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A new approach to prepare highly loaded aqueous alumina suspensions with temperature sensitive rheological properties

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Abstract

Poly(acrylic acid) (PAA)-free alumina suspensions with temperature sensitive rheological properties have been successfully produced using the combination of tri-ammonium citrate and magnesium citrate powders with slurry loading up to 60 vol.%. A new approach using the DLVO concept is proposed to design the suspension composition. Both the shear viscosity and the shear modulus of the suspensions start to increase when the suspension temperature is above a critical value. The flocculation of the suspensions is controlled by the dissolution of the magnesium citrate that increases the ionic strength in the suspensions. The dissolution is controlled by the pH of the suspensions, which decreases with increasing temperature. Compared with the same solid loading suspensions containing PAA, the suspension shear viscosity of 25 °C can be reduced, which is useful in developing new near net shape forming technologies.

Keywords: Al_2O_3; Colloidal processing; DLVO; Gelation; Suspensions; Viscoelastic properties

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1. Introduction

Temperature-sensitive ceramic slurries can be used to fabricate complex-shaped ceramic parts.[1] Temperature Induced Coagulation Casting (TICC),[2] Temperature Induced Gelation (TIG)[3,4] and Temperature Induced Forming (TIF)[5–8] are new near-net-shape ceramic forming techniques that utilize temperature sensitive slurries to induce physical gelation. The common point of these three techniques is the use of polymers to cause flocculation. For the TICC process, the electrosterically stabilized slurry with a minimum amount of polymer dispersant for colloidal stabilization can be flocculated by increasing temperature. The flocculation might be due to the entropy driven increase in polymer adsorption, which suggests that the amount of polymer required for full coverage increases with temperature. Since there is no additional free polymer in solution, the only way to fill the empty sites is by bridging. Therefore, flocculation occurs at elevated temperatures for slurries that have an exact balance of adsorbed polymer. In the case of excessive polymer addition, no flocculation is observed. Limitation for this technique is to use maximum solid loading because the process requires a precise control of the polymer dispersant concentration.[2] Temperature induced gelation (TIG) originates from the incipient flocculation effect of sterically stabilized 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. When the solvency reaches a critical level, the sterically stabilized dispersion agglomerates, so called incipient flocculation. Decrease in solvency of the polymer by temperature change or addition of non-solvent has been utilized in several previous studies to induce flocculation in sterically stabilized concentrated suspensions. TIG produces a fully reversible gel and the gelled saturated bodies must be kept at the solidification temperature to avoid slumping. In principle, all sterically stabilized suspensions should be able to flocculate by making the stabilizing moieties insoluble. For many systems, however, this effect can only be obtained far from

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room temperature, which makes these systems difficult to apply for ceramic processing.[3,4]

Temperature induced forming (TIF) requires a small molecular weight dispersant, i.e. tri-ammonium citrate (TAC) and a larger molecule or polymer, i.e. polyacrylic acid (PAA), as gelling agent. TIF slurry is stabilized at room temperature through electric-double-layer stabilization by the adsorption of citrate anions on the ceramic particle surface. Bridging flocculation of the suspensions can be induced at elevated temperature.[5–8] The strength of the TIF wet gelled body is strong enough to be handled at room temperature and the gelation is irreversible, while the gelled body in the TIG process shows reversible transformation, i.e. from gelation-like state at the solidification temperature that is below room temperature (RT) to fluid-like state again at RT. The reduction of the amount of organic additives (less than 0.5 wt.% of the dry ceramic powder) also permits the elimination of the burnout procedure before sintering. It seems that PAA is a critical component in the TIF of alumina suspensions because it causes bridging flocculation and gel the slurry at elevated temperatures.[8] Our results show that not only the slurry loading increases the viscosity,[8] but also increases in the amount of PAA or its molecular weight. When the slurry loading is 60 vol.% and the amount of PAA (molecular weight of 50,000) is 0.04 wt.%, the room temperature viscosity at 0.1 s^{-1} shear rate is >20 Pa s, which yields a suspension that does not flow easily. Industry needs high solid loading slurries with relatively low viscosity for direct casting in order to fill nonporous molds fast and sufficiently. Therefore, an alternative route must be found to overcome this obstacle.

DLVO (Derjaguin-Landau-Verway-Overbeek)[9] theory proposes that the particles in the suspension may attract one another either when the electric double layer (EDL) is compressed at high ionic strength, or when the net particle surface charge is small at a pH value that is close to the isoelectric point. The dominance of the attractive van der Waals force will cause the suspension to flocculate. The flocculation of the suspension can be accelerated when the counterions are bivalent or trivalent metal ion complexes, which will result in enhanced compression of the EDL thickness. The thickness is commonly identified with the Debye length, which is the inverse of the Debye parameter, κ:

$$1/\kappa = (\varepsilon\varepsilon_0 kT/I)^{1/2} (\text{for } 1{:}1 \text{ electrolyte}) \tag{1}$$

$$I = e^2 \sum \left(n_i z_i^2\right) \tag{2}$$

where e is the electronic charge, n_i the concentration of ions with charge z_i, ε the dielectric constant of the liquid, and ε_0 the permittivity of a vacuum.[9–12]

To increase the ionic strength and flocculate the suspensions, divalent metal salts with concentration of more than 0.01 M (molar/l) are typically required. The challenge is that such an amount of metal salts will cause flocculation of the suspension during the slurry preparation process. As a result, salts containing bivalent metal ions that are insoluble at room temperature but can release the metal ions into solution at elevated temperature would be good candidates. The authors find that magnesium citrate fulfills these requirements. Magnesium citrate powder is observed to have minor dissolution in water at RT when $\mathrm{pH} > 10$, but dissolves completely in water when the pH is decreased to pH 8.0. Magnesium citrate powders carry a negative surface charge at high pH that is reflected in a negative zeta potential (Fig. 1). The dissolution of magnesium citrate in water at lower pH will increase the ionic strength in the suspension. Furthermore, magnesium ions will form oxides on sintering and can be used as sintering aids for alumina. Therefore, magnesium citrate is chosen as a gelling agent to substitute PAA.

