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Temperature Induced Gelation of Concentrated Ceramic Suspensions: Rheological Properties

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Abstract

Concentrated, sterically stabilised ceramic suspensions have been reversibly gelled by changing the temperature. Using an amphiphilic polymer, Hypermer KD3, as dispersant for alumina and alumina-silicon carbide whisker composite mixtures in pentanol resulted in a transition from dispersed to flocculated state close to room temperature. The collapse of the adsorbed polymer layer with decreasing solvency (temperature) in the marginal solvent pentanol induces flocculation when the long-range van der Waals force overcomes the remaining steric repulsion. Temperature induced gelation (TIG) of concentrated suspensions has a drastic effect on the rheological properties. At temperatures above 30°C, the suspensions have a low viscosity and negligible elasticity. When the temperature is lowered below 20°C, the viscosity increases significantly and the viscoelastic behaviour becomes predominantly elastic. The elasticity and the associated particle network strength are sufficiently high for a highly concentrated gelled suspension to support its own weight. The potential use of TIG as a novel forming method was discussed with relation to other new shaping techniques. © 1999 Elsevier Science Limited. All rights reserved

Keywords: temperature-induced gelation, shaping, suspensions, Al_2O_3, SiC.

1 Introduction

An advanced ceramic material should have a microstructure characterised by a small defect size, other phases well dispersed and a homogeneous grain boundary composition to perform optimally at both room temperature and elevated temperatures. It has been shown that such a material can be obtained only if the powder processing steps are successful in producing a well mixed, homogeneous green body with a high density, minimum density variations and a narrow pore size distribution.[1,2]

Present methods of forming ceramic green bodies of a complicated shape include slip casting, pressure casting and injection moulding. Tape casting is also used to produce thin sheets, mainly for the electronics industry. All of these forming methods start with a suspension where the ceramic particulates, which can be powders, whiskers, platelets, etc., are mixed with a liquid or a polymer melt, a proper dispersant and possibly further additives such as binders, plasticisers, anti-foaming agents so that a well dispersed, non-agglomerated ceramic slurry can be made. This suspension is sometimes subjected to an additional processing step such as sedimentation or filtration to remove large hard agglomerates. In this way, it is possible to obtain a well-mixed suspension with all the large agglomerates removed.

The traditional forming methods are unfortunately plagued by generic problems, which usually leads to poor materials properties and reduced reliability of the sintered materials. Drained casting techniques, e.g. slip casting, pressure casting and centrifugal casting, involve a solid–liquid separation process to form a dense green body. The liquid flow is either driven by an external pressure gradient (slip casting, pressure casting) or a body force in a centrifugal force field (centrifugal casting). The liquid flow will affect the suspension microstructure and tend to orient non-spherical constituents such as whiskers. The stress gradient may also lead to nonuniform densities of the green body[3] and cause mass-segregation due to differences in particle size and density.[4]

Undrained, or constant volume, forming methods such as injection moulding have the potential to avoid the foregoing problems. However, the removal of a high volume of high molecular weight polymer cause many problems including slumping

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and crack formation. The polymer removal time increases drastically when the size of the green body increases and it is difficult to produce parts with thick cross sections.[5]

These problems have led several researchers to suggest alternative forming methods, e.g. gel casting,[6] freeze forming,[7,8] and direct coagulation casting (DCC),[9] which all are characterised by a minimisation of the disturbance of the suspension during the formation of the green body. All of the methods require a well dispersed, highly concentrated suspension of reasonably low viscosity to facilitate the mould filling process. The physical process responsible for the formation of a solid green body differ greatly; gel casting is based on polymerisation of monomer dissolved in the continuous medium, in freeze forming, the temperature is reduced below the freezing point of the continuous medium, DCC utilises the destabilisation of electrostatically stabilised suspensions through an enzyme catalysed pH change to flocculate the concentrated suspension. In addition to these methods, it was recently demonstrated how the reversible destabilisation of a sterically stabilised suspension could be used as a novel forming method called temperature induced gelation (TIG).[10]

Temperature induced gelation (TIG) originates from the incipient flocculation effect of sterically stabilised suspensions. The magnitude and range of the interaction between polymer layers can be related to the solution properties of the polymer and the conformation of the polymer at the solid–liquid interface.[11,12] When the solvency reaches a critical level, the sterically stabilised dispersion flocculates, so called incipient flocculation. Decrease in solvency by temperature change or addition of non-solvent has been utilised in several previous studies to induce flocculation in sterically stabilised concentrated suspensions.[13–15] In principle, all sterically stabilised suspensions should be able to flocculate by making the stabilising moieties insoluble. For many systems, however, this effect is only obtained far from room temperature which makes these systems difficult to apply for ceramic processing.

