of 1.2 M HCl required to neutralise a known quantity of NHPA in solution was established, Eq. (4).

$$M^s_{\mathrm{NHPA}} \begin{array}{ll} = 0.0083\alpha & -0.0008 \\ \pm 0.0001 & \pm 0.0007 \end{array} \tag{4}$$

where: M^S_{NHPA} -mass of NHPA in solution/g
α -volume of 1.2 M HCl added/ml

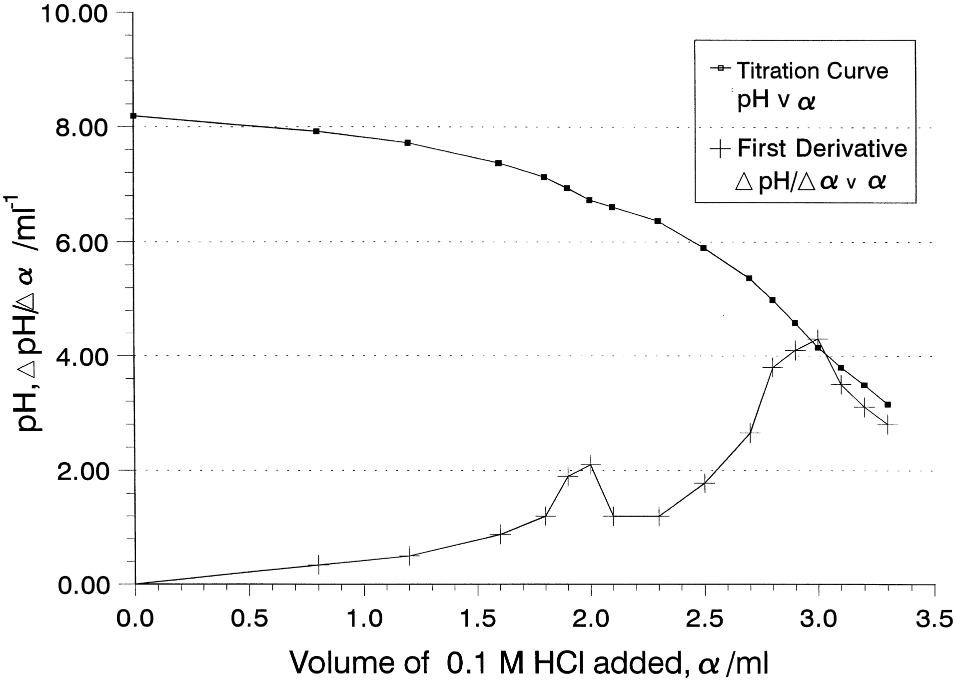

Fig. 2. Typical titration and first derivative plot for adsorption under coagulating conditions at 70 wt% alumina.

The time taken to achieve adsorption equilibrium in the presence of NH_4Cl was experimentally pre-determined. In summary, 1 h after salt addition was found to be sufficient to attain equilibrium adsorption. As a result all adsorption tests were carried out 1 h after coagulation.

2.5. Green density measurements

The densities of green compacts were measured using the mercury immersion method after they had been dried to constant weight. In all cases, at least three different samples were measured to produce each value quoted.

3. Results

3.1. Effect of salt and NHPA concentration on viscosity

Typical flow behaviour of fully coagulated samples under shear sweep conditions is depicted in Figs. 3 and 4. The former shows the behaviour of samples initially dispersed with 1.4 mg g^{-1}, which, from Fig. 1, is the concentration required to achieve the first viscosity minimum. Fig. 4 corresponds to the NHPA concentration associated to the second minimum. In both cases samples were fully coagulated using 1.2 M NH_4Cl. As would be expected, pseudoplasticity was observed at both concentrations, whilst thixotropy was less evident in Fig. 3. Indeed, Table 1 shows that the degree of thixotropy increased gradually with increasing NHPA concentration, whilst the degree of pseudoplasticity remained essentially constant.

Shear stress–shear rate plots for samples initially dispersed at 70 wt% with 1.40 mg g^{-1} NHPA are plotted in Fig. 5 as a function of increasing salt concentration. Addition of salt caused an increase in the stress required to shear the sample up to a plateau region at 0.5 ± 0.1 M NH_4Cl. Above this concentration there was no further effect. This maximum stress was significantly lower than that required to shear a fully flocculated body.

The corresponding maximum viscosity attained on addition of salt was found to depend on the amount of NHPA present, Fig. 6. A plateau level of viscosity occurred for each NHPA concentration. In addition, as the concentration of NHPA increased, the plateau viscosity, η^{p}_{109}, decreased to a minimum at 3.85 mg g^{-1} NHPA, above which a small viscosity increase was observed. The amount of NH_4Cl required to reach the plateau viscosity region increased concurrently with NHPA content. Above 3.85 mg g^{-1} NHPA the plateau region was not distinct; addition of 5.0 M NH_4Cl did not significantly increase the viscosity further. The addition of NH_4Cl to a fully flocculated body caused the viscosity to decrease, although it remained significantly greater than any sample containing NHPA. The stability of the viscosity plateaus can be clearly seen in Fig. 7 by their time independence, indicating that the coagulated samples are distinctly different to flocculated samples.

As already mentioned, the objective of salt induced coagulation was to create a viscous body that possessed a sufficiently high yield stress to permit it to be extruded. The yield stresses for 70 wt% suspensions, calculated using the Casson equation, are plotted in Fig. 8. As can be seen the yield stresses followed a similar pattern to the viscosities shown in Fig. 6.

3.2. Sedimentation

The sediment height of both flocculated and coagulated bodies is plotted in Fig. 9 as a function of time. Coagulated samples sedimented in a similar manner to flocculated bodies; all samples producing a clear supernatant however those containing NHPA gave rise to a smaller sediment volume. The final sediment volume decreased with increasing NHPA concentration up to 3.85 mg g^{-1}.