2. Experimental procedure

The raw materials used in this research are AKP53 alumina powders (Sumitomo, Japan), tri-ammonium citrate (TAC) powders (Aldrich, USA), polyacrylic acid (PAA) (25 wt.% solution in water with average molecular weight of 50000, Polyscience, Niles, IL, USA), and magnesium citrate powders (Alfa Aesar, USA). The chemical formula of magnesium citrate is $MgC_6H_6O_7$. TAC powder is used as dispersant in the slurry and the adsorption of citrate ions on the alumina surface gives a net negative surface charge and potential so that EDL stabilization is yielded. The TAC powder is soluble in water at pH >7. The amount of the TAC in the suspension is fixed to 0.4 wt.% of the dry alumina particles because a fully covered surface can be obtained at this amount, which yields minimum shear viscosity in rheological measurements.[8] The amount of the magnesium citrate is taken as molar percent of the dry alumina particles. The amount of PAA is taken as weight percent of the dry alumina particles.

A planetary ball mill (Fritsch, Pulverisette 5, Idar-Oberstein, Germany) was used to mix the starting materials homogeneously with alumina mill containers and zirconia mill balls (10 mm diameter, E.R. Advanced Ceramics, Inc. East Palestine, OH). The size of the mill container is 105 (outside diameter)×75 (inside diameter)×75 mm (height of the inside cavity). There are 30 mill balls in each container. For the suspensions without PAA, the exact designed amount of the alumina powder, TAC powder and magnesium citrate powder are ball-mill mixed in deionized water at a speed of 250 rpm for 40 min, and the pH of water is adjusted to ~pH 10.5 using ammonium hydroxide (20%, LabChem Inc, USA) before ball milling. The pH of the resultant

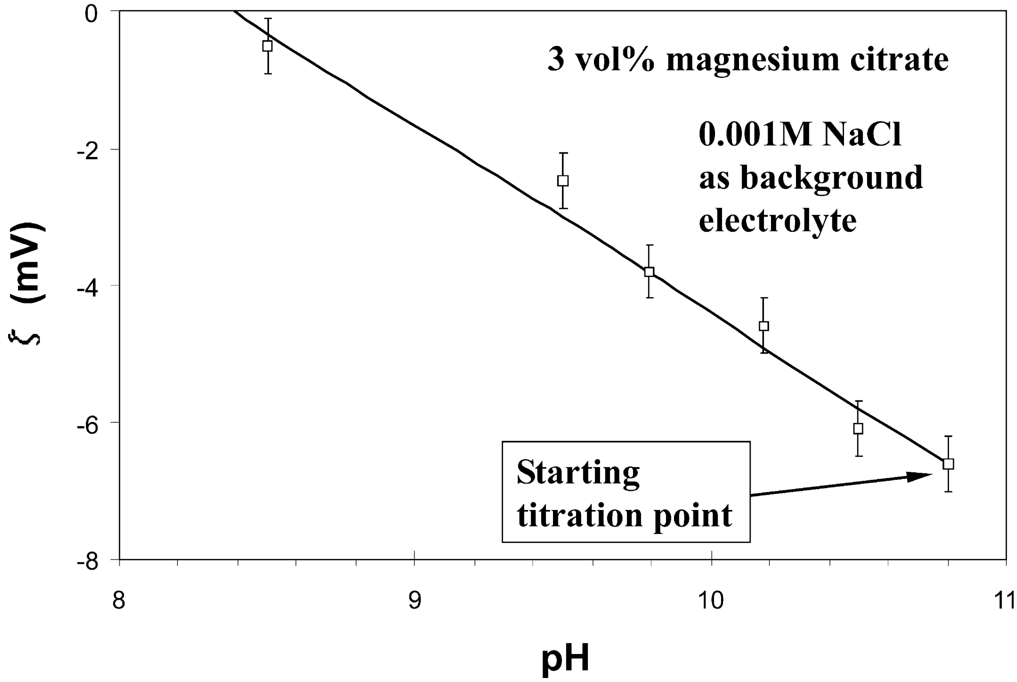

Fig. 1. Variation of ξ potential with pH for the 3 vol.% magnesium citrate powders in water. The titration is conducted at 25 °C from pH 10.8 to pH 8.5 using 1 N HCl acid. The ξ potentials shrink when the pH of the suspension decreases.

suspension is checked and adjusted to pH 10.0 using a 20% ammonium hydroxide solution. Finally the suspensions are transferred into a beaker and stirred for another 2 h before conducting measurements. For the PAA containing suspensions, the exact designed amount of the alumina powder, TAC powder and 0.04 wt.% PAA are ball-mill mixed in deionized water (pH is adjusted to ~pH 10.1 using the 20% ammonium hydroxide solution) at a speed of 250 rpm for 40 min.