In this study, we will demonstrate the thermally induced gel formation of Al_2O_3 and composite Al_2O_3/SiC_w suspensions dispersed with Hypermer KD3. This dispersant has proved to disperse a wide range of ceramic powders in non-aqueous liquids.[16–18] Choosing a continuous medium of intermediate polarity, pentanol, results in a transition temperature close to room temperature. We will present adsorption isotherms and report on the solution properties of KD3. The rheological properties (steady shear and viscoelastic) of the concentrated suspensions will be reported and discussed with respect to the application of this method for forming ceramic green bodies.

2 Experimental

2.1 Materials and methods

The alumina powder used in this study was A16SG obtained from Alcoa, USA with an average diameter around 0·4 μm and a specific surface area of 8·0 m^2 g^{-1}. The silicon carbide whisker was obtained from ACMC, Greer, SC, USA with a specific surface area of 3·9 m^2 g^{-1}. The length and aspect ratio of the silicon carbide was determined by cursory inspection of scanning electron micrographs. The whiskers were subjected to a premilling treatment to reduce the aspect ratio, normally being > 40. The premilled whiskers show a large variation in length, from 1 to 50 μm with an average length of 5·7 μm. The average diameter is 0·6 μm; hence, the average aspect ratio is 9·5. The whiskers are oxidised with an oxygen content ~ 0·7 wt%.

Suspensions were prepared in decahydronaphtahlene (decalin)(99+, Aldrich Chemicals), and pentanol (pro analysi, 99+, Merck). Decalin is an optimal non-polar solvent for model studies because of its high purity and low vapour pressure at room temperature (≈1 mbar). Decalin has a density of 0·896 g cm^{-3} and the viscosity was measured as 3·0 mPas at 25°C. Pentanol is an alcohol of intermediate polarity; it has a density of 0·810 g cm^{-3} and the viscosity was measured as a function of temperature (Table 1). We used a commercial block-copolymer, Hypermer KD3, ICI Chemicals, UK as dispersant. Hypermer KD3 consists of two parts; a multifunctional (having both acid and base functions) polar head group which has a high affinity to the powder surface and a non-polar, polyester-type tail which provides the stabilising polymer layer at the solid/liquid interface. The dispersant is polydispersed with an estimated average molecular weight around 3000 from titration measurements. The temperature dependent cloud-point of KD3 was determined in some alcohols of intermediate polarity by visual inspection of 1% KD3 solutions. Adsorption isotherms of KD3 were determined at room temperature by mixing powder and a known amount of dispersant in decalin or pentanol overnight, followed by centrifugation of the suspension and potentiometric titration of the remaining KD3 in the supernatant with an alcoholic potassium hydroxide solution.[16]

Table 1. Temperature dependence of the viscosity of pentanol

T(°C)	*10*	*20*	*30*	*40*	*50*
η (mPas)	5·8	4·3	3·2	2·5	1·9

2.2 Suspension preparation and rheological measurements

Suspensions were prepared by mixing known amounts of dry powder with solvent and dispersant to obtain the desired volume fraction. Prior to suspension preparation, we dried the solvent by storing over molecular sieves and subjected the powder to an overnight vacuum treatment at 120°C to minimise water contamination. All the composite suspensions were prepared at constant composition Al_2O_3/SiC_w (75/25 wt%) equivalent to 30 vol% SiC_w.

The slurries were ultrasonicated (Soniprep 150, MSE Scientific Instruments, UK) in 5 min intervals until no trace of larger agglomerates could be seen on a spatula which had been dipped into the suspension. An ice bath was used to minimise solvent evaporation during ultrasonication. The suspensions were prepared in 25 ml batches to maximise the effect of the ultrasonic treatment. After ultrasonication, the slurries were placed in an Erlenmeyer flask, sealed, and allowed to stir overnight at an elevated temperature, $T \approx 50°C$ (pentanol slurries) or room temperature (decalin slurries), to ensure that no air remained and that the samples equilibrated after ultrasonication.

