

Estimation of the volume fraction gelation threshold for the temperature induced forming (TIF) alumina aqueous suspensions using rheological measurement

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An approach using a viscoelastic property measurement to estimate the volume fraction gelation threshold of the temperature induced forming (TIF) alumina suspensions is described. The results show that the volume fraction gelation threshold is about 0.15 for 0.04 wt% polyacrylic acid (PAA) addition suspensions. The amount of PAA added (up to 1.0 wt%) does not have significant influence on this volume fraction threshold.

Key words: Gelation threshold, Ceramic forming, Colloidal processing, Viscoelastic property, Alumina, Shear modulus, Percolation.

Introduction

One of the advantages of colloidal processing is the ability to form complex-shaped ceramics [1]. Temperature induced forming (TIF) is a novel direct casting method through colloidal processing to form ceramic green bodies. Generally, a smaller molecular weight dispersant (*i.e.* ammonium citrate) and a larger molecular weight polymer (*i.e.* polyacrylic acid) are used to form stable concentrated aqueous suspensions at room temperature. The weight ratio of the organic additives to that of the ceramic powder is less than 0.5 percent. The suspensions can be induced to bridging flocculation by increasing temperature [2-4]. Compared to other ceramic forming methods, TIF is a physical gel method and has simple operation procedures. Due to the small amount of organic additives, the burnout procedure before sintering can be omitted.

The viscoelastic properties, in particular how the elastic modulus scales with volume fraction, have been modeled based on the assumption that the particle network consists of close packed particle flocs. Two models have been proposed to explain the experimental phenomena, a fractal model and a percolation model. Both models depend on the assumption that the aggregated structure transmits stress through its elastic backbone (a chain of particles). The fractal model assumes that suspensions can gel at all volume fractions; therefore, there is no gelation threshold [5]. In contrast, the models based on percolation concepts describe the importance of the gelation threshold ϕ_g to

the rheological properties of aggregating suspensions. Two equations have been reported to scale and capture the generic mechanical behavior of a particle gel, $G = G_0 (\phi/\phi_g - 1)^s$ and $G' = G'_0 (\phi - \phi_g)^s$. Where, the exponent, s is related to the microstructure of the network. $\phi - \phi_g$ is the distance from the gel transition and thus relates to the number of stress carrying bonds. G_0 and G'_0 characterize the elasticity of the inter-particle bonds, which may be temperature dependent [6, 7]. A higher value of G_0 or G'_0 is expected if more particles are involved in building a denser percolation network because such a particle network can sustain a higher yield stress.

If the percolative network forms in the suspension when the volume fraction of particles is high enough and its temperature is raised, the suspension should have a transition from "fluid-like" to "solid-like", which is reflected by changes in rheological properties, *i.e.* yield stress or shear modulus. The variation of the shear stress and shear modulus at increasing temperature can be measured using a rheometer. The shear stress and shear viscosity can be calculated from the measured torque value when the suspension is sheared at a fixed strain rate. With this method, an apparent elastic response is observed first (linear stress-strain response), followed by a nonlinear "yielding phenomenon" prior to flow (increasing strain at constant stress). The slope of the initial linear region (shear modulus, G) is independent of the applied strain, but the stress where the deviation from linear behavior is observed ("yield stress") is a function of the applied shear rate. A sinusoidal oscillation, at a fixed amplitude and frequency, is used to measure the shear modulus within linear viscoelastic range [8, 9].

We have noticed that there was a "transition" (gela-

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tion) behavior when the temperature of TIF alumina suspensions is raised and this transition can be modeled by the percolation theory. It is also realized that the volume fraction gelation threshold is less than 0.30 according to our qualitative gelation experimental results [10]. In order to interpret the microstructure evolution of the TIF suspensions with temperature both qualitatively and quantitatively, it is imperative to know the volume fraction threshold according to the above equation. In this report, the strain amplitude is determined so that the shear modulus measurement using the oscillation method is within the linear viscoelastic range. Both the temperature dependence of the shear stress and shear modulus are measured and analyzed. The effect of the PAA amount on the determination of the gelation threshold is also reported.

