NANOPARTICLE COLLOIDAL SUSPENSION OPTIMIZATION AND FREEZE-CAST
FORMING

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ABSTRACT
        Nanoparticle suspension and forming are important areas. In this paper, the stability and
rheology of Al_2O_3 nanoparticle suspensions at different dispersant concentration, suspension pH,
and solids loading were studied. The most desirable suspension conditions were 7.5-9.5 for pH
and 2.00-2.25 wt% of Al_2O_3 for poly(acrylic acid) (PAA) dispersant. 45.0 vol% Al_2O_3 solids
loading can be achieved while maintaining good suspension flow for freeze casting. The
maximum solids loading of the Al_2O_3 nanoparticle suspension was predicted to be 50.7 vol%.
The preliminary results of the freeze-cast sample showed that suspension pre-rest before freezing
was critical for achieving defect free microstructures.

INTRODUCTION
        To overcome agglomeration and low packing density issues, colloidal processing is the
preferred approach for nanoparticles. The unique ionic properties of water allow addition of ions
to overcome the problematic particle-particle attraction; this ion-related stabilizing mechanism is
called electrostatic stabilization. Another approach is to add a polymer dispersant to the
suspension; polymer chains adsorb onto the particle surfaces and extend into water, and
physically repel one another; this method of stabilization is called steric stabilization.[1] More
effectively, an ionic polymer dispersant and the ionic properties of water can be used
simultaneously to obtain a well-dispersed suspension; this method is called electrosteric
stabilization.[2] A delicate balance must be maintained in the pH and the dispersant concentration.
Inappropriate pH will result in particle attraction, not repulsion.[3] The adsorbed polymer must be
thick enough to prevent close particle contact and counteract van der Waals forces. Too little
polymer will cause bridging flocculation; too much polymer will cause depletion
flocculation.[4,5,6,7] Ideally, the adsorbed polymer layer should be just thick enough to prevent van
der Waals bonding. Since nanoparticles have much larger specific surface area than micron size
particles, more polymer molecules will be adsorbed to cover the nanoparticle surface of the same
mass; this will correspondingly reduce the solids loading of the nanoparticles even with ideal
polymer layer thickness.
        Viscosity measures the ability of the solid particles to flow relative to one another. A
decrease in the particle size leads to suspensions of high viscosity because the effective solids
loading is increased in the nanoparticle suspensions. The effective solids loading increase occurs
because the particle diameter decrease creates large electrical double layer or adsorbed polymer
layer volume that accounts as part of the effective solids loading. For high solids loading, the
polymer concentration must be controlled with a much higher precision for the nanoparticle
suspension than for the conventional suspensions.[8] The suspension must flow well into the mold
and fill in the complex details or cavities of the mold. Intuitively, the higher the solid loading,

the more viscous and difficult the flow will be. However, high solids loading is necessary to get a fully dense component. A balance must be achieved to address these opposite demands.

Freeze casting is a process that pours the suspension into a nonporous mold, freezes the suspension, demolds the component, and then dries the component under vacuum. Very desirably, freeze casting avoids defect formation by eliminating capillary force during drying and saves tremendous effort in binder removal. The technique is ideally suited for complex shapes and costs very little on tooling, which is a huge saving compared to dry pressing, isostatic pressing, or shock wave compaction.[9,10,11] Flexibility in forming complex shapes at minimal cost is also very suitable for rapid prototyping. Freeze casting also has the advantage of using less expensive and non-toxic dispersing medium, water.

The work reported here is focused on understanding PAA dispersant concentration, suspension pH, and Al_2O_3 solids loading effects on PAA adsorption onto Al_2O_3 nanoparticles and the stability and rheology of the nano-Al_2O_3 suspensions. By measuring the suspension rheology under different conditions, the maximum solids loading for the Al_2O_3 nanoparticle suspension is predicted. Based on the optimized dispersion conditions, the 40 vol% solids loading suspension has been freeze-cast. The preliminary characteristics of the freeze-cast components are reported.

