

# The use of poly (*N*-isopropylacrylamide) microgels as a multi-functional processing aid for aqueous alumina suspensions

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Received 14 September 1999; accepted 3 January 2000

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## Abstract

Two temperature sensitive microgels of poly (*N*-isopropylacrylamide) were prepared, one anionic in nature and the other cationic. The microgels were concentrated by centrifugation and the rheological properties of the microgels measured as a function of temperature. The anionic microgel showed a transition from an elastic gel like structure to a liquid like structure at 32°C, whilst the cationic microgel demonstrated the same transition, but at a slightly higher temperature of 34°C. Both systems were completely reversible. A sub micron sized alumina powder was then mixed into the microgels using an anionic dispersant, (Darvan 821A ) to stabilise the powder. The powder was added until the system was just reversible. The aim was to see which microgel behaved as the best processing aid for the alumina particles, in terms of dispersion, gelation and adhesion after drying. The resulting mixtures were freeze dried, sintered and investigated by electron microscopy. The best microgel / alumina system was the one with similarly charged particles, i.e. the anionic microgel, whereas the system containing the oppositely charged cationic microgel particles flocculated, as would be expected from simple electrostatic theory. The presence of the inorganic particles caused the sharp transition from elastic gel to viscous fluid to broaden and the systems to behave viscoelastically over the whole temperature range. Sintered products made from the two systems were remarkably different. With the cationic microgel the resulting structures crumbled, but with the anionic microgel robust structures were obtained. Hence it is feasible to use similarly charged microgels as processing aids for ceramics as long as both particles are not oppositely charged. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Al<sub>2</sub>O<sub>3</sub>; Microgels; Sol–gel methods; Suspensions

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## 1. Introduction

From ancient times it has been known that colloidal clay and animal dung were used as aids to early ceramic processing. Agents are added to ceramic suspensions in order to enhance the strength and handling ability of the resulting green body. The processing aid remains in the body forming interparticle bridges resulting in much stronger adhesion after the solvent evaporates. The additive can also delay sedimentation through increased suspension viscosity. The processing aid must also meet several other requirements; compatibility with the existing system, ability to function as a stabiliser, ability to

act as a lubricant, should not interfere with solvent evaporation, burn out easily without residues, be effective at low concentrations, possess a high molecular weight and a low glass transition temperature. It should also maximise product uniformity, green density and process reproducibility whilst minimising shrinkage, cracking and porosity. Additives may also be added to ceramic systems to give plastic deformation during extrusion or other such required rheological properties and to control liquid migration.

There are many types of substance either natural or synthetic that can be used as aids for aqueous ceramic systems. These two groups can both be divided into organic and inorganic sub groups. Organic examples include; starches, dextrans, alcohols, celluloses, waxes and natural gums, thermosetting polymers, lignosulphonates, alginates, polyethyleneoxide and perhaps the

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most widely used poly (vinylalcohol). More recent additions to this list would include acrylic emulsions and lattices. Inorganic additives include; kaolin, bentonite, soluble silicates, phosphates and aluminates. Extensive reviews of binders utilised in aqueous ceramic processing have been given by Moreno,<sup>1</sup> Hotza and Greil<sup>2</sup> and Reed.<sup>3</sup>

Materials usually expand on heating due to an increase in their thermal energy. The solubility of most materials also increases when dissolving a material in water. However, a number of polymers in aqueous solution show sharply contrasting behaviour. As the temperature is decreased below a critical point termed the lower critical solution temperature or phase transition temperature they shrink. Below the lower critical solution temperature the polymer is soluble, the chains are extended and surrounded by water molecules. Above the lower critical solution temperature the polymer is insoluble and phase separation occurs.

The driving force for this is the balance between hydrophilic and hydrophobic forces. Examples of polymers that demonstrate this behaviour are;<sup>4</sup> poly (*N*-isopropylacrylamide), poly (vinylmethylether), poly (ethyleneoxide), poly (vinylalcohol), poly (ethylhydroxyethylcellulose) and poly (2 ethyloxazoline). These are termed thermo shrinking polymers in contrast to thermo swelling polymers like starch. Two thermal shrinking polymers that have attracted much interest are poly (*N*-isopropylacrylamide) and poly (vinylmethylether). This is due to the abrupt nature of the transition and the fact that the switch is thermally reversible.

Microgel dispersions have attracted a great deal of attention due to their ability to undergo large size changes in response to small changes in solvent conditions. Temperature and pH are the variables of greatest interest, primarily because of their importance in physiological and biological systems. Thus temperature and pH sensitive microgels offer opportunities for applications in controlled drug delivery. The drug would be released as the microgel contracted at body temperature of 37°C. Additional uses include the removal of heavy metal ions from water systems<sup>5,17</sup> for water purification as the microgels can be recycled.

Murray and Snowden<sup>4,6</sup> review the preparation, characterisation and applications of microgels in two papers. Microgels have been prepared that respond to temperature, pH, electric field or ionic strength. The resulting particles are often characterised by photon correlation spectroscopy and electron microscopy for particle size and size distribution and by electrophoresis or conductometric / potentiometric titrations to establish surface charge characteristics. Microgels have been used mainly as rheological modifiers especially in the paint industry, but they have also found uses in ink jet printing, cements, enzyme immobilization, oil recovery, molecular separation and environmentally sensitive display devices.