3.3. Adsorption

The effect of 1.2 M NH_4Cl addition to dispersed samples is summarised in Fig. 10. As can be seen, the adsorbed plateau value was greater in the presence of

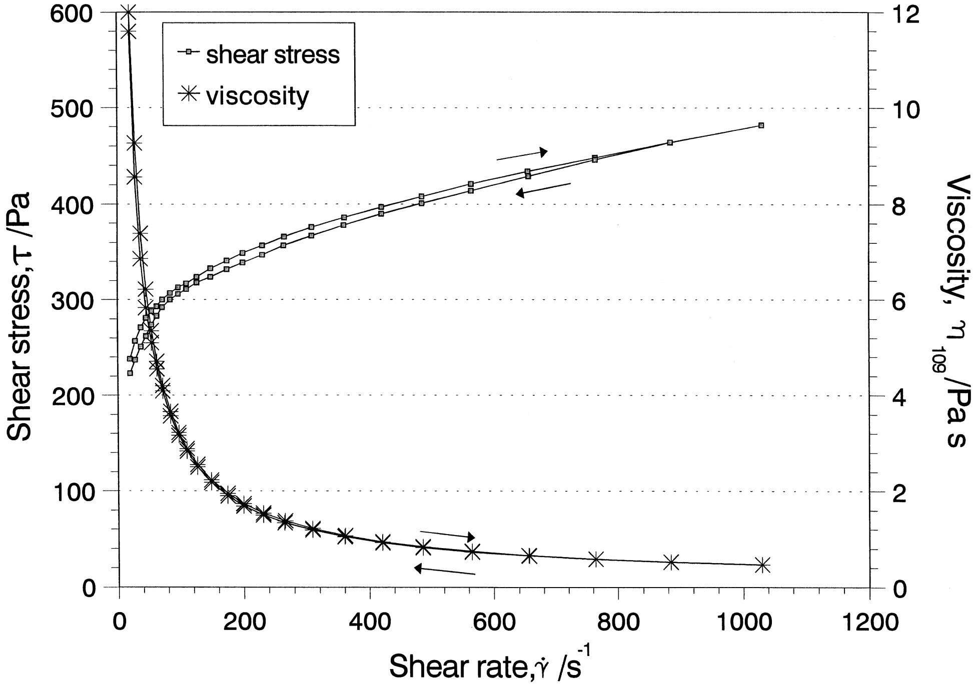

Fig. 3. Typical flow behaviour of a fully coagulated suspension containing 1.40 mg g^{-1} NHPA under shear sweep conditions at 70 wt% alumina.

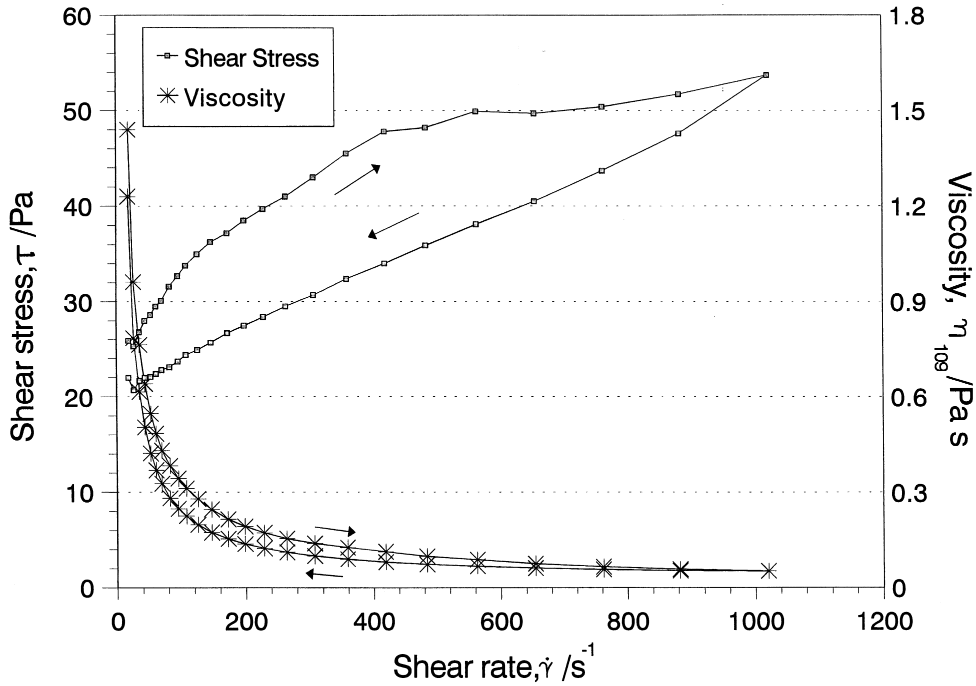

Fig. 4. Typical flow behaviour of a fully coagulated suspension containing 3.85 mg g^{-1} NHPA under shear sweep conditions at 70 wt% alumina.

Table 1
Thixotropic index and pseudoplastic constant for samples fully coagulated with 1.2 M NH_4Cl at 70 wt% alumina

Concentration of NHPA (mg g^{-1})	Thixotropic index, *TI* (% ± 5)	Pseudoplastic constant, $n \pm 0.3$
1.40	0	0.60
2.15	18	0.56
2.80	18	0.60
3.85	28	0.63

NH_4Cl (pH 8.0) than in the dispersed state and complete equilibrium coverage was achieved at 3.7 ± 0.2 mg g^{-1} NHPA compared to 2.5 ± 0.2 mg g^{-1} NHPA in the dispersed state. Therefore, the addition of 1.2 M NH_4Cl induced an extra 1.2 mg g^{-1} of NHPA to be adsorbed from solution. At concentrations below this, no NHPA was detected in solution. However, the process of coagulation using NH_4Cl not only caused an ionic strength increase, but also a pH decrease from the initial dispersion pH of 9.5 down to ~8. When the pH was maintained at 9.5 using concentrated NH_4OH the adsorption data was significantly different, having a plateau value very similar to that of the dispersed suspension and no NHPA adsorbed until 1.4 mg g^{-1} had been to the suspension. The viscosity data are given in Fig. 13; it can be seen that despite the differences in the adsorption data, the pH had no effect on the viscosity.

3.4. Green density

The green densities of 70 wt% alumina coagulated samples as a function of NH_4Cl concentration are given in Fig. 11 along with those for flocculated bodies. In each case the coagulated samples yielded a lower green density compared to their dispersed counterparts (i.e. those containing no NH_4Cl), whilst the green density generally increased with increasing concentrations of NHPA over the ranges tested. It is interesting to note that little difference was observed between the densities of bodies produced from fully coagulated pastes (i.e. those containing $\geqslant 1.2$ M NH_4Cl) originally dispersed with 1.40 mg g^{-1} NHPA and those of flocculated pastes.