Rheological (steady shear and oscillatory) measurements were performed with a controlled strain rheometer (Bohlin VOR, Bohlin Instruments, UK) using a couette geometry (bob diameter 25 mm, bob length 37·5 mm, 1·25 mm gap width). The spring constants of the torque bars were calibrated using standard oils. A cell cover supplied by Bohlin Instruments was used to prevent evaporation loss of solvent. Steady shear measurements were performed over a wide range of shear rates by incrementally changing the shear rate and measuring the shear stress after an equilibration time of 60 s at each shear rate. Viscoelastic measurements were performed by applying a sinusoidal strain and measuring the stress and phase shift between the stress and strain. The amplitude was sufficiently small to be in the linear viscoelastic region where the viscoelastic response is independent of strain. Viscoelastic measurements were only performed on the alumina suspensions; the composite suspensions displayed a very complex viscoelastic response with an absence of a measurable linear region making the results difficult to interpret.

3 Results and discussion

3.1 Polymer adsorption and suspension stability.

The adsorption isotherms (Fig. 1) show that the amphiphilic dispersant, KD3, adsorbs strongly on both alumina and SiC whiskers from both decalin and pentanol. The saturation levels, which correspond to monolayer coverage, varies between $\Gamma_m \approx 10–12$ mg m^{-2} for alumina to $\Gamma_m \approx 5$ mg m^{-2} for the silicon carbide whiskers. This difference in adsorbed amount implies a corresponding difference in specific site density of the SiC whiskers and Al_2O_3 since the multifunctional headgroup ensures strong adsorption to most hydrophilic ceramic surfaces.[16–18]

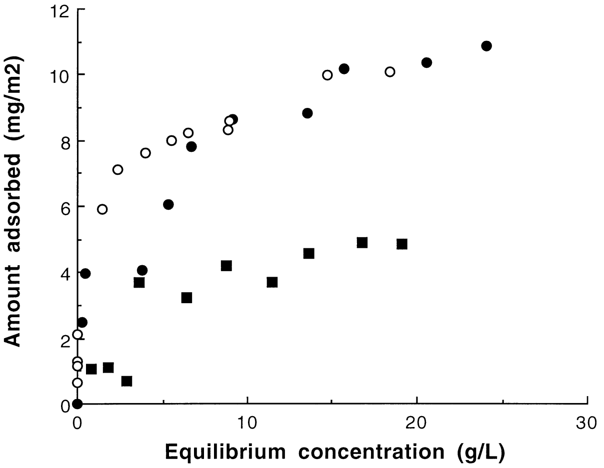

Fig. 1. Adsorption isotherms of Hypermer KD3 on Al_2O_3 (●) and SiC_w (■) from decalin; and on Al_2O_3 from pentanol (○).

In general, the magnitude and range of the polymer induced steric repulsion is determined by the solvent quality, the strength of adsorption, the layer thickness and density.[11,12] For a diblock dispersant like KD3, the strong interaction between the headgroup and the surface ensures a strong attachment while the essentially nonpolar tail that protrudes into the solvent provides a polymer induced or steric repulsion. The effect of surface coverage of KD3 on the rheological properties of alumina suspensions in decalin was investigated in a earlier study.[17] It was found that a minimum surface coverage corresponding to 2·5–3 wt% KD3 is needed to obtain a colloidally stable suspension. This amount is substantially lower than the maximum adsorbed amount (~ 8 wt%) which suggests that an efficient steric repulsion can be created at a rather low surface coverage. In this study, an addition of 4·5 wt% KD3 was used to prepare the alumina suspensions which ensures a sufficiently high surface coverage. For the silicon carbide whiskers, an addition of 2 wt% was used; this corresponds to the maximum adsorbed amount from the adsorption isotherms.