By combining polyNIPAM and polyacrylamide a bigel<sup>4</sup> strip, (similar to a bimetallic strip) can be manufactured. The temperature sensitivity of the polyNIPAM and the acetone sensitivity of the polyacrylamide allows the strip to bend. As the difference in thermal expansion coefficients between the two gels is larger than two metals then a bigel is more sensitive to its environment. This could be put to use in robotics. A polyNIPAM microgel has also been modified to contain a light sensitive chromophore; chlorophyllin. The resulting microgel shrinks on exposure to light and suggested uses include photo responsive muscles, switches and memory devices. Molecular separation has also been obtained with a poly (vinylmethylether) hydrogel. Non ionic surfactants can be adsorbed from waste water at 38°C, the hydrogel can then be removed, cooled to 30°C and the surfactants desorbed. Microgels can also be used in liquid chromatography systems. PolyNIPAM microgels may also be freeze dried<sup>7</sup> without any detrimental effects, the lyophilised products can then find utility as moisture removal devices.

Microgels are discrete cross linked polymer particles<sup>7</sup> falling within the colloidal size range, as a result of the cross linking they become swollen with solvent molecules below a critical transition temperature. The shrinking behaviour is a consequence of the polymer solvent interactions decreasing with increasing temperature promoting more polymer–polymer contacts with the simultaneous exclusion of the majority of the water from the interstitial regions. Another way of thinking of this is an increase in the Flory  $\chi$  parameter.<sup>25</sup>

Temperature sensitive microgels<sup>5,16</sup> can be prepared from *N*-isopropylacrylamide, which has a lower critical solution temperature of 32°C in the linear homopolymer form. Hence, polyNIPAM microgels cross linked with bisacrylamide rapidly swell/deswell on cooling/warming. At temperatures below 32°C poly NIPAM microgel has an expanded *sponge like* structure with the interstitial spaces filled by water. It is colloidally stable because attractive van der Waals forces are negligibly small. On warming above 32°C water in the space is squeezed out. However, the particles are now electrostatically stabilised due to the presence of surface charge groups. About 94% of the water inside a polyNIPAM microgel<sup>8</sup> is driven out on shrinking and the volume change is continuous.<sup>9</sup>

Other microgels apart from polyNIPAM have been prepared. Poly [(methylmethacrylate) co (methacrylic acid)] microgels have been made by Saunders et al.<sup>11</sup> The microgel could be swollen by controlling the pH, addition of methanol or propan 2 ol and the addition of polyethylene glycol. PolyNIPAM microgels are also deswelled in the same solvents and on addition of PEG. Microgels have also been prepared from *N*-ethylacrylamide.<sup>12</sup> This time the transition temperature is much

higher at 78°C. However, this microgel was sensitive to bacterial growth and showed considerable hysteresis on the heating/cooling cycles. Wolfe<sup>13</sup> has prepared polymethylmethacrylate microgels in acetone cross linked with ethyleneglycoldimethacrylate and studied their rheological characteristics. Finally, it is possible to modify the polyNIPAM microgels by copolymerising<sup>14</sup> with acrylic acid. The resultant microgels are not only temperature sensitive, but respond to pH and ionic strength. These microgels then have great advantages over pure polyNIPAM microgels as the transitions can be designed to occur at temperatures greater than 34°C and an additional triggering mechanism can then be used. PolyNIPAM has also been grafted onto polystyrene particles<sup>15</sup> to give core shell particles whose diameter may be carefully be controlled under different pH conditions.

It is the aim of this paper to investigate the effect of mixing two differently charged microgels with a polyelectrolyte stabilised alumina powder, in an attempt to study the use of microgels as processing aids for ceramic systems. Cationic polyNIPAM microgels have been mixed with other colloidal particles before, namely anionic polystyrene latex,<sup>18</sup> but this is the first study of mixing cationic and anionic microgels with inorganic particles. The anionic polystyrene latex mixed with cationic polyNIPAM microgel was stable at 20°C, but increasing the temperature caused heteroflocculation at certain microgel concentrations. The system could be redispersed on cooling, but only at elevated pH values. This is believed to be the first example of temperature induced heteroflocculation. At 20°C the system is stable due to low charge density on the microgel so any electrostatic attraction is small. Additionally the microgel particles are swollen so the Hamaker constant is small hence the van der Waals attractive force is small. On heating, however, the diameter decreased five fold corresponding to a 25-fold reduction in surface area, corresponding to an increase in charge density. The electrostatic attraction is now greater so flocculation occurs. At higher microgel concentrations the microgel particles completely adsorb onto the polystyrene latex conferring a net positive charge and hence cause re-stabilisation.

In ceramic processing it is vital to eliminate the aggregates which cause flaws in the final product and hence according to the Griffith<sup>19–22</sup> equation the strength. As colloidal particles aggregate naturally due to attractive van der Waals force it is necessary to stabilise the particles against aggregation. Classically, in colloid science this can be achieved in one of two ways.<sup>23–25</sup> Firstly, by adjusting the pH of the system it is possible to alter the nature and magnitude of the naturally occurring surface charge. These charged surface groups lead to the formation of electrical double layers in dispersion. Overlap of which causes the particles to be repelled from one another and hence do not form

aggregates. This process is termed electrostatic stabilisation. The second method is via the adsorption of polymeric materials onto the particle surface. The polymers then physically prevent the particles coming close enough to one another for van der Waals attraction to occur, a process known as steric stabilisation.

Traditionally in the ceramic industry polyelectrolytes are used to deflocculate systems, these impart stability to particles via electrosteric stabilisation. The optimum amount of the dispersant required to stabilise the alumina powder has been previously estimated from acoustophoresis experiments. The use of acoustophoresis to measure the adsorption of polyelectrolytes onto ceramic powders has been reported previously.<sup>26–29</sup> The objective of this paper is, therefore, to decide which microgel is suitable as a processing aid for forming a ceramic body. From simple electrostatic theory it would be expected that stable systems would be obtained when both particles have the same charge, whereas flocculation would occur for oppositely charged particles.