The shear viscosity is measured using a Modular Compact Rheometer (MCR 300, Paar Physica) with a concentric-cylinder measurement system (CC27), the inner cylinder having a diameter of 27 mm. Steady state shear flow curves are measured at a shear rate range between 0.1 and 1030 s^{-1}, the duration between measuring points is 15 s and each measurement lasts 6 min. The temperature ramp rotation mode is used to measure the temperature dependence of the slurry viscosity. The shear rate is set at 20 s^{-1}, and the temperature is raised at a rate of 1 °C/ min with a starting temperature of 25 °C. The final temperature is 85 °C and a total of 60 points are recorded for each sample. The temperature dependence of the storage and loss modulus are measured using the temperature ramp oscillation mode at a fixed shear strain amplitude and a fixed frequency, and the temperature ramp of 1 °C/ min. The starting and final temperatures are 25 and 85 °C, respectively. Typically, ceramic slurries require a longer relaxation time so that the shear modulus of the slurry remains relatively invariant at high frequencies.[13] Experiments showed that a frequency of 1 Hz is sufficient to satisfy the requirements for the present ceramic system. Our experimental results show that the slurry is in the linear viscoelastic region at a frequency of 1 Hz at 1% strain amplitude. During the temperature ramp rotation or oscillation measurements, a thin layer of vegetable oil is used to cover the slurry surface to prevent the evaporation of the dispersing medium, i.e. water. For the measurements of the concentration of magnesium ions, six 100 ml beakers are filled with 40 ml DI water (R~18.2 MΩ), and the pH is adjusted by 30 wt.% potassium hydroxide (LabChem Inc., USA) to pH 11.2, 10.8, 9.8, 8.9, 8.3, 7.6, respectively. Then 0.404 g of magnesium citrate is dispersed into each beaker while stirring. After stirring for 24 h, the above suspensions are centrifuged in PE tubes (Centrifuge 5810, Eppendorf) at 3600 rpm for 1.5 h. The clear supernatants are drawn out carefully and diluted using DI water. The Mg^{2+} concentration in the supernatant is measured using ICP Emission Spectroscopy (Perkin-Elmer, Optima 3200 RL).

3. Results

3.1. *Effect of the amount of magnesium citrate on shear viscosity*

The shear viscosity (at a shear rate 20 s^{-1}) of the 40 vol.% AKP53 alumina suspensions started to increase when the temperature is above 80 °C when the amounts of magnesium citrate powders are 0.01 and 0.02% (molar percent). But below 80 °C, the suspension viscosity decreases with initial temperature increase, similar to the PAA addition suspensions.[8] This viscosity decrease is thought to be due to the viscosity decrease of water with temperature, as can be described in the following expression that is fitted to data from the CRC Handbook, $\eta_{\mathrm{Water}} = 0.0017 - (4.73\times10^{-5})\ T + (7.45\times10^{-7})\ T^2 - (6.25\times10^{-9})\ T^3 + (2.13\times10^{-11})\ T^4$, where T is the temperature of the suspension with the unit of degree centigrade (°C). Fig. 2 gives the variation of the relative viscosity with temperature for these suspensions in order to remove the effect of the solvent. It can be seen that the relative viscosity does not vary with temperature up to 80 °C for slurries with 0.01 and 0.02% magnesium citrate powders. For the suspension containing 0.05% magnesium citrate powders, its relative viscosity starts to increase from 30 °C. It is proposed that weak agglomerates may start to form at a lower temperature in the suspension with 0.05% magnesium citrate powders, which has a small magnitude negative ζ potential at 25 °C (Fig. 1). When the shear rate increases, these weak agglomerates can be broken up so that the suspension yields shear thinning behavior, as shown in Fig. 3.

3.2. Effect of slurry loading on the steady shear flow character

Fig. 4 gives the steady shear flow curves for the 0.02% magnesium citrate addition suspensions with different volume fractions of alumina. The 60 vol.% suspension with 0.4% TAC and 0.04% PAA (Mw ~50,000) are also shown. It seems that the suspension shows enhanced shear-thinning when the volume fraction of particles is increased. If the suspension were to form weak agglomerates, then a shear-thinning behavior is expected at small shear rates because of breaking down agglomerates under shear. Therefore, from the shear flow data, it can be concluded that the 40 vol.% alumina suspensions with 0.01 and 0.02% magnesium citrate powders do not have a significant amount of agglomerates in the as prepared state (Fig. 3). When the slurry loading is above 50 vol.%, agglomerates start to form after the preparation of the suspensions. Comparing the same volume fraction suspensions, it can be concluded that introducing magnesium citrate powder instead of PAA can dramatically decrease the shear viscosity in the low shear rate range, which is favorable for industrial applications of direct casting. The relative viscosity data of the alumina suspensions with 0.4 wt.% TAC and 0.02 mol% magnesium citrate powders can be fitted by the expression, $\eta_r = (1-\phi/0.72)^{-2.5\times0.72} + (130\phi - 41)$, in the whole experimental slurry loading range, as is shown in Fig. 5, where ϕ is the volume fraction of alumina in the suspension. The first part of the expression is the modified Dougherty–Krieger (D-K) equation with the fitting parameters of $[\eta] = 2.5$ and $\phi_m = 0.72$. The