Materials and Methods

The raw materials and preparation of the suspensions are described as follows. The starting materials are AKP 53 α -alumina powder (Sumitomo, Japan), triammonium citrate (TAC) powder (Aldrich, USA, 98%), and poly (acrylic acid) (PAA) (Polyscience, USA, 25wt% solutions in water, the average molecular weight is $\sim 50,000$). The purity of α - Al_2O_3 powder is $>99.999\%$ according to the manufacturer. The particle size is measured by an LS Particle Size Analyzer (COULTER) yielding $d_{50}=0.45\ \mu\text{m}$. The surface area of the alumina powder is measured by standard BET (NOVA 1200) N_2 adsorption giving $14.8\ \text{m}^2/\text{g}$. The TAC powder is dissolvable in water and is used as dispersant. The PAA is used here as a gelling agent, not a dispersant. The amount of TAC powder and PAA are based on the weight of dry alumina powders. The amount of TAC powder is fixed as 0.4 wt%.

The preparation of the suspensions is done by a planetary ball mill (Fritsch GMBH, Pulverisette 5, Germany. Alumina mill jars and zirconia mill balls). The exact amount of alumina powders, 0.4 wt% TAC and respective amount of deionized water are mixed for 30 minutes at a speed of 250 rpm. Then the pH is adjusted to about 9.3 with analytical 4.94 N ammonium hydroxide (Aldrich, USA) before adding the exact amount of PAA. The above suspensions are then ball-milled for about 20 minutes to get the final suspensions. The pH value of the final suspension is 9.0.

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 1 – $1030\ \text{s}^{-1}$, the time duration for each measurement point is 20 s and a total of 30 points are obtained for each suspension. The temperature ramp rotation measurements are conducted to measure the temperature dependence of suspension viscosity. The shear rate is $20\ \text{s}^{-1}$, and the

temperature is raised at a rate of $1^\circ\text{C}/\text{min}$ with the start temperature at 25°C . The temperature dependence of the storage and loss moduli are measured using the temperature ramp oscillation mode with a fixed shear strain amplitude of 1%, frequency of 1 Hz, and a temperature ramp of $1^\circ\text{C}/\text{min}$.

Results and Discussions

Determination of the strain amplitude for oscillation measurement

Figure 1 illustrates the results of a typical strain sweep experiment, showing the linear viscoelastic region, *i.e.* where the storage modulus G' is nearly invariant with strain and a nonlinear region with decreasing values of G' . It can be seen that a 1% strain amplitude is in the linear viscoelastic region at a frequency of 1 Hz. Therefore, a 1% strain amplitude is used in the measurements.

Volume fraction dependence of the steady shear flow

Figure 2 gives the steady shear flow curves for the 0.04 wt% PAA addition alumina suspensions. The volume fraction of the suspended particles varies from 0.1 to 0.3. The high shear-rate viscosity increases with volume fraction of solids. It seems that in varying the volume fraction from 0.1 to 0.2, the suspensions have Newtonian flow behavior at lower shear rate. A shear thickening behavior occurs at higher shear rate. But the 0.3 volume fraction alumina suspension shows shear-thinning behavior at the lower shear rate range and a shear thickening at high shear rate. The shear thinning might be due to the evolution of the suspension structure during shear flow so as to minimize the dissipation of energy, making it easier for the suspension to flow. The preferential flow structures during shear can be two-dimensional sliding layers or strings. The