## 2. Experimental

### 2.1. Characterisation of alumina powder and dispersants

The AAO4 alumina powder was supplied by the Sumitomo Chemical Company, Japan. The surface area and particle size distribution of this powder has been reported previously,<sup>28</sup> but for convenience are also reported here. The powder impurity levels have also been reported previously.<sup>28</sup> The dispersant used was Darvan 821A supplied by R.T. Vanderbilt, USA. This is an ammonium salt of polyacrylic acid. Its molecular weight is 6000 Daltons and is supplied as a 40% active solution.

### 2.2. Microgel preparation

The anionic microgel was prepared in the following manner. A 5 l round bottom flask was charged with 3200 ml of double distilled water and 2 g of potassium persulphate initiator. The flask was secured in a water bath and heated to 70°C. To the four neck positions the following were connected: a nitrogen bubbler, a condenser and a glass stirrer connected to an electric motor, the final position was stoppered. Eighty grammes of N isopropylacrylamide and 2 g of *N,N*-methylenebisacrylamide (cross linker) were then dissolved in 800 ml of double distilled water. The beaker was heated to approx. 40°C whilst being stirred. Once dissolved the solution was added to the 5 l flask. The solution was then left stirring under nitrogen for 6 h.

The cationic microgel was prepared in exactly the same manner but using 2 g of 2,2 azobis(2 amidinopropane) as the initiator. However, prior to the preparation the glassware was silanated to prevent the product

adhering to the flask walls. The resulting 4 l of microgel was then cleaned by filtering through glass wool to remove large flocs and then centrifuging and redispersing in double distilled water. The microgel was then stored in glass bottles in the fridge.

### 2.3. Concentration of the microgels

The microgels as prepared are not nearly concentrated enough to behave as binders in concentrated ceramic suspensions, so they were further concentrated by successive centrifugation/redispersion cycles. The resulting concentrated gels were then redispersed by gently heating a centrifuge tube full of microgel to about 40–50°C in a water bath and mixed gently with a spatula. The concentration of polymeric material in the microgel was then noted by drying a small proportion of the microgel in an oven to drive off all the water.

### 2.4. Addition of alumina powder

In the colloidal processing of ceramics it is necessary to work at high solids loading, i.e. volume fractions in the region of 0.50 and above. Hence, the next part of the experiment was to see how much alumina powder could be added to each of the microgels and still be reversible on heating/cooling. A small known mass of powder was added to the warm microgel suspension, (kept in a beaker of warm water at 40–50°C,) followed by the optimum amount of dispersant (to stabilise all the added powder). The suspension was then cooled to see if it gelled (i.e. centrifuge tube was inverted to see if the microgel demonstrated a yield value i.e. did not fall). The microgel was then warmed up to see if the microgel/alumina mixture was fluid i.e. flowed. If both conditions were met then the process was deemed reversible and more powder was added and the experiment repeated. Eventually a point was reached where no more powder could be reversibly mixed into the suspensions, this was then determined to be the maximum alumina loading.

### 2.5. Freeze drying / sintering

Once the concentrated alumina / microgel systems had been prepared it was necessary to dewater the system to produce the green body. This can be achieved in several ways for example, tape casting and slip casting, but in this case it was decided to remove the water by freeze drying. The samples were placed into small plastic bags and placed in a commercial freeze drier overnight (LSL Selfroid, Lyolab F.) The resulting green bodies were then split into two batches. One half of the sample was then sintered whilst the other was left alone. Both samples were then examined under the SEM. The following sintering profile was used: from ambient 1°C/

min up to 500°C, then 5°C/min up to 1600°C. The dwell time at 1600°C was for 1 h and then cooled at 10°C / min.

### 2.6. Rheology

The rheological properties of the microgels and the microgel alumina mixtures were measured in two different rheological experiments. Firstly in steady shear rate mode the upper cone is rotated at a fixed shear rate ( $\dot{\gamma}$ ) and the resulting stress ( $\sigma$ ) was recorded, hence the viscosity ( $\eta$ ) of the material can be recorded as;

$$\eta = \frac{\sigma}{\dot{\gamma}} \quad (1)$$

The second mode of operation of the rheometer was oscillation. In this experiment a sinusoidally varying stress of known amplitude ( $\sigma_0$ ) is applied to the sample and the resulting sinusoidally varying strain (amplitude  $\gamma_0$ ) is recorded. Due to the viscoelasticity of the sample the strain is out of phase with the stress by an angle  $\delta$  (phase angle) but has the same frequency dependence. From this the complex modulus,  $G^*$  can be defined as:

$$G^* = \frac{\sigma_0}{\gamma_0} \quad (2)$$

This can then be split into two components, the elastic (or storage) modulus,  $G'$  and the viscous (or loss) modulus,  $G''$ . These are related to the complex modulus and the phase angle by the following;

$$G' = G^* \cos \delta \quad (3)$$

$$G'' = G^* \sin \delta \quad (4)$$

The complex modulus can then be expressed as;

$$G^*(\omega) = G'(\omega) + iG''(\omega) \quad (5)$$

Where  $i$  is the square root of  $-1$ . It is important to note the frequency dependence of these moduli. For a perfect Newtonian fluid, the phase angle,  $\delta$ , is 90° whilst for a perfect Hookean solid the phase angle is 0°. Viscoelastic materials have a phase angle of something in between. These three moduli must be measured in the linear viscoelastic region (LVER), where  $G^*$  is independent of the applied stress and the structure of the material is not destroyed. The LVER was always measured prior to any oscillation experiment.