EXPERIMENTAL PROCEDURE

Al_2O_3 nanoparticles with average particle size of 38 nm and specific surface area of 45 m^2/g were used in this study (Nanophase Technologies, Romeoville, IL). The Al_2O_3 was reported from the vendor to have 70:30 of δ: γ phases. Even though the average particle size was much less than 100 nm, the particle size distribution was wide and there was a small percent of large particles close to 100 nm. PAA (M_W 1,800, Aldrich, St Louis, MO) was used as a polymer dispersant with the polymer segment as $[-CH_2CH(CO_2H)-]$.

For the preparation of the Al_2O_3 suspensions, 10 wt% glycerol ($C_3H_8O_3$, water basis, Fisher Chemicals, Fairlawn, NJ) was mixed with water and the mixture was homogenized for 5 min using a ball mill. Glycerol was used to lower the freezing temperature of the suspension and refine the ice microstructure for homogeneous component formation during freeze casting.[12] Al_2O_3 powder was added for a specific solids loading in 10 g increments along with an appropriate amount of PAA dispersant. Since low pH promotes PAA dispersant adsorption onto the nano-Al_2O_3 particles, HCl solution was added to lower the pH to 1.5.[13] The suspension was ball milled for 12 hrs with periodic adjustment of pH to 1.5. This procedure was used to make suspension of approximately 20 vol% Al_2O_3. NH_4OH was then used to adjust the suspension to the desired pH level. Depending on the final solids loading desired, nano-Al_2O_3 was added again in 10 g increments, along with the appropriate amount of PAA dispersant and the adjustment of the suspension pH. The suspension was then mixed for 24 hrs for complete homogenization. NH_4OH was again used to adjust the suspension to the desired pH level.

For suspension characterization, the pH of the suspensions was measured by a pH meter (Denver Instrument, Arvada, CO). Potentiometric titration was used to determine the amount of PAA dispersant adsorbed onto the Al_2O_3 particles in a suspension.[14,15] pH was adjusted to 9.5±0.05 before titrant HCl solution was added in order to promote the dissociation of PAA dispersant in water. Adsorption curve was developed for known PAA concentration blank solutions first. To measure the adsorption of PAA dispersant in an actual suspension, the suspensions with PAA dispersant and different solids loading were centrifuged at 2,500 rpm for 45 min before collecting the resulting supernatants. A known volume of the supernatant was

titrated and the amount of un-adsorbed PAA dispersant was determined using the standard curve from the blank PAA solutions. The viscosities of the suspensions were measured by a rheometer with a cone-plate geometry (AR 2000, TA Instruments, New Castle, DE). All the suspensions were pre-sheared at 200 s^{-1} to impart similar shear history. The measurements were performed at equilibrium shear with controlled shear rates.

Slurries of 40 vol% solid loading were used for freeze casting. Freeze casting molds were developed using poly (dimethylsiloxane) epoxy (RTV 664, General Electric Company, Waterford, NY) and a fully dense flexural test specimen as a pattern. After curing, the flexural test specimen was removed, leaving a cavity in the epoxy. A transfer pipette was used to place the well dispersed Al$_2$O$_3$ suspension into the mold to reduce air bubbles and promote filling. The Al$_2$O$_3$ suspension filled epoxy mold was placed in a freeze dryer (Labconco Stoppering Tray Dryer, Labconco, Kansas City, MO) and cooled to -35° C for 2 hrs. The samples were demolded after freezing and then exposed to low pressure (<10 x 10^3 Pa) for 36 hrs to allow the ice to sublimate. The microstructures of the freeze-cast samples were examined by a LEO 1550 field emission scanning electron microscope (Carl Zeiss MicroImaging, Inc, Thornwood, NY).