The green densities of suspensions initially prepared at 80 wt% alumina are given in Fig. 12. Two features may be noted in comparison to Fig. 11. Firstly, the recorded values were generally higher than those prepared at 70 wt% solids, whilst secondly the samples prepared with 1.40 mg g^{-1} NHPA give rise to green densities that were slightly higher than the corresponding flocculated samples. These results were repeated several times to ensure validity.

4. Discussion

The following section discusses the effect of NH_4Cl induced coagulation of initially dispersed suspensions.

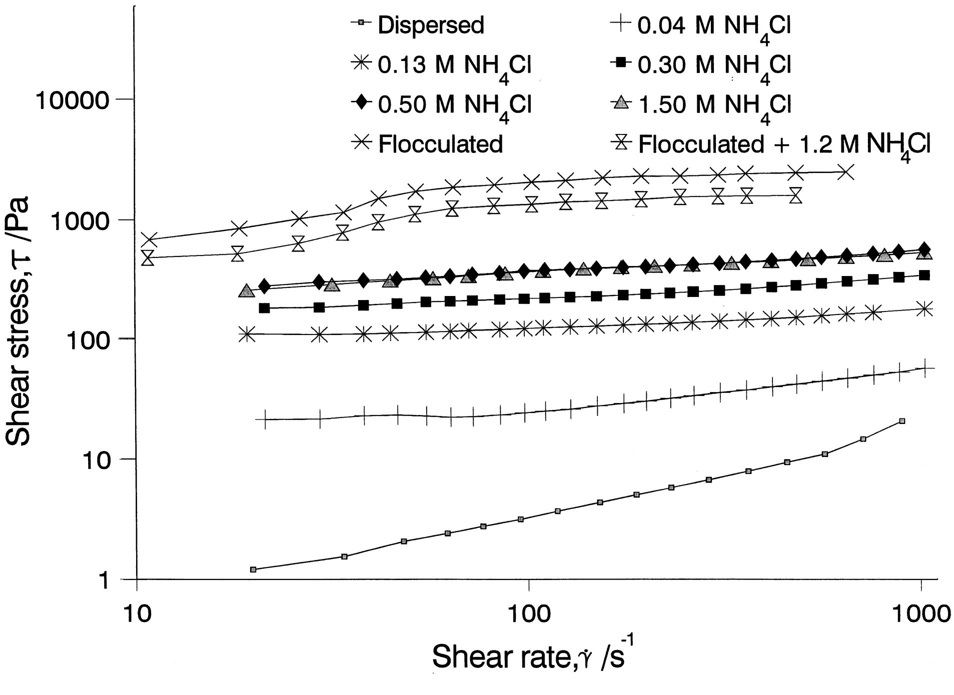

Fig. 5. Flow behaviour during increasing shear of a suspension originally dispersed with 1.40 mg g^{-1} NHPA at 70 wt% alumina plotted as a function of NH_4Cl concentration.

Particular attention is given to suspensions initially dispersed with 1.4 mg g^{-1} NHPA, the concentration required to achieve the first viscosity minimum, Fig. 1, and which, when coagulated, gives rise to a rheology suitable for extrusion at high enough solids loading.

Fig. 6 indicates that the addition of NH_4Cl induced a gradual increase in viscosity up to a plateau region. This can be attributed to the gradual shielding of the negative electrostatic charges on the adsorbed NHPA by the positive NH_4^+ counter-ions. This caused a gradual contraction of the electrosteric double layer, leaving only the steric barrier provided by the NHPA to oppose the van der Waals forces. Complete neutralisation of the electrostatic charge corresponds to the attainment of the

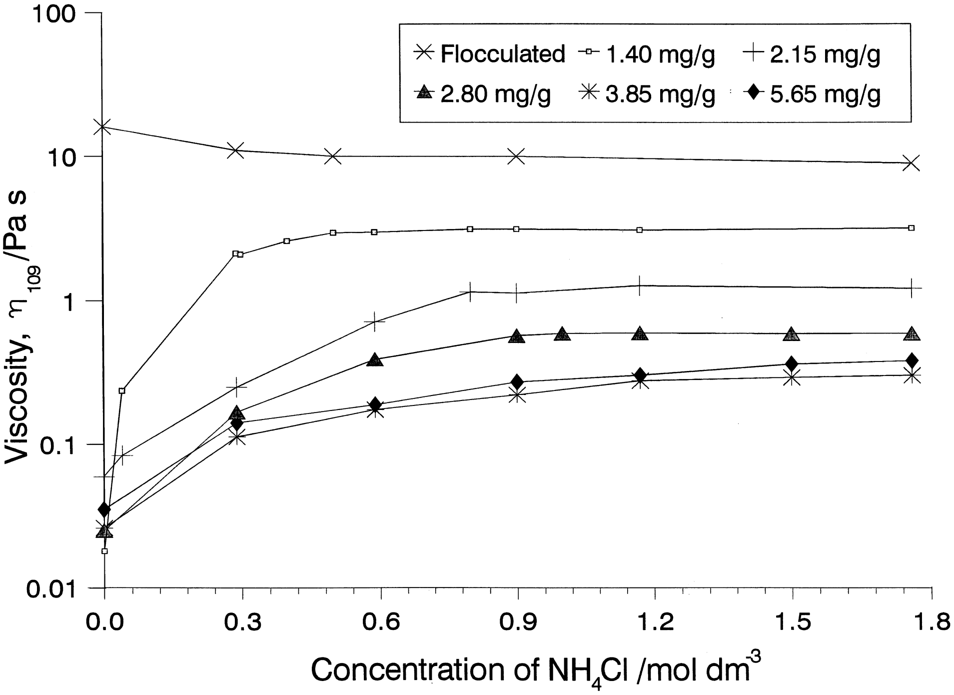

Fig. 6. Viscosity versus added NH_4Cl concentration for samples prepared with varying quantities of NHPA at 70 wt% alumina.