The pure concentrated microgel suspensions were then rheologically characterised using an AR1000 controlled stress rheometer (TA Instruments) equipped with cone and plate geometries (6 cm 2° cone). Initially the shear viscosity as a function of temperature was

measured over the temperature range 4 – 40°C. The temperature was ramped from 4 to 40°C (10 min) then directly 40 to 4°C (10 min) with the shear viscosity measured at a constant shear rate of 5 s<sup>-1</sup>. The temperature was controlled directly using a peltier plate. In oscillation mode, the linear viscoelastic region was initially observed at 40°C. It was assumed that the LVER would decrease with increasing temperature, hence the LVER for the microgel was noted at 40°C and assumed to be valid for the entire temperature range. Oscillation experiments were carried out across the temperature range 40–4°C (10 min). The elastic modulus ( $G'$ ), viscous modulus ( $G''$ ), and phase angle ( $\delta$ ) were measured at a constant oscillatory stress of 25 Pa and a frequency of 1 Hz.

The same rheological experiments were then carried out under the same experimental conditions on the mixed systems.

### 3. Results and discussion

#### 3.1. Characterisation

The surface area of the powder as reported previously<sup>28</sup> was measured to be 4.3 m<sup>2</sup>/g. The particle size distribution was reported to be  $d_{10}=0.32\ \mu\text{m}$ ,  $d_{50}=0.50\ \mu\text{m}$ ,  $d_{90}=0.80\ \mu\text{m}$ , with 95% of the particle size distribution under 1  $\mu\text{m}$ . Previous acoustophoresis<sup>28</sup> experiments on the same alumina powder and dispersant under the same conditions have revealed that the optimum active amount of Darvan 821A needs to be 0.59 mg/m<sup>2</sup>.

#### 3.2. Microgel preparation and concentration

The microgels were easily prepared and then concentrated by centrifugation. The cationic gel was concentrated to 11.9% by weight, whilst the anionic gel was concentrated only to 8.4% by weight.

#### 3.3. Alumina addition

It was possible to add 49.3% by weight of alumina to the cationic microgel, whilst a slightly higher solids loading of 57.0% could be added to the anionic microgel. This is an early indication of the former system being flocculated, whilst the other is stable.

#### 3.4. Rheological results

Firstly the rheological properties of the pure systems will be discussed followed by the rheology of only one of the microgel / alumina mixtures. This is because the systems containing oppositely charged particles flocculated and could not be measured under the same experimental conditions as the other systems.

Fig. 1 shows the viscosity (at a fixed shear rate of 5 s<sup>-1</sup>) as a function of the temperature for the anionic microgel alone. There are two curves one for increasing temperature and one for decreasing the temperature. At low temperatures from 5°C to 20°C the viscosity of the microgel is constant at about 170 Pas. After 20°C the viscosity starts to decrease slightly with an abrupt decrease occurring at 32°C (mid point of the transition). This corresponds to the temperature at which the particles have de-swollen and shrunk. At 35°C the viscosity of the system is very low (0.03 Pas) approaching the viscosity of the underlying medium. The viscosity of water at 40°C is 0.65 mPas.<sup>30</sup> There is a small degree of hysteresis probably due to the timescale of the experiment which was a total of 20 min for ramping up in temperature and then down.

Fig. 2 shows the viscosity temperature profile for the cationic microgel alone (again at a constant shear rate of 5 s<sup>-1</sup>). The curve is similar to Fig. 1 with a constant plateau viscosity ( $\approx 220$  Pas) at low temperatures and a lower viscosity ( $\approx 0.1$  Pas) at the higher temperatures. However, the transition temperature at which the microgel particles shrink occurs at a slightly higher temperature of 34°C. Again there is a small degree of hysteresis, again attributed to the experimental timescale. The plateau viscosities and final viscosities are higher than for the anionic microgel as the cationic gel was slightly more concentrated than the anionic one. This is as expected from the Krieger–Dougherty equation,<sup>31</sup> which relates the volume fraction ( $\phi$ ) to the relative viscosity ( $\eta_r$ ) of a particulate suspension;

$$\eta_r = (1 - \phi/\phi_m)^{-[\eta]\phi_m}$$

where  $[\eta]$ =intrinsic viscosity, which is taken to be 2.5 for spheres and  $\phi_m$  = maximum packing fraction, which for monodisperse hard spheres under low shear rates is taken to be random close packing, i.e. 0.63. (The maximum packing fraction for *microgel* particles is difficult to estimate due to their deformability when closely packed.) Hence, a more concentrated microgel would have a greater volume fraction, therefore, a greater viscosity is expected for the same sized particles.

Thus, the viscosity temperature profiles show how both systems transform from a viscous material at low temperatures to a fluid at temperatures above the transition temperature. The experiment also reveals the slightly different transition temperatures the two microgels possess, which are in agreement with other results in the literature.