RESULTS/DISCUSSION
1) PAA Adsorption and Suspension Rheology
Hydrogen bonding is a ubiquitous mechanism for polymer adsorption onto hydrophilic surfaces. Mathur et al. studied the nature of oxide surface hydroxyls and indicated that isolated surface hydroxyls constitute the surface of Al$_2$O$_3$.[16] Based on this understanding, PAA adsorption onto Al$_2$O$_3$ is expected to be affected by the PAA concentration. However, how such adsorption mechanism plays a role in high solids loading suspensions has not been examined. To study the PAA concentration effect on its adsorption onto Al$_2$O$_3$ nanoparticles in a high solids loading suspension, the solids loading of the suspension was fixed at 30 vol% while the PAA concentration was varied between 1.00-2.50 wt% of Al$_2$O$_3$ as shown in Fig. 1. As the PAA concentration increases up to 2.00 wt% of Al$_2$O$_3$ PAA concentration, the adsorbed PAA amount onto Al$_2$O$_3$ particles also increases. As more PAA is added to the suspension, the adsorbed PAA amount reaches a plateau at 0.31 mg/m^2. The adsorption plateau represents a saturation adsorption level at which the Al$_2$O$_3$ particle surfaces are fully covered by PAA dispersant. For the studied system, the minimum PAA concentration needed is 2.00 wt% of Al$_2$O$_3$. On the other hand, the relative amount of PAA adsorbed onto the Al$_2$O$_3$ nanoparticles decreases monotonically as more PAA is added, due to the blocking of some active sites from the adsorbed PAA polymer onto the solid surface; this means free PAA concentration increases along with total PAA concentration increase. After the adsorbed PAA amount reaches the saturation plateau for monolayer coverage, additional PAA dispersant only exists as free polymer in the suspension, resulting in 'overdispersing'.
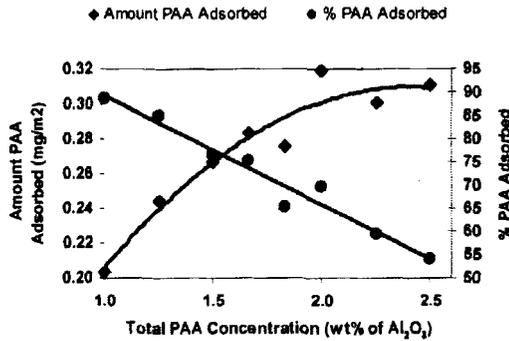
Fig. 1. PAA dispersant adsorbed amount and the adsorbed relative percent vs. the total PAA concentration.

The viscosity measurements at different shear rates for the suspensions of 30% solids loading and different PAA concentrations are shown in Fig. 2. The suspension has the lowest viscosity at 2.00-2.25 wt% of Al_2O_3 PAA concentration. As the PAA content increases or decreases, the viscosity increases. The viscosity increase at low PAA concentration can be explained by a shortage of PAA adsorption onto Al_2O_3 (incomplete PAA coverage of Al_2O_3) and the resultant bridging flocculation. The viscosity increase at high PAA concentration can be explained by the presence of free polymer in the suspension--depletion flocculation. A balance needs to be maintained in the PAA adsorbed onto the nano-Al_2O_3 particles and the free PAA dispersant in the suspension. The results in Fig. 2 serve as an important guide in optimizing the dispersion conditions. For the studied system, the optimal PAA content is 2.00-2.25 wt% of Al_2O_3.
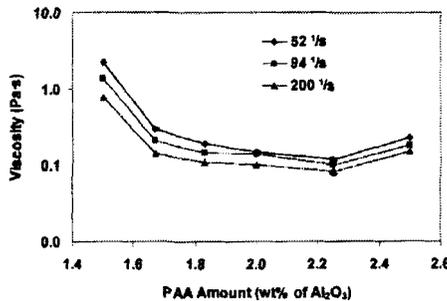

Fig. 2. PAA concentration effect on the suspension viscosity at 30 vol% Al_2O_3 solids loading.