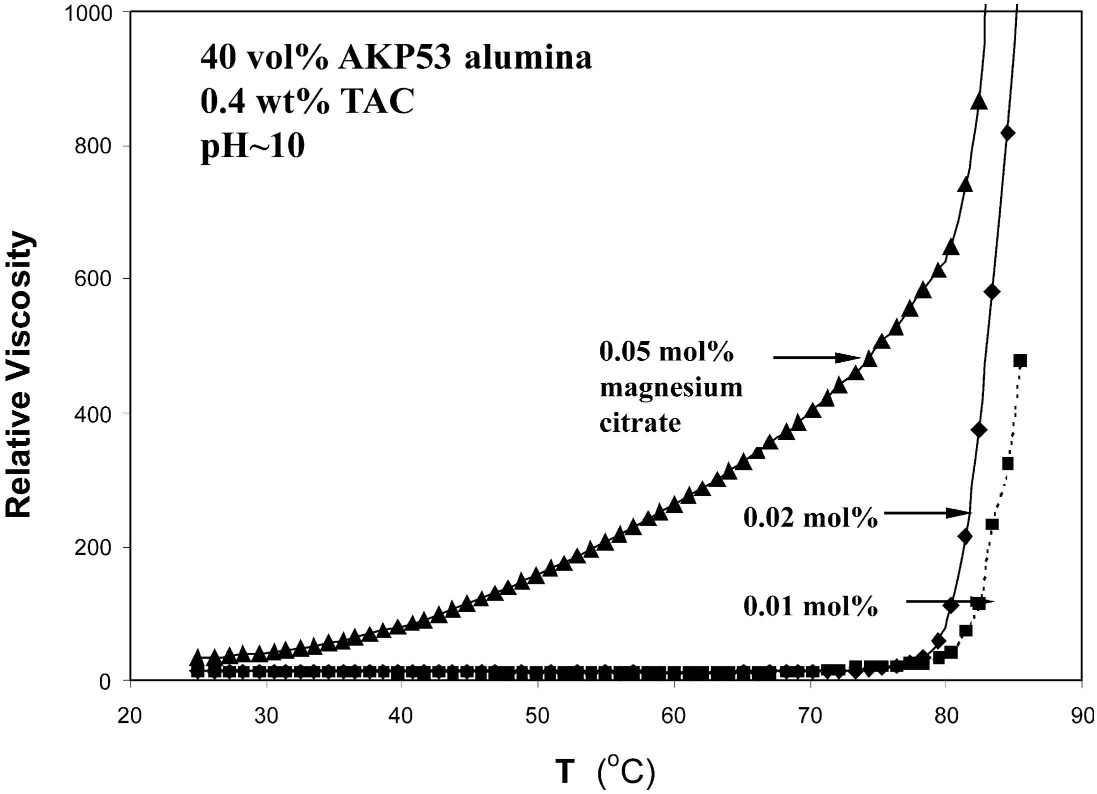

Fig. 2. Effect of the amount of magnesium citrate on the temperature dependence of the relative viscosity of 40 vol.% AKP53 alumina suspensions. The here presented relative viscosity is defined as the ratio of the measured viscosity at a shear rate of 20 s^{-1} divided by that of water at each temperature point. Starting pH = 10, with pH decreasing with increasing temperature.

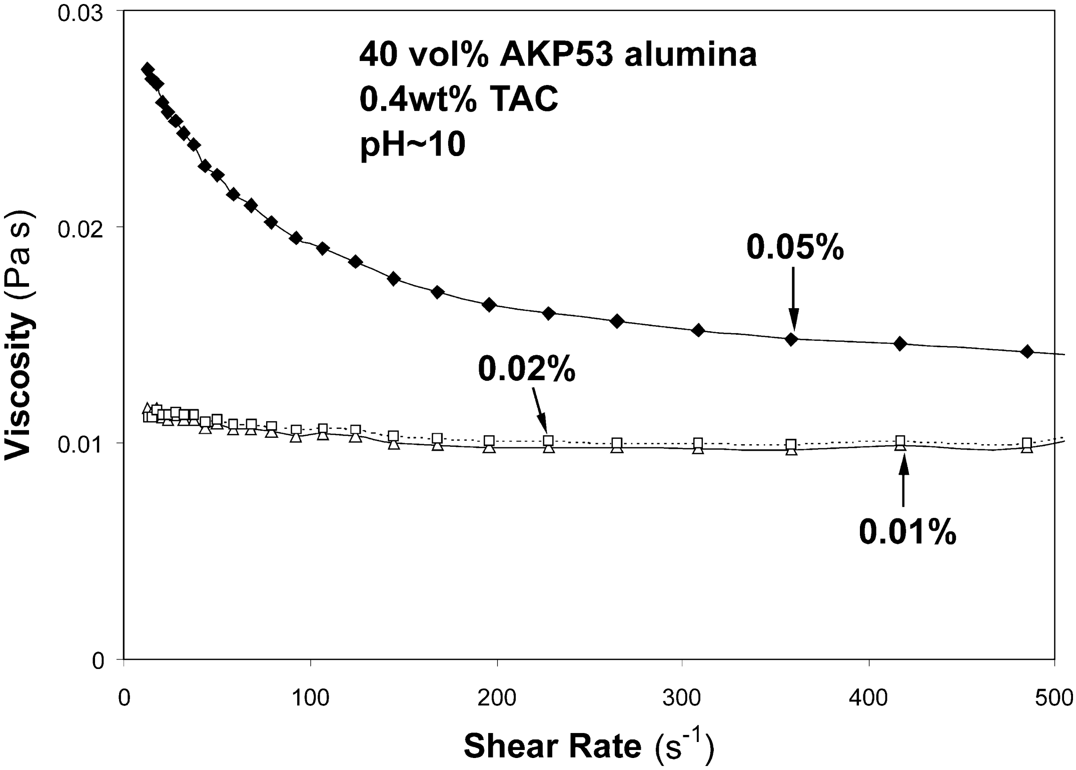

Fig. 3. Steady shear flow (at 25 °C) of the same amount magnesium citrate containing 40 vol% alumina suspensions as in Fig. 2. All suspensions contain 0.4 wt.% TAC. All three suspensions show shear-thinning behavior at low shear rates.