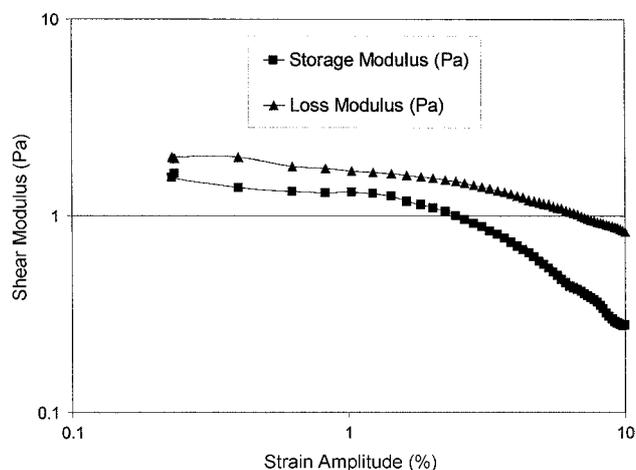


Fig. 1. Variation of shear modulus with strain amplitude for the 40 vol% AKP53 alumina suspension with 0.4 wt% TAC and 0.04 wt% PAA 50,000. The frequency is 1 Hz.

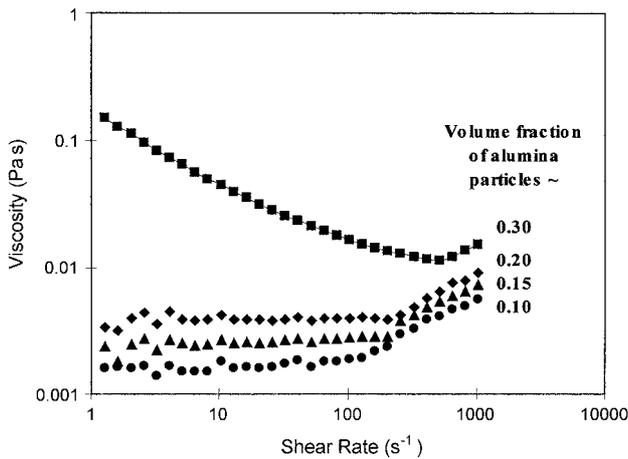


Fig. 2. Variation of steady shear-flow with volume fraction of particles for suspensions with 0.4 wt% TAC and 0.04 wt% PAA 50,000.

shear thickening usually follows that of the shear thinning. The layered arrangement is unstable, and is disrupted above a critical shear stress. The ensuing random arrangement increases the viscosity [11-13]. The critical shear rate at which this type order-to-disorder transition is to occur increases with the volume fraction from 0.1 to 0.3, which is in agreement with the results of Barnes *et al.* [13]. But it is difficult to extract the volume fraction gelation threshold from the steady shear flow data only.

Temperature dependence of the viscoelastic properties

Figure 3 shows the temperature dependence of the shear stress under a constant shear rate of 20 s^{-1} when the suspension temperature is raised at $1^\circ\text{C}/\text{min}$. The shear stress for the 0.1 volume fraction suspension seems independent of temperature. The shear stress starts to increase above a critical temperature, T_θ , when the volume fraction is higher than 0.15. The higher the

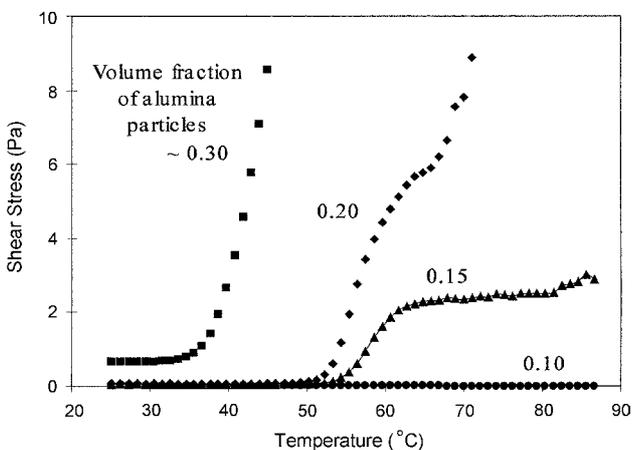


Fig. 3. Temperature dependence of the shear stress at shear rate of 20 s^{-1} for different volume fraction suspensions. The temperature is raised at a rate of $1^\circ\text{C}/\text{min}$.