Based on the PAA concentration effect on the suspension stability, PAA concentration of 2.00 wt% of Al_2O_3 was used for the pH effect study while the solids loading was kept at 30 vol%. pH was studied from 5.5 to 10.5. As shown in Fig. 3, PAA has the highest adsorption at pH 5.5. This is consistent with the theory that low pH promotes PAA adsorption onto Al_2O_3

nanoparticle surfaces. As pH increases, both PAA adsorption concentration and the relative amount of the adsorbed PAA decrease. From pH 5.5 to 10.5, the PAA adsorption concentration decreases from 0.44 mg/m^2 to 0.27 mg/m^2, a 38.6% decrease, while the adsorbed PAA percent decreases from 92.0% to 57.5%, a relative 37.5% decrease.

It should be noted that the PAA adsorption concentration is only one aspect of the polymer stabilization mechanism. PAA conformation on the Al$_2$O$_3$ nanoparticle surface also plays important roles. At low pHs, PAA tends to have more train configuration on the Al$_2$O$_3$ surfaces and hinders suspension stabilization. At high pHs, PAA has more loop and tail configurations and provides electrosteric stabilization. When the pH value is too high, PAA adsorption onto Al$_2$O$_3$ particles is too low, depletion flocculation results and viscosity increases. The viscosity measurement (Fig. 4) shows that at pH 5.5, the suspension is very viscous and there is substantial shear thinning. At pH 10.5, there is also noticeable shear thinning and high viscosity. At pH 7.5-9.5, the suspension has low viscosity and is the most desirable pH range for stabilizing the Al$_2$O$_3$ nanoparticles.
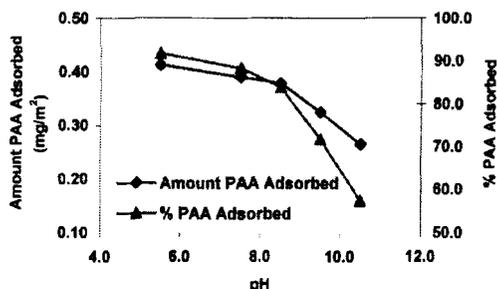

Fig. 3. Suspension pH effect on PAA adsorption at 30 vol% solids loading and 2.0 wt% of Al$_2$O$_3$ PAA concentration.
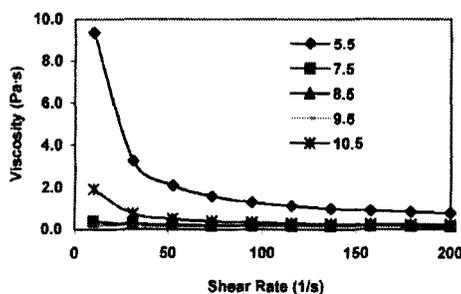

Fig. 4. Viscosity change vs. shear rate for the 30 vol% solids loading and 2.0 wt% of Al$_2$O$_3$ PAA concentration suspensions at different pH values.

For the solids loading effect study, all the suspensions were controlled at 2.00 wt% of Al$_2$O$_3$ for the PAA concentration and 9.5 for the final pH. Fig. 5 shows that as the Al$_2$O$_3$ solids