The oscillation experiments, however, give more insight into the nature of the systems. Fig. 3 shows the elastic ( $G'$ ) and viscous ( $G''$ ) moduli and the phase angle ( $\delta$ ) of the anionic microgel as a function of temperature. At low temperatures  $G' \gg G''$  i.e. 4000 Pa  $\gg$  200 Pa and the phase angle was almost zero. Hence at these temperatures the microgel was behaving like a perfectly

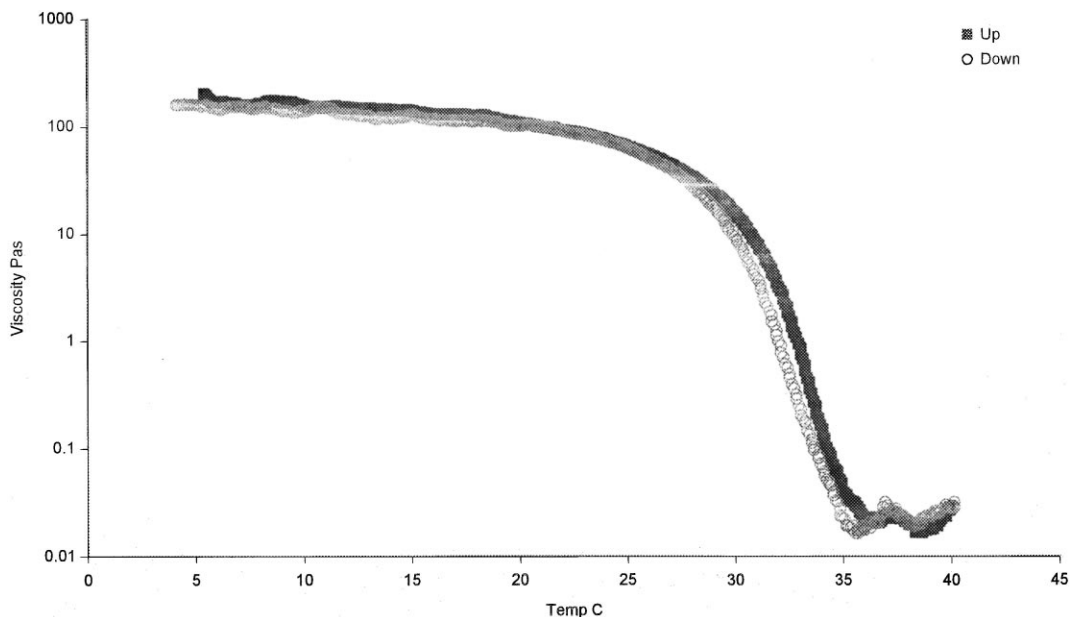


Fig. 1. The effect of temperature on the viscosity of the concentrated anionic microgel, shear rate  $5 \text{ s}^{-1}$  concentration 8.4%.

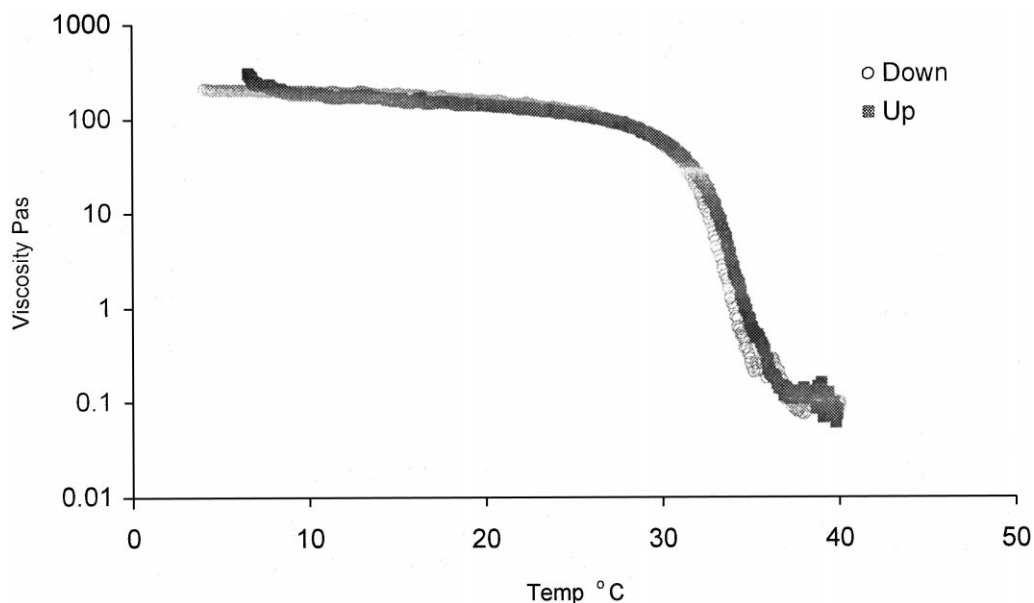


Fig. 2. The effect of temperature on the viscosity of the concentrated cationic microgel, shear rate  $5 \text{ s}^{-1}$  concentration 11.9%.

elastic body. The microgel continues to behave elastically until about  $20^\circ\text{C}$ . As the transition temperature was reached the microgel particles shrink so are no longer touching one another and the elasticity was lost so  $G'$  falls drastically. In fact at low temperature  $G'$  was an order of magnitude higher than  $G''$ , whilst at higher temperature  $G''$  was an order of magnitude higher than  $G'$ . The phase angle also changes dramatically such that at higher temperatures it was approaching  $90^\circ$ , the theoretical phase angle for a perfectly viscous system. At higher temperatures both  $G'$  and  $G''$  were low, but  $G''$  was significantly greater than  $G'$ , again indicating that the system was greatly more viscous than it is elastic.

The temperature at which  $G' = G''$  i.e. when the phase angle is  $45^\circ$  can be identified as occurring at  $31\text{--}32^\circ\text{C}$ , which of course corresponds with the transition temperature.