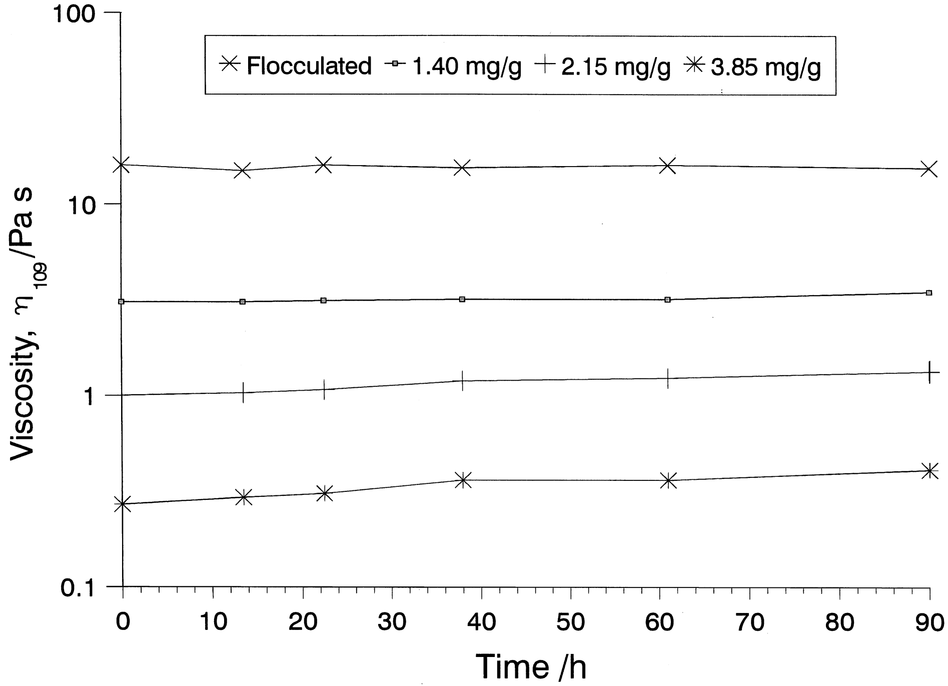

Fig. 7. Ageing of coagulated and flocculated samples containing 1.2 M NH_4Cl, prepared at 70 wt% alumina.

viscosity plateau. The magnitude of the plateau is therefore dictated by the effectiveness of the steric barrier offered by the adsorbed NHPA against the van der Waals forces. It has been established that linear polymers of molecular weight less than 10,000 are generally unable to provide a steric barrier of sufficient thickness to extend beyond the scope of the van der Waals forces, Napper.[8] Since the NHPA used in this research had a molecular weight of only 3,500, it is perhaps not surprising that the loss of the surface electrostatic charge caused a loss of dispersion.

In all samples containing NHPA the magnitude of the viscosity plateau was much lower than that produced by fully flocculated samples prepared at pH 8.0, the same

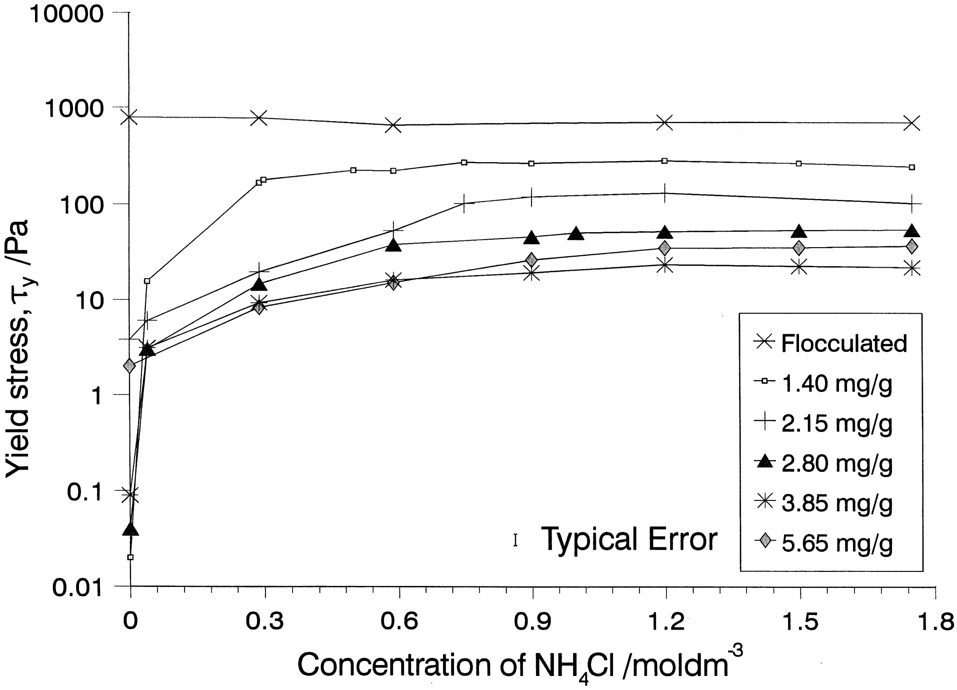

Fig. 8. Casson yield stress developed upon coagulation, plotted as a function of both NH_4Cl and NHPA concentration at 70 wt% alumina.

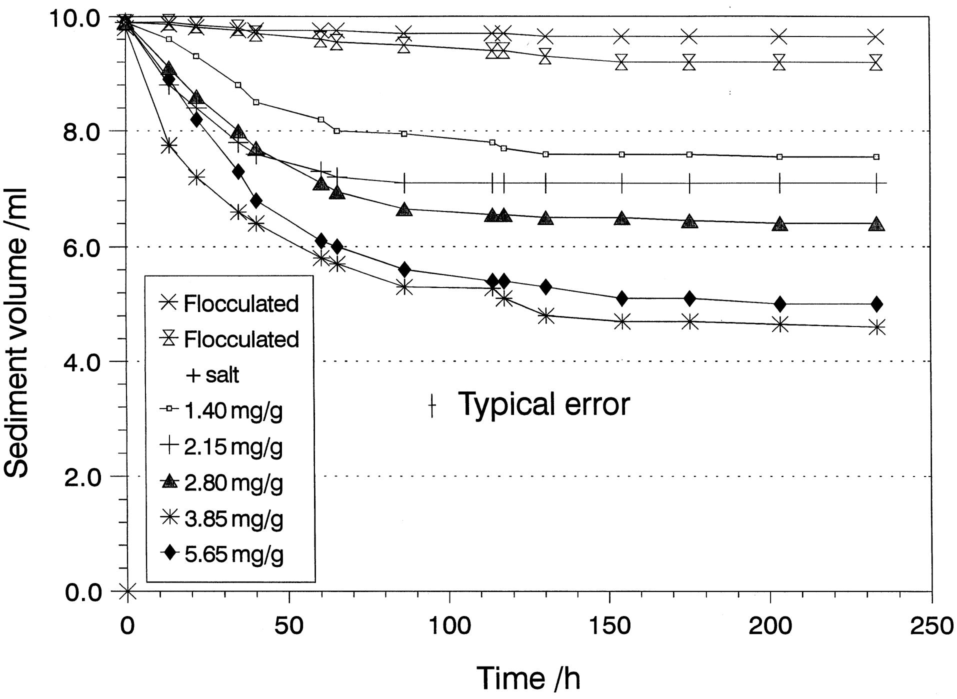

Fig. 9. Sedimentation of coagulated and flocculated suspensions as a function of time at 30 wt% alumina. All samples contained 1.2 M NH_4Cl.