Providing that the adsorbed polymer layer is strongly adsorbed and that the surface coverage is sufficiently high, we expect the particle interactions to be mainly controlled by the solvent quality. In decalin, which is a good solvent for the stabilising moieties, KD3 provides colloidal stability to suspensions of Si_3N_4,[16] Si[18] and Al_2O_3.[17] However, SiC whisker suspensions were weakly flocculated, probably due to the vdW interactions being of longer range than the steric repulsion.[17] This effect points to another requirement for efficient polymeric stabilisation of colloidal suspensions; the adsorbed polymer layer should be thick enough to prevent the particles from approaching close enough for the van der Waals force to generate a net attraction. Apparently, the KD3 layer thickness is sufficient to stabilise the equiaxed, submicron alumina particles but too thin for the long, relatively thick silicon carbide whiskers. Direct measurements of the interaction range of adsorbed KD3 layers in decalin[19] corroborates this conjecture. The measurements indicate a layer thickness in the order of 9–15 nm[19] which is too thin to overcome the van der Waals attraction between two silicon carbide rods but sufficient to stabilize the small alumina particles.

Changing the solvent to pentanol, which is a more polar solvent than decalin, resulted in a temperature sensitive colloidal stability. The alumina suspensions were stable above 30°C while they flocculated at temperatures below 30°C. This is easily observed in dilute suspensions where the onset of flocculation increases the settling rate dramatically. The SiC whiskers are flocculated at all temperatures, becoming more strongly flocculated as the temperature is lowered. The decrease in solvency when lowering the temperature of KD3 stabilised suspensions in alcohols of intermediate polarity affects both the magnitude of the free energy of mixing, ΔG_m, upon polymer layer overlap, and the conformation and thickness of the adsorbed polymer layer. The decrease in the magnitude of the polymer-induced repulsion with solvency can be estimated from the temperature scaling of ΔG_m

$$\Delta G_m \propto \left(1 - \frac{\theta}{T}\right) = \frac{\Delta T}{T} \tag{1}$$

where θ denotes the temperature where ΔG_m becomes zero. This relation shows that thermodynamically limited flocculation is expected close to the θ-temperature where ΔG_m becomes very small and eventually changes sign.

Comparing cloud points for KD3 solutions in various alcohols with the flocculation temperature of dilute suspensions of alumina particles dispersed with KD3 in the respective solvents should give some guidelines regarding the dominating cause of the observed temperature induced flocculation. We find that both the cloud point, T_c, and the flocculation temperature, T_f, increases with decreasing polarity of the solvent; hence, the higher alcohols are better solvents for KD3; in pentanol, T_c and T_f are -7 and 30°C, respectively while in butanol $T_c = 7$°C. Using the cloud point measurements at one polymer concentration as a crude estimate of the θ-temperature, the large difference between T_c and T_f in pentanol, $\Delta T \approx 40$°C, indicates that the dispersion flocculates in significantly better than θ-solvent conditions.

These results suggest that the major cause for flocculation in the KD3-stabilised alumina system is not a decrease in the magnitude of the polymer induced repulsion but originates in the van der Waals forces between the alumina particles acting beyond the polymer layers. A lowering of the temperature of the pentanol system decreases the degree of solvation of the polymer which causes the attached polymer chains on the particle to coil up. Hence, the polymer layer thickness will decrease and at some critical point, the total interparticle force will change from repulsive to attractive and thus result in flocculation of the suspension (Fig. 2). In a recent study on a system consisting of submicron alumina particles dispersed with poly(12-hydroxy stearic acid) in hexanol, we found a similar behaviour.[20] Simple estimates of the range and magnitude of the attractive van der Waals forces and the steric repulsion suggested that the interparticle well depth at low temperatures were on the order of 5–10 kT.

3.2 Rheological properties and gel formation

The effect of temperature on the rheological properties of a concentrated alumina suspension in pentanol are displayed in Figs 3 and 4. The viscosity of the suspension, η, can be normalised with respect to the viscosity of the medium, η_s, by using the relative viscosity, η_r, defined as

$$\eta_r = \eta / \eta_s \tag{2}$$

Using this expression, a direct comparison between suspension dispersed at different temperatures can be made.

The steady shear properties, Fig. 3, for the pentanol suspension at 30°C and the reference, temperature independent, decalin suspension at a slightly higher volume fraction, are closely related; both suspensions display a relatively weakly shear

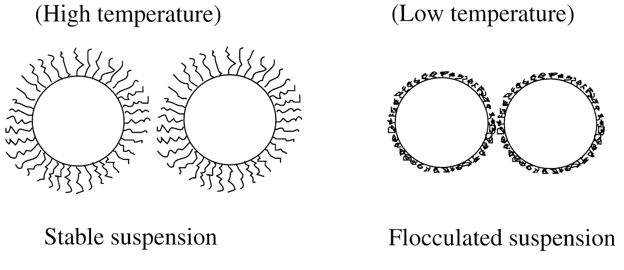

Fig. 2. Schematic figure describing the mechanism behind temperature induced flocculation of sterically stabilised suspensions.

thinning behaviour approaching a constant viscosity at high shear rates, characteristic for a highly concentrated, stable suspension. The slightly higher relative viscosity for the decalin suspension can be explained by a somewhat higher volume fraction; the viscosity is a very strong function of volume fraction at these concentrations.