loading increases from 20.0 to 45.0 vol%, the PAA adsorbed amount and the relative amount of PAA adsorbed onto Al_2O_3 nanoparticles increase. Since most of the prior research was focused on very dilute systems (< 20 vol%), this observation revealed trend that has not been detailed before. The reason can be traced back to the more favorable PAA adsorption onto the Al_2O_3 surfaces at lower pH. During the Al_2O_3 solids loading adjustment, Al_2O_3 and PAA additions shift the suspension pH to more acidic conditions from pH 9.5. This suspension adjustment process promotes the PAA adsorption onto Al_2O_3 nanoparticles as demonstrated in Fig. 3. After the PAA adsorption at the more acidic condition, the final adjustment of pH to 9.5 does not change the bonding between PAA and Al_2O_3 and the higher PAA adsorption. From 30.0 to 45.0 vol% Al_2O_3 solids loading, the PAA adsorption difference is similar to the adsorption difference for a pH decrease from 9.5 to 8.5 for the 30 vol% solids loading suspension. This solids loading and PAA adjustment effect can probably be minimized by controlling pH at 9.5 with very small increment of Al_2O_3 and PAA additions. However, this is not very practical since the suspension needs to be mixed thoroughly for homogenization at each small addition. Instead, Fig. 5 provides practical information for the optimal dispersion conditions at different Al_2O_3 solids loading levels.
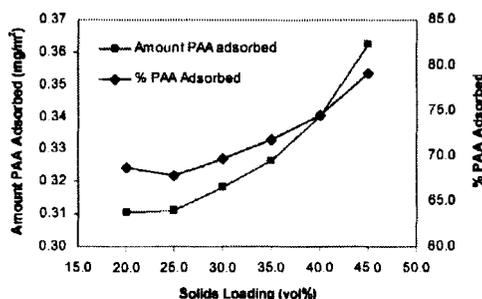

Fig. 5. Solids loading effect on adsorbed PAA amount and relative percent of PAA adsorbed onto Al_2O_3 nanoparticles.

Fig. 6 shows that the suspensions have reasonably low viscosity and are well dispersed from 20.0-45.0 vol% solids loading, consistent with the prior measurement that the suspensions have about -40.0 mV zeta-potential.[17] It can also be easily observed that the viscosity is a strong function of Al_2O_3 solids loading. With the solids loading increase, the viscosity increases. As the shear rate increases, the viscosity decreases monotonically. The viscosity becomes more sensitive to the Al_2O_3 solids loading increase at high solids loading levels.
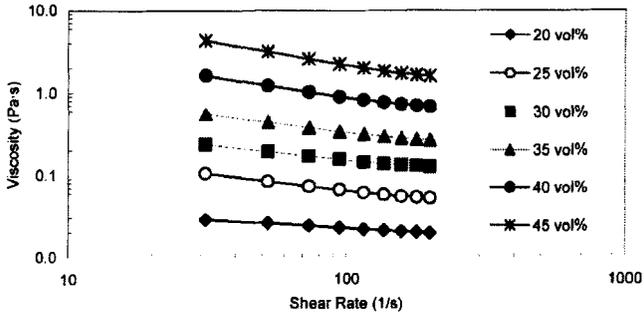
Fig. 6. Viscosity vs. shear rate change at different Al₂O₃ solids loading levels.

2) Maximum Solids Loading Prediction

Nano-Al₂O₃ has large specific surface area that adsorbs large amount of dispersant PAA, which can quickly reduce the particle packing efficiency. When excessive PAA dispersant is used, some PAA polymer chains stay freely in the suspension, further decreasing the achievable maximum solids loading. Mathematical models have been developed to relate the amount of the solids loading with the viscosity. Among these is the semi-empirical Krieger-Dougherty equation:

$$\eta_r = \frac{\eta}{\eta_0} = \left(1 - \frac{\phi_{eff}}{\phi_{max}}\right)^{-n\phi_{max}}$$ (1)

where η_r is the relative viscosity, η is the suspension viscosity, η_0 represents the viscosity of the suspension medium (water), and $\dfrac{\phi_{eff}}{\phi_{max}}$ represents the solids loading over the maximum solids loading (~0.64). Here, n is a constant representing the intrinsic viscosity of the suspension.[18] Liu showed that most of the equations describing particle packing-viscosity behavior at high strain rate (~100 s⁻¹) follow the simple form:

$$1 - \eta_r^{-\frac{1}{n}} = a \cdot \phi + b$$ (2)