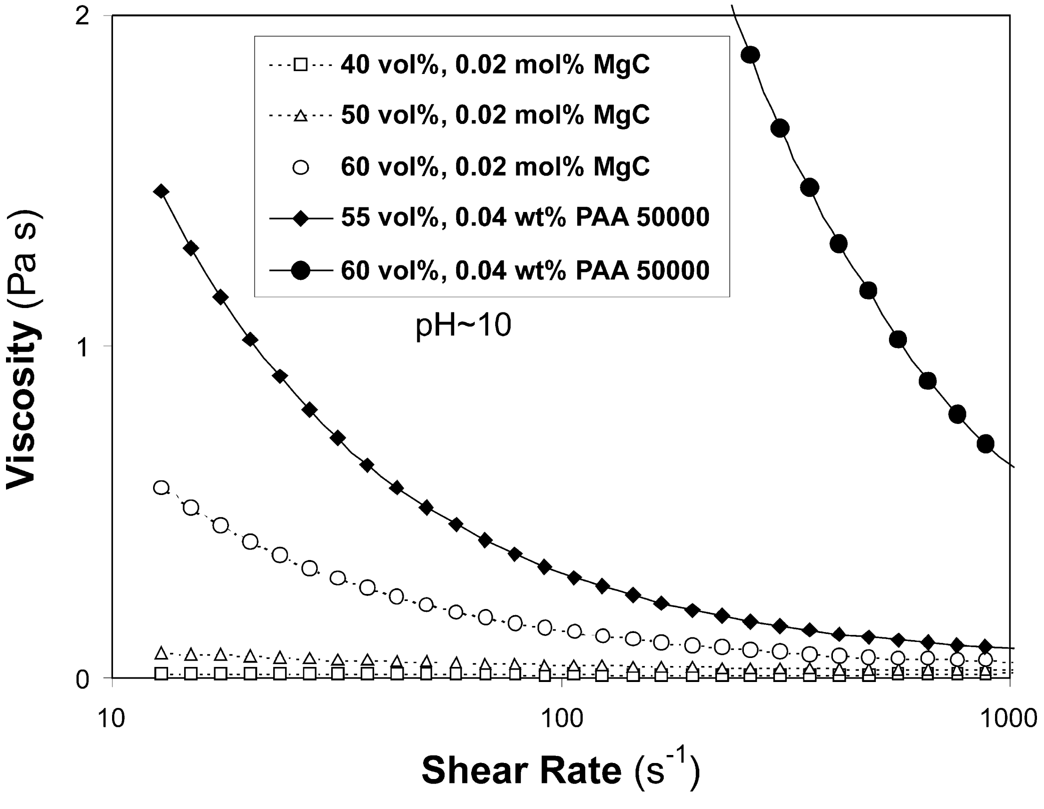

Fig. 4. Steady shear flow curves (at 25 °C) for the 0.02 mol% magnesium citrate (MgC) containing suspensions with different volume fractions of alumina. All suspensions also contain 0.4 wt.% TAC. The 55 and 60 vol.% suspensions with 0.4% TAC and 0.04% PAA (Mw ~50,000) are also shown.

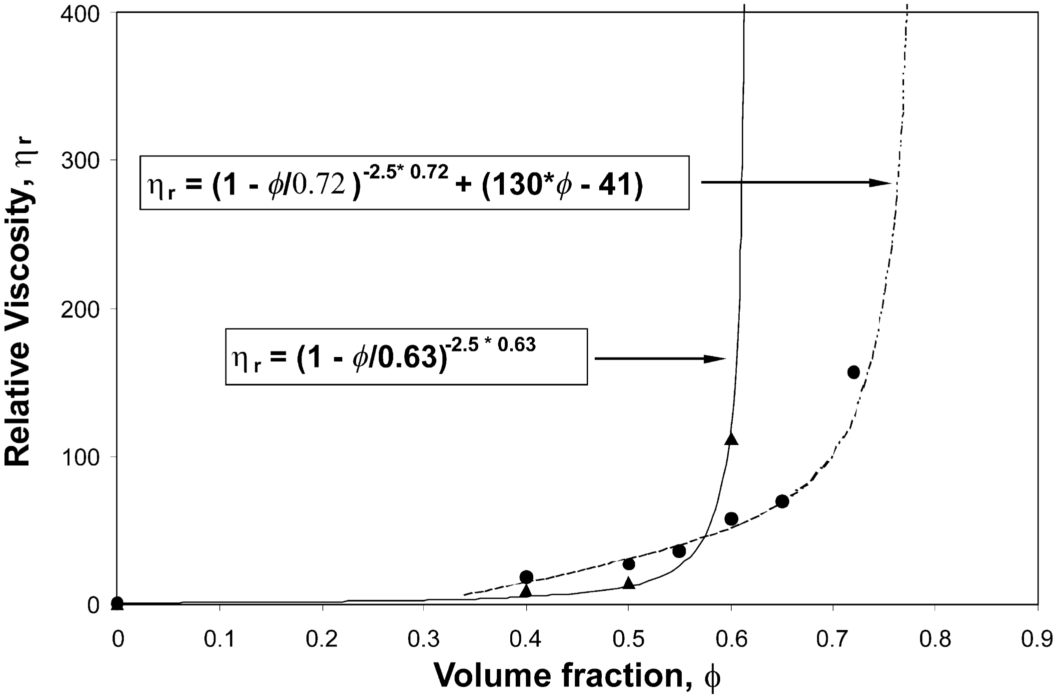

Fig. 5. Variation of the relative viscosity (at shear rate of 1030 s^{-1} and 25 °C) with the volume fraction of alumina for the suspensions with 0.4 wt.% TAC only (▲) and the suspensions with both 0.4 wt.% TAC and 0.02 mol% magnesium citrate (●). The modified Dougherty–Krieger equations (lines in the figure) are used to fit the experimental data (symbols). The relative viscosity is defined as the ratio of the measured suspension viscosity to that of water at the same temperature.