pH as the suspensions after coagulation. This indicated that although the steric barrier was not sufficient to maintain dispersion, it provided a lubricating layer that assisted the flow of particles during shear and perhaps prevented van der Waals attractive forces acting to their full extent. The reduction of the plateau value with increasing NHPA up to 3.85 mg g^{-1} is reflective of the increasing efficiency of the steric barrier against van der Waals forces, a possible consequence of the different adsorbed polymer configurations in the dispersed state, Davies and Binner.[5] Solvency effects may also influence the efficiency of the steric barrier and hence the magnitude of the viscosity plateaux, although it would appear that the thinness of the adsorbed layer is the dominating factor.

The viscosity as a function of shear rate for increasing NH_4Cl concentrations took an identical form to that observed by Velamakanni et al.,[1] who studied the effect of NH_4Cl on electrostatically dispersed alumina suspensions

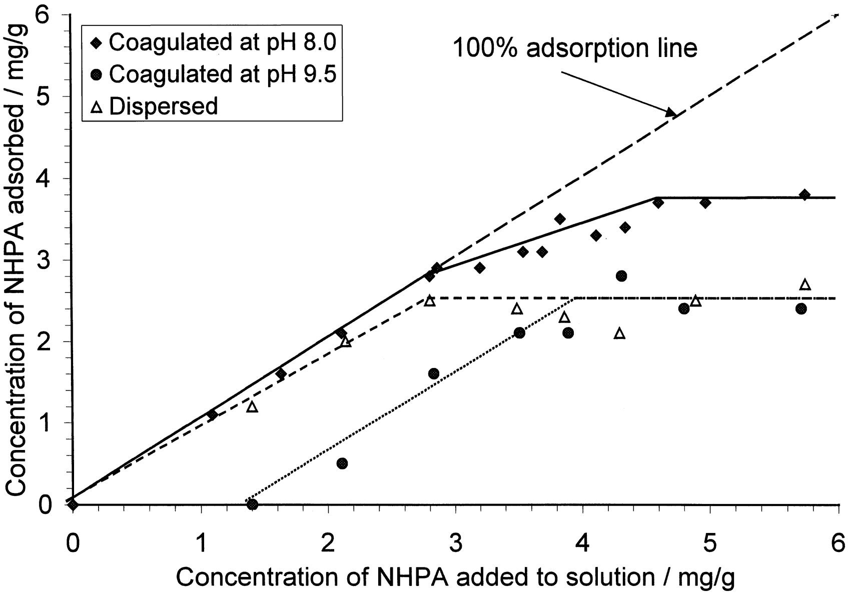

Fig. 10. Summary of adsorption of NHPA onto alumina after coagulation at 70 wt% alumina.

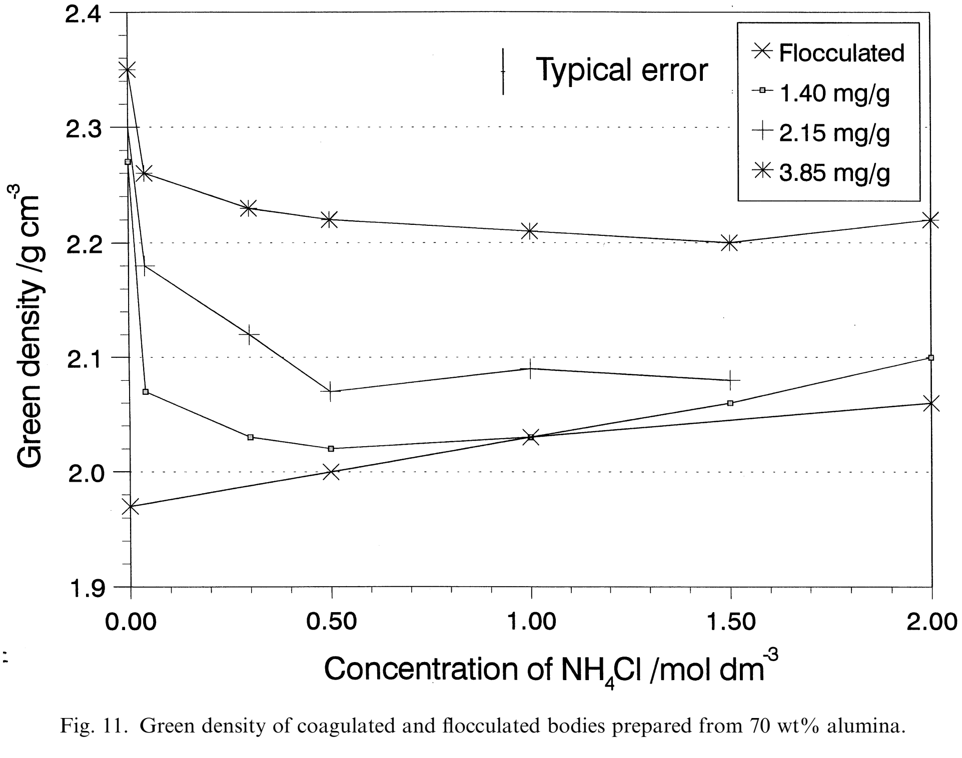

Fig. 11. Green density of coagulated and flocculated bodies prepared from 70 wt% alumina.

at pH 4.0. The plateau viscosity they observed was attributed to the formation of a layer consisting of hydrated Cl^- ions bound to the positive surface charge by electrostatic attraction. This thin hydration layer acted as a barrier preventing the particles being attracted into the deep primary minimum associated with flocculated networks, although the overall coagulated network was weakly attractive. It was also noted that such viscous bodies exhibited plasticity when sufficiently loaded with powder. The formation of an extensive hydration layer is considered unlikely in this research, however, since at pH 8.0 the powder is effectively uncharged. In this case it is