When the temperature of the pentanol dispersion is lowered to 10°C, both the relative viscosity and the degree of shear thinning increases significantly. This change of the steady-shear properties is directly related to the temperature induced flocculation of the pentanol suspension. When the particles aggregate, clusters form in the suspension which immobilise some of the continuous medium. With increasing shear, the clusters are broken down to smaller and smaller units, thus releasing the immobilised liquid. At high shear rates, there is only a small difference in viscosity between the stable and flocculated suspensions, suggesting that the clusters are nearly destroyed by the shear forces. At low shear rates, however, there is a large difference in relative viscosity, with the pentanol suspension at 10°C displaying a higher viscosity than the pentanol suspension at 20°C. This supports the notion that a lower temperature corresponds to a stronger flocculation.

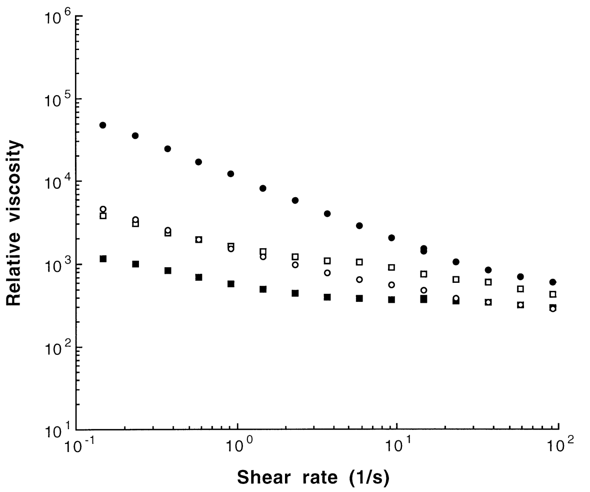

Fig. 3. Steady shear relative viscosity of an Al_2O_3 suspension at 50 vol% in pentanol with 4·5 wt% KD3 added at different temperatures; $T = 30°C$ (■), $T = 20°C$ (□), $T = 10°C$ (●). As a reference, the steady shear behaviour of an Al_2O_3 suspension in decalin at 50·4 vol% is also included (○).

Oscillatory measurements at small deformations offer an alternative, less destructive, method for probing the temperature induced gelation. At a sufficiently high volume fraction of particles, and sufficiently strong interparticle attraction, a space filling gel will form. The gel transition, and the mechanical properties of the particle networks, can easily be probed by measuring the mechanical properties while continuously lowering the temperature at constant volume fraction. The viscoelastic measurements, Fig. 4, show that the alumina suspension changes from being predominantly viscous at high temperature to displaying a strongly elastic behaviour at lower temperatures. The magnitude of the storage modulus, G', increases strongly and G' becomes less dependent on frequency with decreasing temperature. At temperatures $T < 10°C$, only minor changes in the viscoelastic response could be detected. This suggests that the KD3 can not collapse further although the solvency is decreased. It should be noted that decreasing the temperature even below the cloud point ($T_c \approx -7°C$) does not affect the viscoelastic properties significantly.

Figure 5 shows how the particle gel responds to an increasing amplitude of the oscillation. In accordance with previous studies, we find that stronger gels also are more brittle; the maximum strain a gel can take before it breaks decreases with

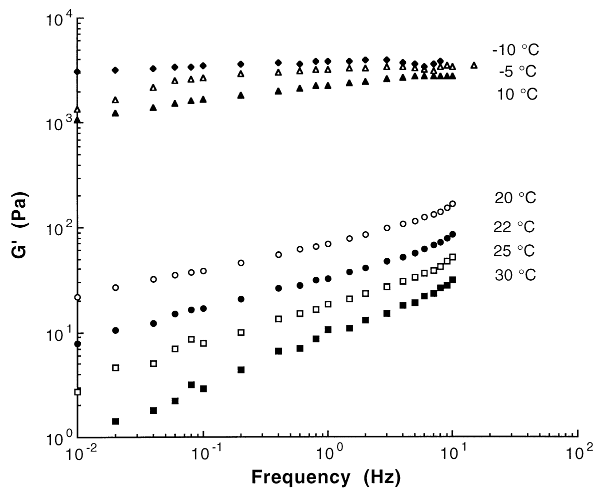

Fig. 4. Effect of temperature on the storage modulus, G', of an Al_2O_3 suspension at 50 vol% in pentanol.