D-K equation is $\eta_r = (1-\phi/\phi_m)^{-[\eta]\,\phi_m}$, where ϕ_m is the maximum packing fraction. The physical meaning of the linear part, $(130\phi - 41)$, is still under investigation. Comparatively, for the alumina suspensions with 0.4 wt.% TAC only, the relative viscosity data can be fitted well to the D-K equation with $[\eta] = 2.5$ and $\phi_m = 0.63$.[8]

3.3. Variation of the shear viscosity with temperature and slurry loading

Fig. 6 shows the effect of volume fraction of alumina on the temperature dependence of the viscosity for suspensions with 0.02% magnesium citrate. A higher suspension viscosity in the lower temperature range is observed with increased volume fraction of alumina, which might be due to the extensive overlapping of the electric double layers. The temperatures where the slurry viscosity starts to increase significantly are at about 80, 70 and 55 °C for the 40, 50 and 60 vol.% suspensions, respectively.

3.4. Variation of the shear modulus with temperature

Experimental data in Fig. 7 illustrate that both the storage modulus, G', and the loss modulus, G'', increase with temperature when the temperature is above a critical value. A "cross-over" is observed between the G' and G'' curves. When the temperature is lower than the "cross-over" point, $G'' > G'$, the suspension is fluid-like; at a temperature higher than this "cross-over" point, $G' > G''$, the suspension is approaching solid-like behavior. The "cross-over" temperatures are ~82 and 72 °C for the 40 and 50 vol.% suspensions, respectively, which are higher than the temperatures where the viscosity starts to increase for the same solid loading suspension containing PAA.

4. Discussion

In the as-prepared suspensions, the surface potential of the pure magnesium citrate powder is less than negative 8 mV at pH > 10 (Fig. 1). Even though the magnitude is low, a small amount of magnesium citrate can still form stable suspensions with alumina particles, which has a negative zeta potential with absolute value > 50 mV. When the temperature is raised, the pH value of the suspension starts to decrease, as is shown in Fig. 8 (curve a). The pH decrease may be in part due to the increasing dissolution of alumina with temperature as is also shown in Fig. 8 (curve b). Any further decrease of pH at higher temperatures may be due to evaporation of ammonia as gas. It is also observed that during the pH measurements, agglomerates start to form at ~60 °C, which is correspondent to a pH value of about 8.8.

Fig. 9 illustrates the variation of magnesium ion concentration with pH. The magnesium ion concentration

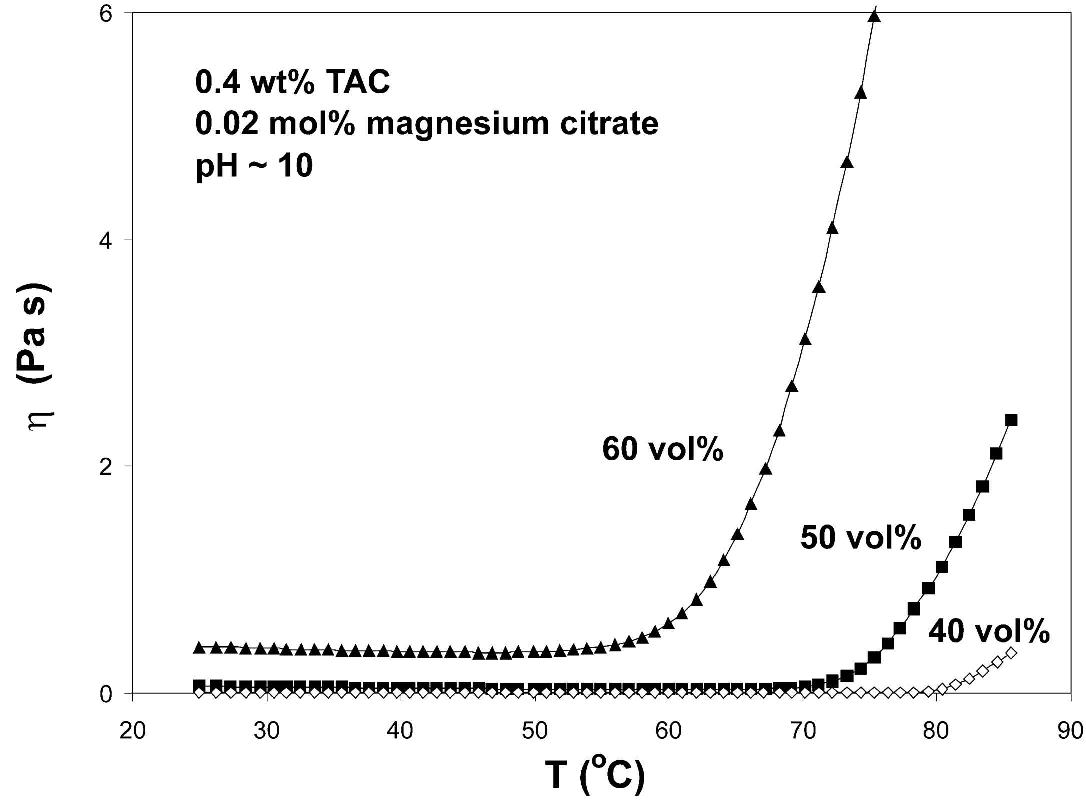

Fig. 6. Effects of volume fraction of alumina and temperature on the viscosity of the alumina suspensions with 0.02 mol% magnesium citrate. Measurements are conducted at a shear rate of 20 s^{-1} with a temperature ramp of 1 °C/min. The starting temperature is 25 °C and the final temperature is 85 °C.