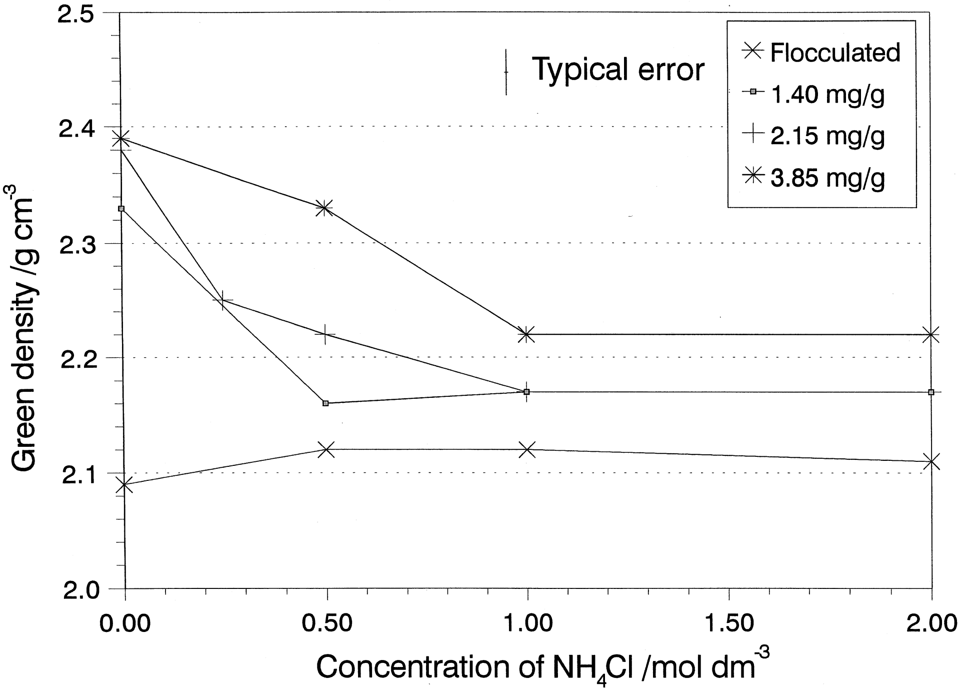

Fig. 12. Green density of coagulated and flocculated bodies prepared from 80 wt% alumina.

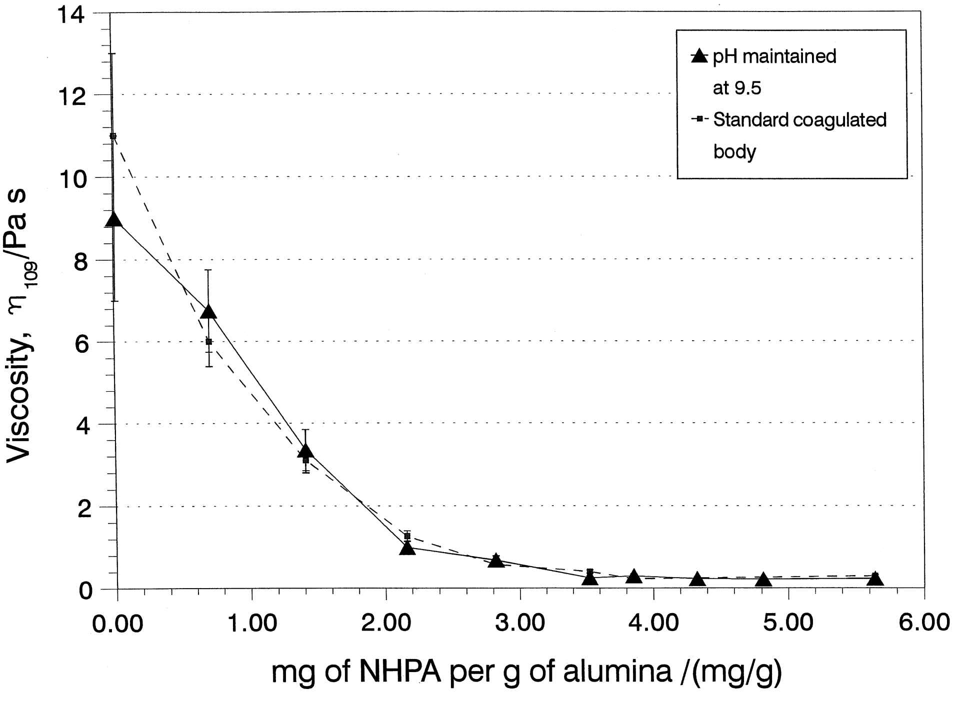

Fig. 13. Viscosity of coagulated samples in which pH is maintained at 9.5 plotted as a function of NHPA content, compared to standard coagulated bodies.

likely that the barrier was primarily provided by the adsorbed NHPA with perhaps only a minor contribution from the counter-ions (hydration layer).

The calculated yield stresses, Fig. 8, indicate that if sufficiently loaded, coagulated suspensions prepared with 1.4 mg g^{-1} would be suitable for plastic forming operations. Indeed, at solids loadings above 81 wt% coagulation transformed an initially pourable suspension into a stiff paste possessing a yield stress sufficiently large to support its own weight. Processing of such a paste is dealt with in a following paper, Davies and Binner.[9] This type of paste formation was also remarked upon in the work by Velamakanni et al.[1]

The increase in degree of thixotropy with increased NHPA content under fully coagulated conditions, Table 1, is reflective of the decreasing influence of van der Waals attractive forces. The degree of pseudoplasticity remained relatively constant, however, suggesting that other suspension properties dominate this characteristic.

The sedimentation behaviour given in Fig. 9 followed a similar trend to the plateau viscosity data shown in Fig. 6; both decreasing with NHPA concentration up to the limit of 3.85 mg g^{-1} NHPA. Furthermore, it was noted that in all samples containing NHPA the final sediment volume was much lower than for flocculated bodies. This suggests that greater particle packing was achieved in coagulated suspensions, the degree of which increased with increasing NHPA concentration up to 3.85 mg g^{-1} NHPA. Of particular interest is the lower sediment volume of samples prepared with 1.4 mg g^{-1} compared to flocculated samples, indicating a higher degree of packing or a higher degree of homogeneity, a factor critical to the final component strength.

From the adsorption data, Fig. 10, it can be seen that the process of coagulation causes enhanced adsorption of NHPA from solution. The equilibrium concentration of NHPA adsorbed on the alumina surface was 3.7 mg g^{-1} NHPA, 1.2 mg g^{-1} greater than for the originally dispersed suspensions shown by the dotted line and measured in Davies and Binner.[5] This value of adsorbed NHPA agrees very well with the observed sedimentation and viscosity data described above. Such enhanced adsorption from solution must be accounted for by enhanced coiling of the adsorbed species, at least for the loose loop and tail configuration associated with concentrations above the second viscosity minimum of the dispersed state.[5] It will be shown later that the pH decreases from 9.5 to 8.0 induced by coagulation may also play a significant role.