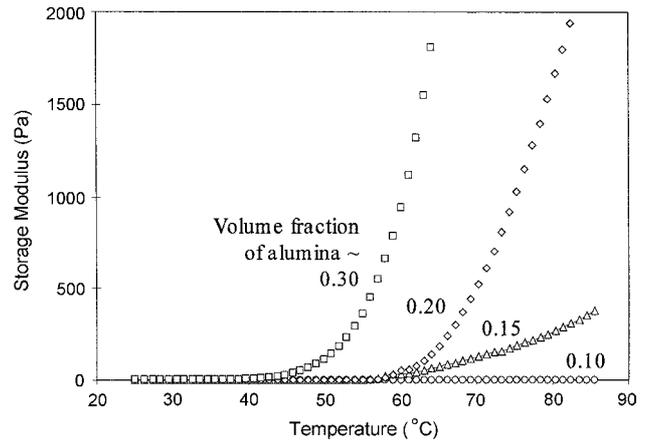


Fig. 4. Temperature dependence of the storage modulus for various volume fraction suspensions with 0.4 wt% TAC and 0.04 wt% PAA. The strain amplitude is 1%, the frequency is 1 Hz, and the temperature is raised at a rate of $1^\circ\text{C}/\text{min}$.

volume fraction, the lower this critical temperature and the more sharply the increase of the shear stress required to make the suspension flow under a shear rate 20 s^{-1} . At volume fraction of 0.15, the shear stress starts to increase at 53°C but levels off from about 64°C . But for higher volume fraction suspensions, the shear stress continues to increase without leveling off. These data indicate that 0.15 might be around the volume fraction gelation threshold, and above this volume fraction the number of alumina particles might be sufficient to form a space-filling network with 0.04 wt% PAA addition when the temperature is raised. The shear stress increase is due to the bridging agglomerate formation [4] and growth in the suspension [14]. The higher volume fraction of solids will result in a higher number density of the agglomerate floc. Furthermore, these flocs will grow with increasing temperature because more and more particles will fill into the interstices of the bridging flocs, and these flocs can connect with each other to form a larger floc. Therefore, the shear stress will be further increased. If the volume fraction of solids is small, aggregation flocs will cease to grow when all the particles are located in the flocs and the leveling off occurs for the shear stress shown in Figure 3, e.g., for the 0.15 volume fraction suspension.

In Figure 4, the variation of the storage modulus with temperature of the suspensions is shown. The damping factor is also illustrated in Figure 5. When the volume fraction of solids is above 0.15, the storage modulus starts to increase above a critical temperature, T_θ' . Figure 5 clearly shows that the damping factor decreases and levels off to nearly zero when the suspension temperature is above T_θ . Since the damping factor is the ratio of the loss modulus to the storage modulus, decreasing of the damping factor indicates that the storage modulus value increases faster than the loss modulus. A nearly zero value of the damping factor is an indication that the storage modulus of a suspension

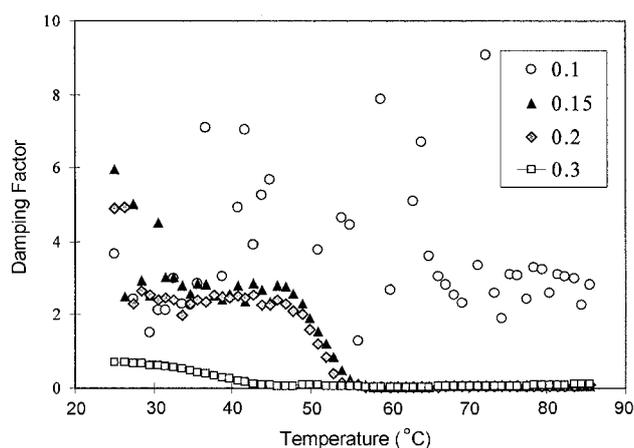


Fig. 5. Temperature dependence of the damping factor for various volume fraction suspensions with 0.4 wt% TAC and 0.04 wt% PAA. The strain amplitude is 1%, the frequency is 1 Hz, and the temperature is raised at a rate of 1°C/min.