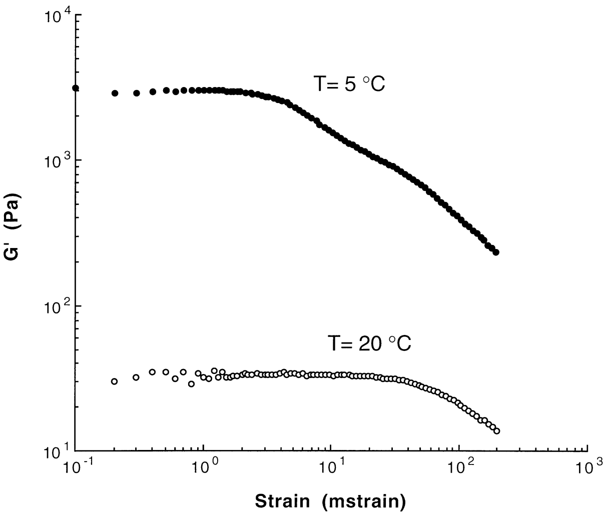

Fig. 5. Strain sweep tests of an Al_2O_3 suspension at 50 vol% in pentanol at $T = 5°C$ (●), and $T = 20°C$ (○).

decreasing temperature.[20,21] For all the oscillatory measurements, a low strain well within the linear viscoelastic region was used.

These rheological measurements correlate nicely to simple test tube experiments where a concentrated alumina suspension in pentanol changes from being easily flowable at 30°C to showing only a very slow plastic flow when turned upside down at 0°C. Increasing the temperature back up to 30°C results in a break-up of the particle gel and the flowable state is retained. This reversible effect is a manifestation of the change in the interparticle forces, from being repulsive at high temperature to becoming increasingly more attractive when the temperature is lowered. Hence, the results clearly illustrate that a drastic change of the rheological properties can be obtained when the temperature is changed a mere 30°C.

Preliminary tests of making green bodies based on the TIG method suggest that the inferred strength (yield stress) is sufficiently high to allow a moulded particle gel to be handled without shape distortion. Not surprisingly, we found that the wet body strength is a strong function of the solids loading; it is necessary to maximise the solids loading to obtain sufficiently strong wet green bodies. The gelation rate appears to be relatively fast being mainly controlled by the heat transfer from the body to the mould. Using the crude method of putting a brass mould containing the suspension into the freezer, we were able to mould simple rectangular shapes with characteristic dimensions 10–15 mm within a period of 20 min. With a more optimised mould design and cooling system, it should be possible to decrease the moulding time substantially.

Changing the solid material from equiaxed alumina to a composite containing rod-like whiskers does not change the nature of the temperature dependent effect to any significant degree. Figure 6 shows that the relative viscosity increases with decreasing temperature, in accordance with the results on the alumina suspensions in pentanol. At temperatures $T > 30$°C, the reduction in viscosity becomes rather small and can almost entirely be referred to the temperature dependency of the pentanol viscosity. The relative viscosity of the pentanol suspensions at $T > 40$°C is almost identical to the decalin suspension.

Figure 7 shows the volume fraction dependence of the relative viscosity for composite suspensions. The high shear data for composite suspensions suspended in decalin are taken from an earlier study[17] while the data in pentanol at 30 and 50°C are from this study. The experimental points of the decalin data were fitted to a an empirical expression relating the relative viscosity to the volume fraction of solids, ϕ

$$\eta_r = (1 - \phi/\phi_m)^{-n} \quad (3)$$

where ϕ_m is the maximum volume fraction; both ϕ_m and n are used as fitting parameters. The best fits were obtained with $\phi_m = 0{\cdot}58$ and $n = 3{\cdot}3$, suggesting that relatively high volume fractions should also be attainable in this complex system. The viscosity data for composite pentanol suspensions falls right on the data from the decalin suspensions, thus supporting our previous conclusion that pentanol is as good a solvent as decalin for KD3 at these high temperatures.