It has been proposed[5] that the adsorbed configuration associated with dispersions containing 1.4 mg g^{-1} NHPA is significantly different to that at 2.8 mg g^{-1} and above. The former was believed to be a very unstable, dangling tail configuration whilst the latter was a more stable, loose loop and tail configuration. During coagulation it is very likely that the unstable configuration would be significantly affected. From the adsorption data, it would appear that such changes resulted in incomplete surface coverage of the powder and it is implicit that the increase in viscosity as NH_4Cl is added is indeed primarily due to the gradual exposure of van der Waals forces.

In summary, it would appear that a concentration of 3.85 mg g^{-1} would be optimum in terms of the final packing characteristics and hence ultimate mechanical properties, although such suspensions would have a rheology unsuitable for extrusion. On the other hand, a concentration of 1.4 mg g^{-1} would appear ideal for achieving the desired rheological properties for extrusion, although its homogeneity would be much lower. However, of interest here is whether or not the lower NHPA level is capable of producing more homogeneous and potentially stronger components than those achieved by simple flocculation. The sedimentation data would suggest this to be the case, although the tests were performed in a very dilute environment, very much removed from actual processing conditions. Further evidence in the form of green densities provided a more realistic indicator.

The green density of samples prepared at 70 wt% alumina, presented in Fig. 11, clearly indicate that all coagulated suspensions possessed a lower green density, and hence lower degree of homogeneity, than the initial dispersed suspensions without NH_4Cl. The green densities decreased to plateau levels with increasing NH_4Cl concentration, a feature also apparent in the results of Velamakanni et al.[1] but not remarked upon. As expected coagulated samples prepared at 3.85 mg g^{-1} NHPA exhibited the highest densities, with the density decreasing with increasing NHPA concentrations, until, most significantly, no difference could be distinguished between flocculated samples and those initially dispersed with 1.4 mg g^{-1} NHPA.

The green density values recorded for samples prepared at 80 wt% alumina, Fig. 12, were markedly different, however. All samples produced higher green densities than at 70 wt%, but most significantly coagulated samples prepared with 1.4 mg g^{-1} yielded higher densities than flocculated samples. Whilst the typical error shown in the figure reflects the majority of results, additional experiments on flocculated and 1.4 mg g^{-1} NHPA coagulated samples consistently showed there to be a significant difference between the two. This is clearly supportive of the hypothesis behind this research. Despite a large degree of homogeneity being lost upon the addition of NH_4Cl, as can be seen from the decrease in green density with and without salt addition, a small degree of homogeneity must be retained within the suspension for a difference in green density to be measured between the coagulated and flocculated samples. Therefore the approach of initial dispersion followed by coagulation can be of potential benefit to the creation of extrudable pastes with improved homogeneity over samples prepared by a flocculated route. Another paper deals with the extrusion of such pastes and the results obtained, Davies and Binner.[9]

Systems in which adsorbed polymers do not effectively disperse suspensions but produce high density components have been the focus of research by Yin et al.[10] and Bergstrom et al.[11]

The greater degree of particle packing in samples prepared at 80 wt% can be explained in terms of the packing behaviour of the particles in the dispersed state, as suggested by Bergstrom. The free volume for particle movement is severely restricted at solids loadings approaching the maximum packing volume fraction due to the shear quantity of particles present. Closely packed structures with a degree of ordering tend to form within the dispersed suspension as a result of the surface repulsive potential forcing the particles to assume positions that minimise their free energy. The addition of salt removes the repulsive barrier, inducing instantaneous coalescence of particles where they first make contact. Since particles are already in relatively ordered positions, a more highly packed coagulated network ensues. In contrast, in more dilute suspensions particles are more randomly distributed. Thus upon removal of the repulsive barrier particles are unlikely to be attracted to the positions required for a closely packed arrangement, resulting in a less uniform, lower density network.

The mechanical process of mixing the NH_4Cl into the suspension probably reduces the degree of ordering present. It would be beneficial to sample homogeneity if the coagulation process was initiated from within the suspension. This has recently been achieved by Graule et al.[12] and McDermott et al.,[13] both utilising chemicals that are initially inactive but decompose in-situ over a period of time to produce chemical species that induce coagulation by either increasing the ionic strength or causing a shift in pH towards the PZC of the powder. Using this approach, initially dispersed suspensions can be cast into complex shape moulds and left to solidify to produce homogeneous, high density components.

4.1. Effect of pH on coagulation

As already mentioned briefly, the process of coagulation using NH_4Cl not only caused an ionic strength increase, but also a pH decrease from the initial dispersion pH of 9.5 down to ~8, due to the acidic nature of NH_4Cl that undergoes the reversible reaction:

$$NH_4^+ \leftrightharpoons NH_3 + H^+ \tag{5}$$

Experiments were performed to determine if this pH shift had a major impact on the recorded results. During coagulation the suspension pH was maintained at 9.5 using concentrated NH_4OH. The viscosity of the resultant suspensions was within error of that observed for normally coagulated samples, Fig. 13. This suggested that pH had no influence on the coagulation process. The adsorption data indicated otherwise, however, Fig. 10. Complete equilibrium coverage was reached at an NHPA concentration of 2.4 mg g^{-1} NHPA, similar to that observed for dispersed samples,[5] rather than the 3.85 mg g^{-1} observed at pH 8.0. It could, therefore, be concluded that enhanced adsorption is a function of pH rather than NH_4Cl concentration, although this may be an over simplification considering the chemical reactions taking place. Most interesting however, was the desorption of NHPA at 2.8 mg g^{-1} and below. This is likely due to the excess of hydroxyl and chloride co-ions in solution over the ammonium counter-ions as a result of the hydroxyl anion removing hydrogen ions from solution. Following Le Chatelier's principle, the removal of hydrogen ions forces the equilibrium reaction in Eq. (5) to the right causing the evolution of ammonia gas and hence the loss of counter-ions. Maintaining the pH at 9.5 during coagulation using the process described in this research would therefore likely be of no benefit over preparation via a flocculated route. The development of a very weak hydration layer, similar to that described by Velamakanni et al.,[1] may partly explain the similar viscosities recorded at pH 9.5 and those described in this section at 8.0.