at a temperature dominates over the loss modulus, and this can be a reflection of the occurrence of gelation, or the “transition” from “fluid-like” to “solid-like”. This “transition” temperature might be the point where the number density of the bridging floc is large enough so that the three-dimensional space-filling network (particle percolative network) starts to form [14]. Compared with Figure 3, it can be seen that $T_0 < T_0'$. This temperature difference is an indication of the growth of the agglomerates during this time period before a space-filling network can be formed. Only after the formation of the space-filling network can the shear modulus show an increment with further increasing of temperature. Above this temperature T_0' , the excessive isolated particles might fill into the interstices of the primary particle network so as to increase the packing density of the network. Therefore, the storage modulus will increase continually above the “transition” temperature, and this increment will be larger for a higher volume fraction suspension. These measurement data also suggest that 0.15 might be the critical volume fraction for this type of suspensions to form space-filling networks when the amount of PAA is ~ 0.04 wt%.

Effect of the amount of PAA on the viscoelastic properties of the near threshold suspensions

One remaining question is whether the amount of PAA will affect the formation of the percolative particle network when the volume fraction of particles is just below the gelation threshold, *i.e.* 0.10. Since PAA is an important component of the bridging flocculation, the amount of the PAA in the suspensions should affect the number of the agglomerate flocs. As a consequence, the viscoelastic properties of the suspensions should vary with the amount of PAA. Figure 6 shows the temperature dependence of the shear stress for the 0.1 volume fraction suspensions with variation in the amount of PAA. When the amount of PAA is raised to

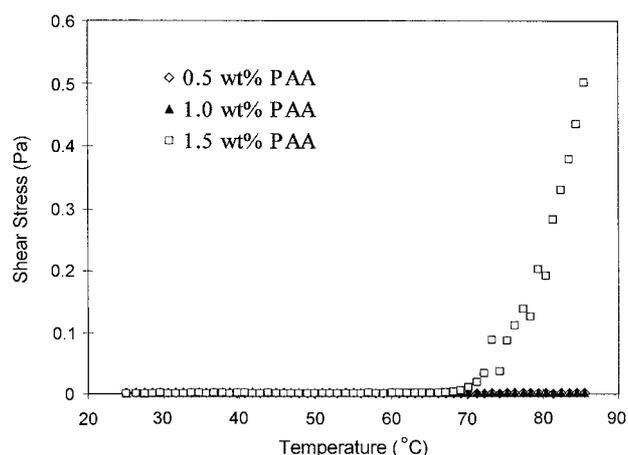


Fig. 6. Temperature dependence of the shear stress (at a shear rate of 20 s^{-1}) for the 0.1 volume fraction suspensions with various amount of PAA. The suspension temperature is raised at a rate of 1°C/min.

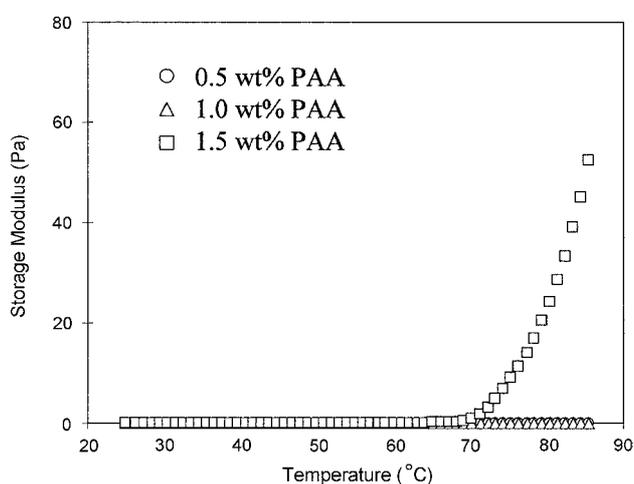


Fig. 7. Temperature dependence of the storage modulus for the 0.1 volume fraction suspensions with various amount of PAA. The strain amplitude is 1%, the frequency is 1 Hz, and the temperature is raised at a rate of 1°C/min.