Fig. 4 shows the same parameters as Fig. 3 for the pure cationic microgel. Again as expected the trends are similar to that of the anionic microgel. At low temperatures  $G' \gg G''$  with a phase angle of near zero indicating strong elastic behaviour, whilst above the transition temperature  $G'' \gg G'$  and the phase angle was almost  $90^\circ$  i.e. the system is behaving in a viscous manner. The temperature at which  $G' = G''$  can be identified at  $33\text{--}34^\circ\text{C}$ , again consistent with the transition temperature

for swelling or deswelling of the microgel. So the oscillation experiments clearly demonstrate the dramatic change from elastic behaviour at temperatures below the transition temperature to viscous behaviour above the transition temperature. This can not be seen from the viscosity temperature profile alone. Both sets of experiments do, however, clearly show the transition

temperatures of 32°C for the anionic microgel and 34°C for the cationic microgel. These results are then in agreement with the observations of Kiminta et al.<sup>10</sup> They noted that the viscosity and the elastic modulus of the microgels decreased with increasing temperature, which they attributed to the change in effective volume fraction. Below the critical transition temperature the

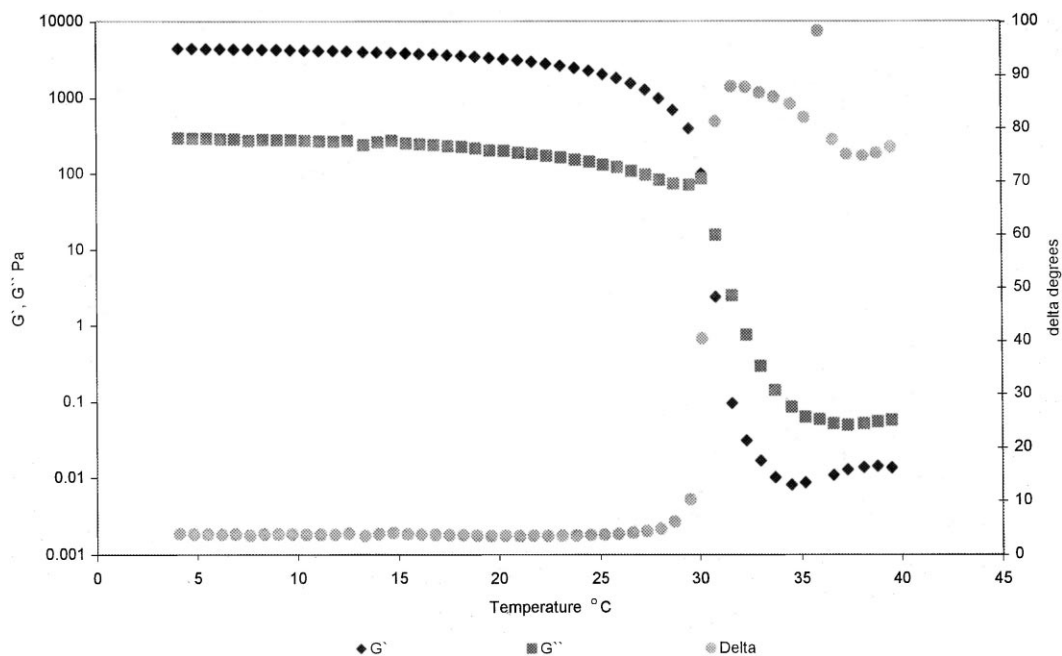


Fig. 3. Oscillation experiment on the concentrated anionic microgel as a function of temperature, (frequency 1 Hz and constant oscillatory stress 25 Pa).

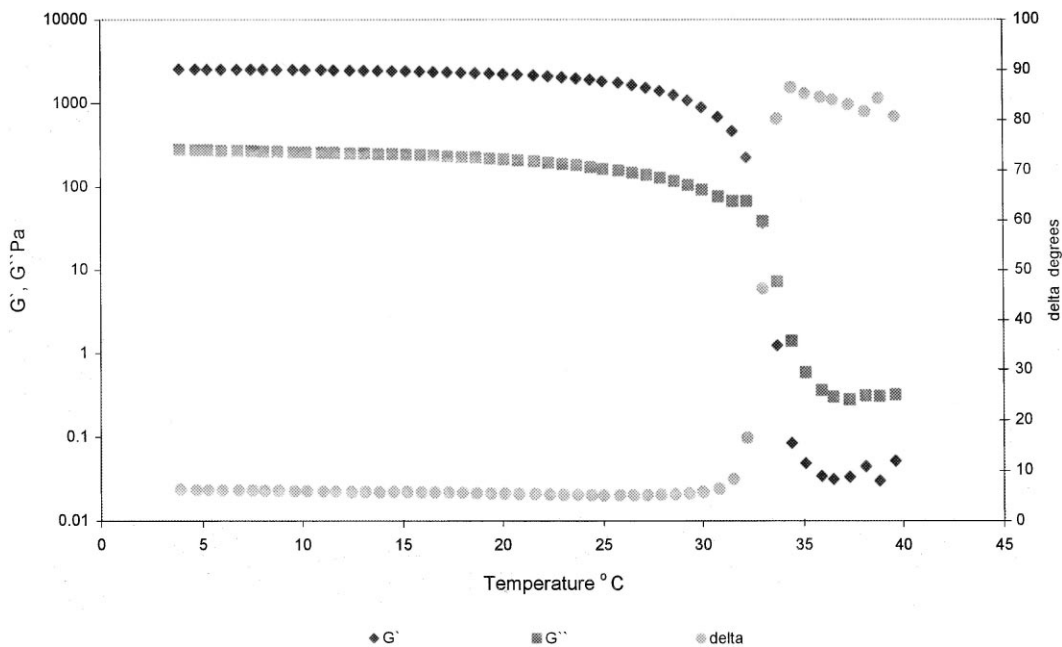


Fig. 4. Oscillation experiment on the concentrated cationic microgel as a function of temperature, (frequency 1 Hz and constant oscillatory stress 25 Pa).

microgel behaved as an elastic gel, but above the transition temperature the microgel behaved as a viscous liquid.