4.2. Lubricating effect of NH_4^+ counter-ions

One final feature worthy of mention is the lubricating nature of the ammonium chloride itself. This is apparent in a number of the graphs. Firstly, in Fig. 5 the flocculated sampling containing 1.2 M NH_4Cl clearly exhibits a lower shear stress and hence viscosity than the corresponding flocculated sample without salt. Sedimentation data also exhibit these effects, Fig. 9. Such effects were also apparent in the work of Velamakanni et al.,[1] although absent in a similar study by Chang et al.[14] Both papers also report that salt had no effect on the density of flocculated bodies. Whilst the recorded

Table 2
Final sediment volumes and viscosities of flocculated bodies

Sample type	Final sediment volume for 30 wt% alumina (ml ± 0.2)	Viscosity, η_{109}, for 70 wt% alumina (Pas ± 2)
Flocculated at pH 8.0	9.7	16
Flocculated at pH 8.0; 1.2 M NH_4Cl added; resultant pH 7.4	9.2	9
Flocculated at pH 8.0; 1.2 M NH_4Cl added; pH maintained at 8.0	8.8	9

values at 80 wt%, Fig. 12, support this, the results at 70 wt% do not, the green density increasing with NH_4Cl concentration. Table 2 shows that the lubricating effect is not due to the associated pH shift, since even when the pH was maintained at 8.0 during salt addition the measured viscosities were lower than samples without salt addition. It is possible that these salt effects may be attributed to the formation of very weak hydration layers of salt ions bound to the charged sites on the ceramic particles even though the net particle surface charge is essentially zero charge at pH 8.0.

5. Conclusions

The effect of coagulation induced by ammonium chloride salt on alumina suspensions initially electrosterically dispersed with ammonium polyacrylate, NHPA, has been investigated. In general, coagulation resulted in a decrease in suspension pH, a viscosity increase, enhanced adsorption, and reduced green density or homogeneity compared to the initial dispersion.

At 70 wt% solids content the optimum concentration of NHPA with respect to ultimate suspension properties was found to be 3.85 mg g^{-1} NHPA. This was the concentration at which the minimum viscosity was recorded, complete surface coverage was achieved and the maximum green density, albeit less than under dispersed conditions, was reached. Unfortunately these suspensions were pseudoplastic, possessed a low viscosity and yield stress, and hence were rendered unsuitable for subsequent plastic forming operations.

Coagulation of suspensions initially dispersed at 1.4 mg g^{-1} NHPA, the minimum concentration found to be sufficient to achieve maximum suspension fluidity, resulted in a sharp viscosity increase to a paste consistency, loss of thixotropy and the introduction of a high yield stress, characteristics suitable for plastic processing by extrusion. Viscosity data indicated the pastes to be clearly distinct from flocculated samples despite the increase in inter-particle attraction introduced by the addition of ammonium chloride. At 70 wt% solids content, however, the resultant properties, in particular the green density, indicated that the coagulated samples were indistinguishable from flocculated samples suggesting that the homogeneity achieved during initial sample dispersion was completely lost during coagulation, despite the lower viscosity. At 80 wt% solids content, however, the green densities were greater than those of flocculated samples indicating a degree of homogeneity had been retained in the sample, believed to be associated with the close packing achieved in the dispersed phase.

It can, therefore, be concluded that the approach of initially dispersing a suspension followed by coagulating it could be of potential benefit for the production of viscous pastes suitable for extrusion with a higher degree of homogeneity compared to those prepared by a flocculation route.

References

1. Velamakanni, B. V., Chang, J. C., Lange, F. F. and Pearson, D. S., New method for efficient colloidal particle packing via modulation of repulsive lubricating hydration forces. *Langmuir*, 1991, **6**, 1323–1325.
2. Cesarano, J., Aksay, I. A. and Bleier, A., Stability of aqueous α-Al_2O_3 suspensions with poly(methacrylic acid) polyelectrolyte. *J. Am. Ceram. Soc.*, 1988, **71(4)**, 250–255.
3. Lyklema, J. and Fleer, G. J., Electrical contributions to the effect of macromolecules on colloid stability. *Colloids and Surfaces*, 1987, **25**, 357–368.
4. Williams, P. A., Harrop, R. and Phillips, G. O., The relationship between polyelectrolyte configuration and colloid stability. In *The Effect of Polymers on Dispersion Properties*, ed. Th. Tadros. Academic Press, 1982, pp. 361–377.
5. Davies, J. and Binner, J. G. P., The role of ammonium polyacrylate in dispersing concentrated alumina suspensions. *J. Eur. Ceram. Soc.*, 2000, **20**(10), 1539–1553.
6. Casson, N., A flow equation for pigment-oil suspensions of the printing ink type. In *Rheology of Dispersed Systems*, ed. C. C. Mill. Pergammon Press, 1959, pp. 84-101.
7. Barnes, H. A., Shear-thickening (dilatancy) in suspensions of nonaggregating solids particles dispersed in newtonian liquids. *J. Rheol.*, 1989, **33(2)**, 329–366.
8. Napper, D. H., *Polymeric Stabilisation of Colloidal Dispersions*. Academic Press, 1983, chapters 1,2,4 & 6.
9. Davies, J. and Binner, J. G. P., Plastic forming of alumina from coagulated suspensions. *J. Eur. Ceram. Soc.*, 2000, **20**(10), 1569–1577.
10. Yin, T. K. and Aksay, I. A., Lubricating polymers for powder compaction. In *Ceram. Trans., Ceram. Powd. Sci. IIB, Vol. 1*, ed. G. L. Messing et al., Am. Ceram. Soc., Westerville, 1988, pp. 654–662.
11. Bergstrom, L., Schilling, C. H. and Aksay, I. A., Consolidation behaviour of flocculated alumina suspensions. *J. Am. Ceram. Soc.*, 1992, **75**(12), 3305–3314.
12. Graule, T. J., Baader, F. H. and Gaukler, L. J., Shaping of ceramic green compacts direct from suspensions by enzyme catalysed reactions. *Ceram Forum Int*, 1994, **71**, 317–322.
13. McDermott, A. In situ coagulation moulding of ceramic suspensions, PhD thesis, University of Nottingham.
14. Chang, J. C., Lange, F. F. and Pearson, D. S., Viscosity and yield stress of alumina slurries containing large concentrations of electrolyte. *J. Am. Ceram. Soc.*, 1994, **77(1)**, 19–26.