where a and b are constants. Assuming that the Al₂O₃ nanoparticle suspensions follow the model, the viscosity of the suspensions under different solid loading levels can be used to extrapolate the theoretical maximum solids loading, at the point where viscosity is infinite.[19] In this study, the maximum solids loading at pH 9.5 and PAA concentration 2.00 wt% Al₂O₃ can be predicted based on the viscosity at lower solids loading levels, which is 50.7 vol% as shown in Fig. 7 (it is assumed n=2 here as in most models). In this study, up to 45.0 vol% Al₂O₃ solids loading has been achieved with good suspension flow, which is even higher than that of some dry compaction processes.
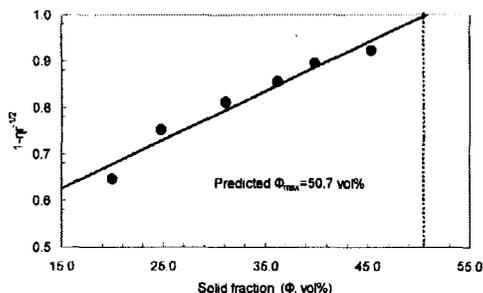
Fig. 7. Maximum solids loading prediction for the Al_2O_3 nanoparticle suspensions when PAA is at 2.00 wt% Al_2O_3, pH is at 9.5, and strain rate is at 94.0 s^{-1}.

3) Freeze Casting

In this study, the 40.0 vol% solids loading Al_2O_3 suspension was freeze cast. It was observed that the pre-rest of the filled suspension has significant effect on the freeze cast sample quality. After mold filling. the trapped air bubbles should be allowed to escape from the suspension under zero shear stress. This is necessary for the studied system due to the high solids loading. The fracture surfaces of the samples under different pre-freezing treatment are shown in Fig. 8 at different magnifications. All the samples were frozen under the same conditions as outlined in the experimental section. As Fig. 8 shows, there is no cracking for the sample with pre-rest (a) but extensive cracking for the sample without pre-rest (b) at low magnification. At high magnification, the sample with pre-rest shows more flat fracture surface and uniform structures. For the sample without pre-rest, very rough fracture surface and micro-voids can be easily seen. Further work is needed to optimize the freeze casting conditions, evaluate the macroscopic properties of the sample, and study the fundamental freeze-casting mechanisms.
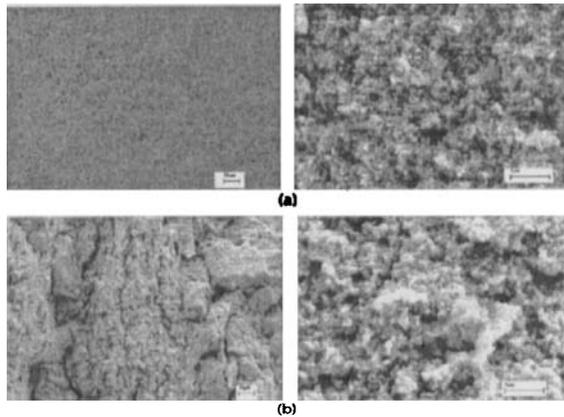
Fig. 8. Freeze cast sample fracture surface microstructures at different pre-freezing conditions: (a) with pre-rest, (b) without pre-rest.

CONCLUSIONS

PAA dispersant concentration, suspension pH, and Al_2O_3 solids loading effects on PAA adsorption onto Al_2O_3 nanoparticles were studied; the stability and rheology of the nano-Al_2O_3 suspensions under different levels of the above three parameters were examined. The most desirable suspension conditions were identified to be 7.5-9.5 pH and 2.00-2.25 wt% of Al_2O_3 PAA concentration; and the highest Al_2O_3 solids loading can be achieved at more than 45.0 vol%. The maximum solids loading of the nano-Al_2O_3 suspension was predicted to be 50.7 vol%. Pre-rest of the suspension was vital for achieving desirable solid samples.

ACKNOWLEDGMENTS

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