The next two Figs. 5 and 6 show the effect of mixing the alumina particles in with the anionic microgel. The amount of alumina powder by weight was 10%, as addition of any more alumina made the samples too viscous to measure under the same conditions. Fig. 5

shows the viscosity temperature profile (again at a constant shear rate of  $5 \text{ s}^{-1}$ ). The first thing to note is that the system is still reversible, but the degree of hysteresis is much greater than the pure system alone. Secondly, the constant viscosity plateau still exists but only until approx.  $15^\circ\text{C}$ , above this temperature the viscosity starts to decrease though there was only a two orders of magnitude change compared to the four orders of magnitude

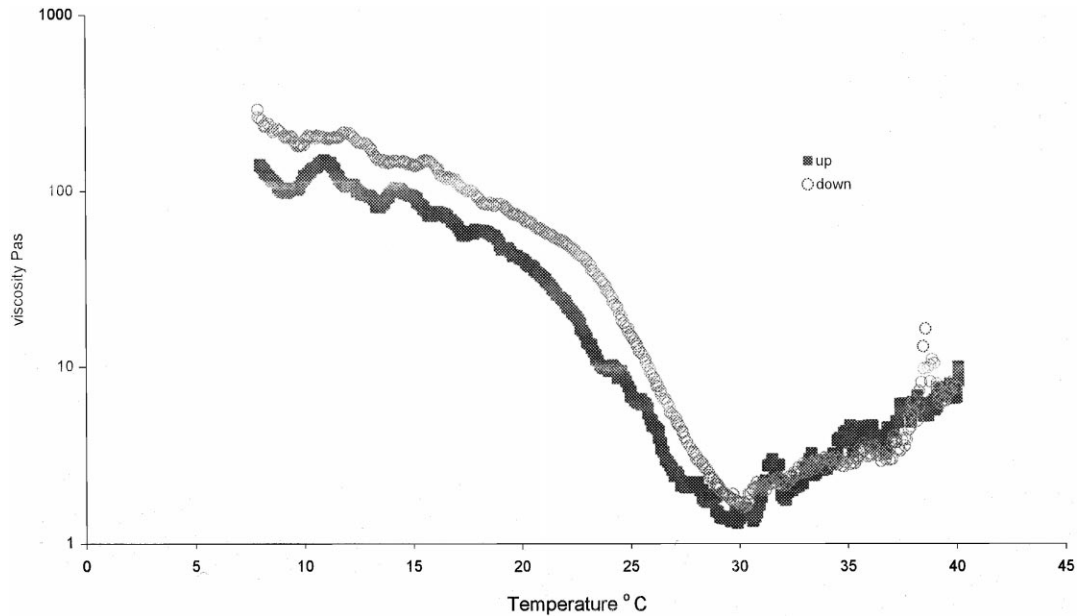


Fig. 5. The effect of temperature on the viscosity of the anionic microgel mixed with negatively charged alumina particles (shear rate  $5 \text{ s}^{-1}$  concentration 10% alumina particles by weight).

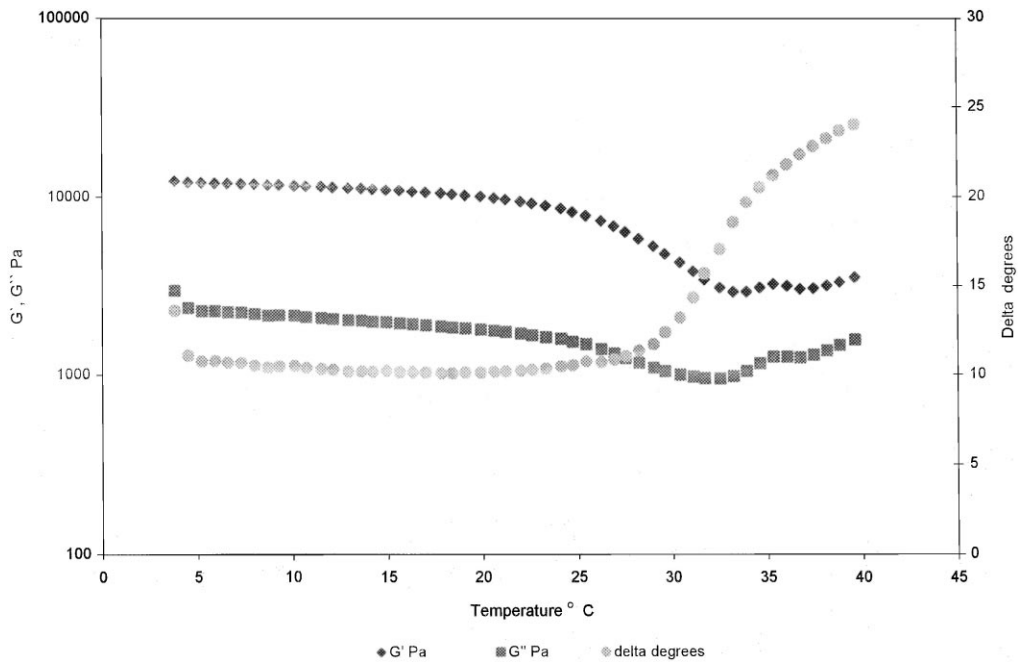


Fig. 6. Oscillation experiment for the anionic microgel mixed with negatively charged alumina particles. (Frequency 1 Hz and constant stress 25 Pa, concentration 10% alumina particles by weight).



change in the microgel alone. The sharpness of the transition is also lost due to the presence of the alumina particles.