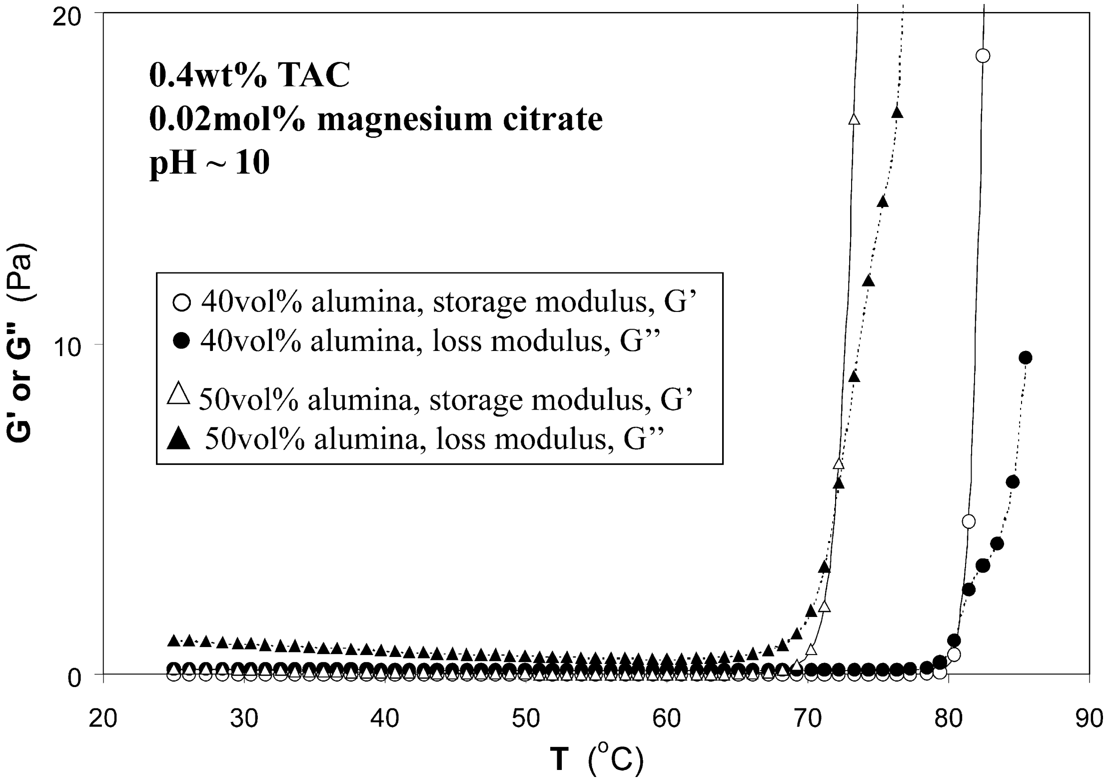

Fig. 7. Variation of the shear modulus with temperature for 40 and 50 vol.% alumina suspension with 0.4 wt.% TAC and 0.02 mol% magnesium citrate. The initial pH of the suspension is ~pH 10. Measurements are conducted at a 1% strain amplitude and a frequency of 1 Hz. The temperature is increased by 1 °C/min from 25 to 85 °C.