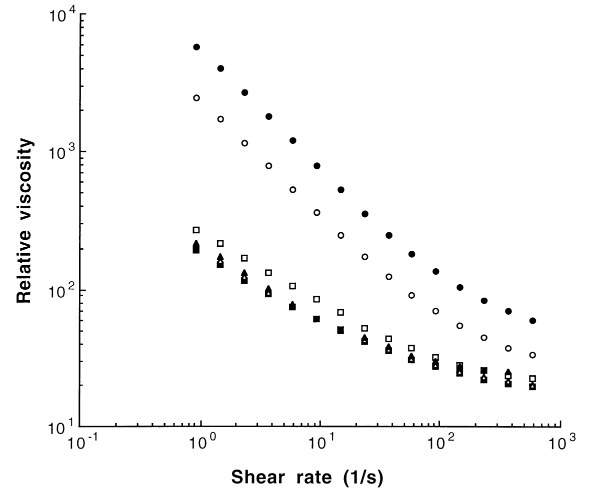

Fig. 6. Steady shear relative viscosity of a composite suspension at 34·5 vol% solids in pentanol at different temperatures; 10°C (●), 20°C (○), 30°C (□), 40°C (■), 49°C (△). As a reference, the data for an composite suspension in decalin at 25°C is also included (▲).

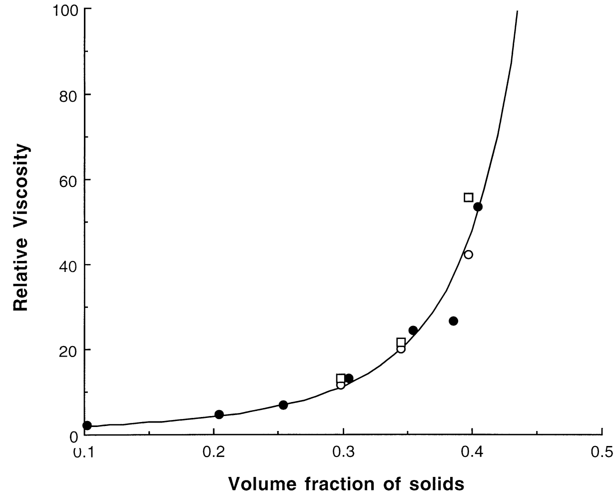

Fig. 7. Relative viscosity versus volume fraction of solids for composite suspensions in decalin (filled symbols) and pentanol at 30°C (○), and 50°C (□). The solid curve is the best fit to eqn (3).

4 Summary and conclusions

The colloidal stability, and thus the rheological behaviour, of sterically stabilised ceramic powder suspensions can be controlled by temperature providing that an appropriate combination of dispersant and solvent is chosen. It was demonstrated that alumina and alumina-silicon carbide whisker suspensions dispersed with Hypermer KD3 in pentanol display such a reversible temperature induced aggregation. At high temperatures, $T > 30°C$, the alumina suspension is well stabilised and have a low viscosity. When the temperature is lowered below 20°C, the viscosity increases significantly. Oscillatory measurements at small deformations show that the viscoelastic behaviour changes from predominantly viscous at high temperatures to a solid-like response at $T < 20°C$. The particle network strength is sufficiently high for a highly concentrated gelled suspension to support its own weight.

Temperature induced flocculation (TIG) of sterically stabilised suspensions has the potential to form the basis for a simple and versatile method to form ceramic green bodies of complex shape. The tuneable interparticle force makes it possible to keep a dense suspension in a fluid state (repulsive forces) during mould filling and then turn on the attraction by changing the temperature to form green bodies with sufficiently high strength. There are several benefits of this novel forming method: the forming method is reversible, hence, it is possible to remould a part, and green bodies are formed in the mould with negligible volume change, hence, the particle microstructure is subjected to a minimum disturbance during shaping. In many respects are TIG similar to another novel forming method—DCC. Both TIG and DCC utilises the introduction of strongly attractive interparticle forces to create a strong particle network, the major difference, however, is that TIG is a reversible process while DCC is irreversible.

Acknowledgements

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