Oscillation experiments were also carried out on the particle microgel mixture. Fig. 6 shows the elastic and viscous moduli and phase angles as a function of temperature for the anionic microgel with negative particles. As with the pure system at low temperatures  $G' > G''$  and the phase angle was low (approx. 10 compared to almost zero for the pure microgel) indicating almost elastic like behaviour. However, increasing the temperature and shrinking the microgel particles does not have such a dramatic effect as before. The elastic modulus falls slightly whereas the viscous modulus remains almost the same. The phase angle increases from 10 to 25°, so the system is behaving with increased viscoelasticity at higher temperatures, whereas before, at these temperatures, the pure microgel was behaving in a purely viscous manner. Additionally there was no swap over of  $G'$  and  $G''$  on increasing the temperature. This suggests that there was still a lot of residual elasticity in

the system. No rheological experiments were possible with the cationic microgel/alumina particles system because it was flocculated and the viscosity was too great to be measured at a shear rate of  $5 \text{ s}^{-1}$ .

### 3.5. SEM results

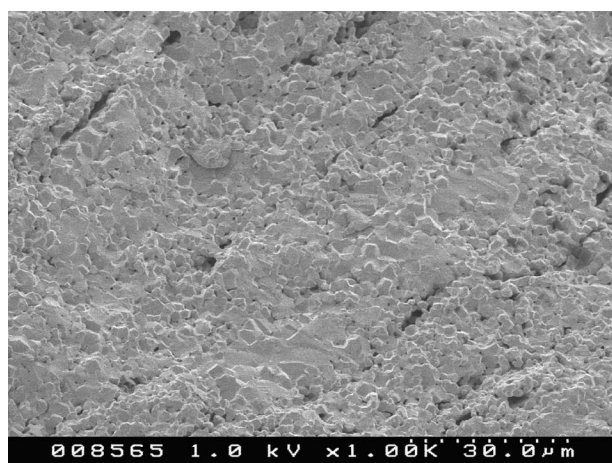
On sintering the ceramic bodies made from the anionic microgel were robust whilst the bodies made from the cationic microgel were crumbly, indicating a poor structure. Figs. 7(a) and 7(b) shows the SEM pictures of the two systems after sintering. Fig. (7a) shows the microstructure obtained with the anionic microgel mixed with the alumina. There is a good microstructure with very few pores. The grain size in the range 0.5–3  $\mu\text{m}$ . The microstructure for the cationic gel mixed with the alumina particles is vastly different, see Fig. 7(b). Here the microstructure is extremely poor with large voids, indicative of the flocculated structure of the particles prior to sintering. Thus agreeing with the strength observations made before.

## 4. Conclusions

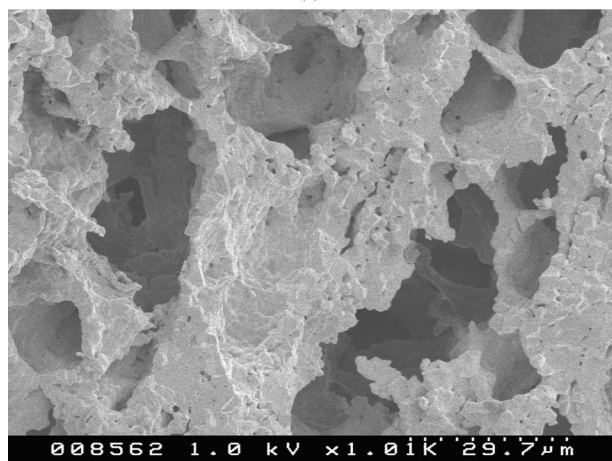
Pure cationic and anionic microgels behave in a similar manner, in that below the transition temperature the microgels behave like elastic gels whilst above the transition temperature they behave like viscous fluids. The transition between the two was very sharp and showed little hysteresis demonstrating its complete reversibility. The rheological behaviour can be attributed to the change in volume fraction on deswelling. The transition temperatures for the cationic microgel was 34°C, whilst that of the anionic microgel was 32°C.

Once the alumina powder was added this behaviour changes significantly. The maximum amount of alumina powder that could be added to the microgels varied from 49 to 57% by weight. The highest loadings were obtained when like charged particles were mixed together. When oppositely charged particles were mixed together the system flocculated as would be expected from simple electrostatic theory, because of this flocculation the rheological properties could not be measured under the same experimental conditions. The presence of the inorganic particles in the microgel broadened the transition from elastic to viscous behaviour and the system behaved viscoelastically.

The best microgel for the formation of ceramic bodies was the anionic microgel, i.e. a system of similarly charged particles. The system containing the oppositely charged microgel particles did not form good green bodies and crumbled on handling. The SEM pictures showed the systems containing the cationic microgel particles had large macropores and a poor microstructure. Whilst systems containing those made from



(a)



(b)

Fig. 7. S.E.M. picture of the sintered product (a) when the anionic microgel was mixed with the alumina particles; (b) when the cationic microgel was mixed with the alumina particles.

like charged microgel particles had a much better microstructure. Hence, it is feasible to use microgels as a processing aid for aqueous ceramic suspensions.

### Acknowledgements

Thanks to David Harley of Keele University for the preparation, concentration, and mixing of the alumina particles to the microgels. Thanks also to Olivier Bellon for the S.E.M. work.

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