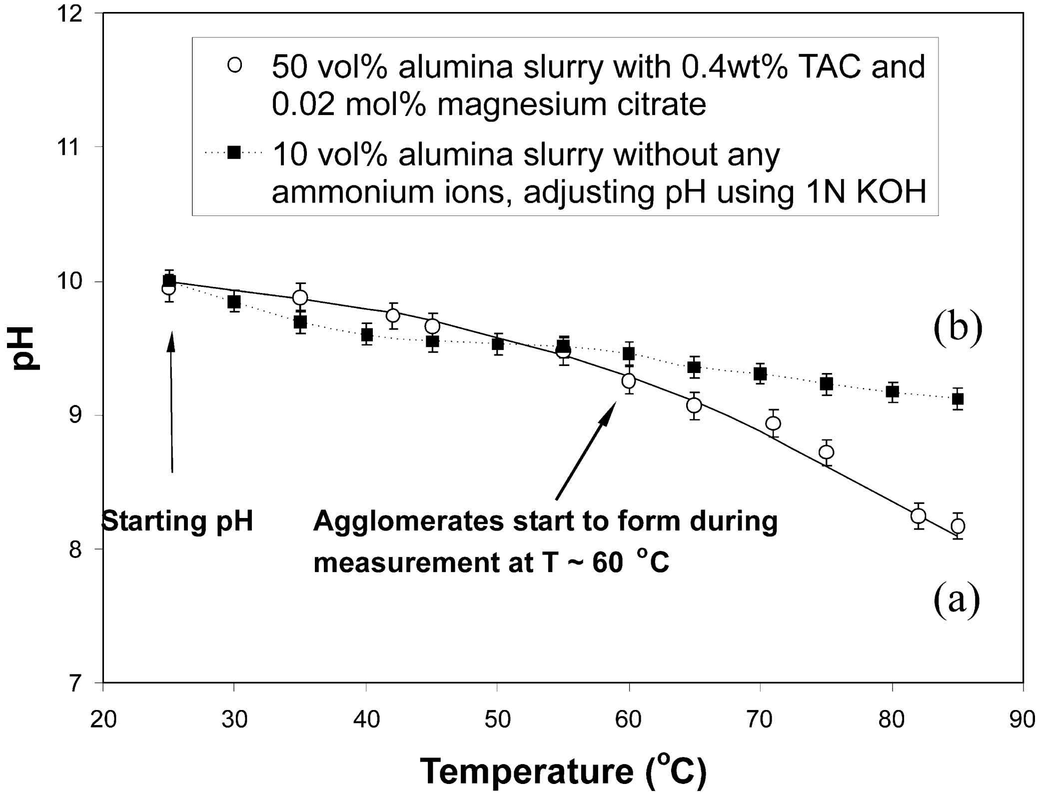

Fig. 8. Variation of pH with temperature for 50 vol.% alumina suspension with 0.4 wt.% TAC and 0.02 mol% magnesium citrate. The initial pH of the suspension is ~pH 10.

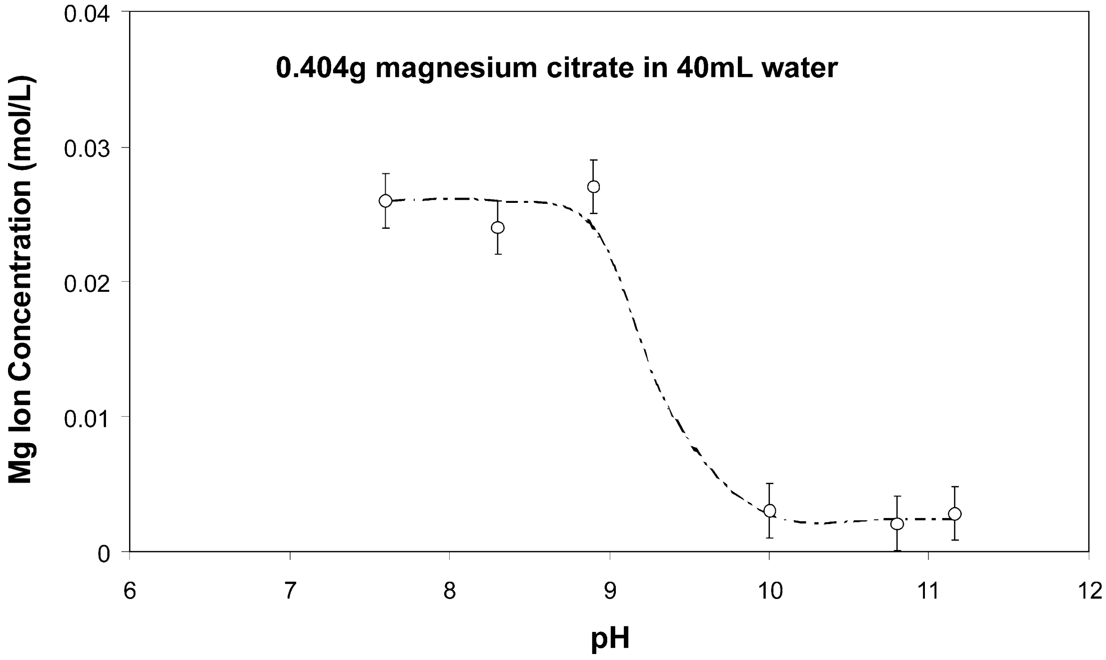

Fig. 9. Variation of the concentration of Mg ions with pH for the pure magnesium citrate powder suspensions. The Mg ion concentration in the supernatant is measured by ICP Emission Spectroscopy (Perkin-Elmer, Optima 3200 RL).

increases sharp with decreasing pH from ~pH 10. This result reflects that dissolution of magnesium citrate powders that takes place in the suspensions with decreasing pH yield the increase of the ionic strength in the suspensions at elevated temperature. The variation of the solubility with pH between pH 9 and pH 10 might be due to a kinetic effect, i.e. a competition in between citrate and hydroxyl triggering the formation of a protective layer on the magnesium citrate particles at high pH. It is also observed that magnesium citrate powders can dissolve gradually into water with the increasing acidity in the solution. The ionic strength in the suspensions can be greater than 0.01 M (mol/l). According to DLVO theory, this ionic strength will compress the EDL thickness and allow that the particles fall into the primary minimum to cause flocculation of the suspension.

The increase of the shear viscosity and the shear modulus with temperature might be due to the growth of agglomerates and the formation of a particle percolation network.[14] As discussed above, the ionic strength increase induces the flocculation of the suspensions and particle agglomerates form. Further increase of the temperature causes these agglomerates to form larger size agglomerates and the viscosity of the suspension may start to increase when the size of the agglomerates reaches a critical value. At the "cross-over" temperature, the growing agglomerates may connect to give a space-filling particle network and the value of the storage modulus becomes larger than that of the loss modulus. Higher volume fraction of solid particles in the suspensions may accelerate the growth of the agglomerates so that the particle space-filling network can be formed at a lower temperature range.

5. Summary

PAA-free alumina suspensions with temperature sensitive rheological properties have been successfully produced using the combination of tri-ammonium citrate and magnesium citrate powders. The flocculation of the suspensions is induced by the dissolution of the magnesium citrate powder that increases the ionic strength in the suspensions. The dissolution of the magnesium citrate powder is controlled by the pH of the suspensions, which decreases with increasing temperature. The combination of tri-ammonium citrate and magnesium citrate can dramatically decrease the shear viscosity of the same pH and solid-loading alumina suspension containing tri-ammonium citrate and polyacrylate. The solid loading of these new slurries is found to be up to ~70 vol.%, which is very promising for enhancing near net shape forming technologies.

Acknowledgements

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