0.5 and 1.0 wt%, the shear stress does not change measurably compared with that of the 0.04 wt% PAA addition suspension in the experimental temperature range. When the amount of PAA is further increased to 1.5 wt%, the shear stress starts to increase when the suspension temperature is above 68°C. The variation of the storage modulus of these suspensions with temperature follows the same trend, as shown in Figure 7. There is no difference in storage modulus between the 0.5 and 1.0 wt% PAA addition suspensions. The suspension with 1.5 wt% PAA seems to have a sharp increase in storage modulus when the temperature is above 70°C, and the highest storage modulus is only 60 Pa at 85°C. Figure 8 gives the damping factors for these suspensions. The scattering of the damping factors for the 0.5 wt% PAA addition suspension might be due to the sensitivity of the rheometer when the

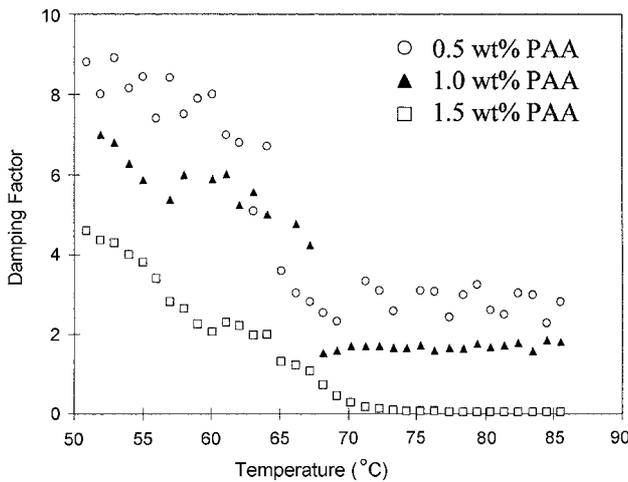


Fig. 8. Temperature dependence of the damping factor for the 0.1 volume fraction suspensions with various amount of PAA. The strain amplitude is 1%, the frequency is 1 Hz, and the temperature is raised at a rate of 1°C/min.

shear modulus of the suspension is very low. Even though the damping factor of the 1.0 wt% PAA addition suspension decreases and levels off at about 70°C, the damping factor is still about 2, implying that the loss modulus is larger than the storage modulus and the “gelation” transition does not occur. When the PAA amount is increased to 1.5 wt%, the damping factor levels off to zero when the temperature is above 70°C, indicating that the storage modulus starts to increase and dominate over the loss modulus and a “fluid-like” to “solid-like” “transition” occurs. Again we can see that the critical temperature T_{θ}' , at which the “fluid-like” to “solid-like” transition occurs is higher than the critical temperature T_{θ} , where the shear stress of the same suspension starts to increase. Therefore, both the shear stress and storage modulus data illustrate that the amount of PAA does not have evident influence on the viscoelastic properties of the 0.1 volume fraction suspensions when the amount of PAA is increased up to 1.0 wt%. But for the higher volume fraction suspensions, the effect of the amount of PAA might be significant.

Conclusions

Variation of the viscoelastic properties, i.e. shear stress

and shear modulus, with increasing temperature is used to estimate the volume fraction gelation threshold for the TIF alumina suspensions. The results show that the volume fraction gelation threshold is about 0.15 for the 0.04 wt% PAA addition AKP53 alumina suspensions. The amount of PAA does not have significant influence on this volume fraction threshold when the amount of PAA is increased up to 1.0 wt%.

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