

Effect of Polyvinylpyrrolidone Additions on the Rheology of Aqueous, Highly Loaded Alumina Suspensions

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The control of the rheological behavior of highly loaded ceramic/polymer suspensions affords the development of near-net shape forming techniques. In this study, suspensions containing sub-micrometer diameter alumina (up to 56 vol%) were fabricated using an anionic dispersant (≈ 4 vol%) and water-soluble polyvinylpyrrolidone (PVP). The amount and ratio of molecular weights of PVP in the suspension were varied to influence flow behavior. The final pH of the system, ≈ 9.5 , was higher than the isoelectric point (IEP) of alumina implying that the alumina powder possesses a negative surface charge. In the case of alumina at this pH, PVP does not adsorb onto the surface of the powder. The flow behavior of the PVP-containing suspensions displayed yield-pseudoplastic characteristics that closely agreed with the Herschel–Bulkley fluid model. The addition of PVP significantly changed the rheology of the system, increasing the shear yield stress and altering flow behavior. Intersurface interaction approximations of the suspensions were modeled to correlate with experimental observations.

I. Introduction

STUDY of the rheological response of highly loaded ceramic suspensions is vital to enable fabrication of ceramic components into useful geometries and near-net shapes. By carefully engineering the rheological behavior it is possible to adapt colloidal suspensions to a variety of processing methods including tape casting, injection molding, and extrusion for application in electronics, aerospace, pharmacy, energy, and other sectors of industry.^{1,2} Colloidal formulations that have been designed for typical ceramic casting methods are usually complex.^{3–5} Depending on the adsorption behavior of a polymer added to a dispersant/ceramic slurry, suspensions can be further stabilized by either steric and/or depletion interactions.³

In steric stabilization, the polymer attaches to the powder surface, and its tail prohibits adjacent powders from approaching and agglomerating. In a colloidal system with nonadsorbing polymer, the interparticle distance may become small enough that polymer molecules are unable to fill all of the space between particles. As a result, depletion zones consisting of only solvent develop, causing depletion floccula-

tion via osmotic gradients.⁶ This colloidal mechanism may transition to another regime depending on the achievable conformations of the nonadsorbed polymers. In a similar case in which polymers do not bond to the powder surface, and the dispersant does not promote their adsorption, the polymers can be located in the volume between particle surfaces, thus restabilizing the suspension. This change results in depletion stabilization.^{7–9} There the polymers can constitute a barrier for contact between particles depending on their concentration and molecular weight with respect to the surface area and size of the powders.^{8,10}

Polyvinylpyrrolidone [PVP, chemical structure shown in Fig. 1(b)] is a hydrophilic water-soluble polymer that has been adapted for use in a number of applications, as it is nontoxic to both humans and the environment. The adsorption of PVP on the surface of alumina is dependent upon the nature of the dispersant/powder surface interaction that is partly characterized through pH. For a solution of alumina particles (suspension pH > IEP of alumina), an anionic carboxylic dispersant that enhances the negative surface charge of the particles will stabilize the system.^{11–13} This particular design strategy was employed in this study where an anionic dispersant was used to disperse alumina, and PVP, which was neutral at the pH of the suspensions evaluated, was added to modify the flow behavior of the ceramic-loaded suspension via depletion interactions. Investigators elsewhere have achieved high ceramic powder loadings (~ 50 vol%) by adjusting the surface charge state of alumina powders using Dolapix[®] CE64 additions.^{14,15} In this study the inherent pH of the suspensions (~ 9.5) with Dolapix[®] CE64 was always greater than the pH at the IEP for alumina as reported previously,^{11–13} implying a negatively charged surface on the alumina particles.

In terms of the polymer interactions with the dispersant and ceramic powder, the nonionic nature of PVP complicates its adsorption behavior on alumina. Without the aid of a dispersant, PVP does not readily adsorb on the surface of alumina.^{16–20} As demonstrated by Pattanaik and Bhaumik²⁰ for PVP with molecular weights of 10 000, 40 000, and 360 000 g/mol average molecular weight, the IEP for alumina in water is not affected by the presence of the polymer. This effect was observed for each molecular weight and is attributed to the lack of sufficient hydroxyl ions on the surface of the ceramic powder in orientations that would favor an acid-base mechanism via hydrogen bonding.

In summary, by using an alumina/DI water/Dolapix[®] CE64/PVP system it is possible to select a pH range to minimize interaction of the alumina surface with PVP such that the PVP chains locate themselves between the powders and greatly influence the rheological properties of the system.^{10,21} It is possible to control the rheology of these systems by merely selecting polymer concentration and molecular weight, which are very sensitive variables for different forming approaches.²² The addition of neutral PVP modifies the rheology without having to employ more complex steric,

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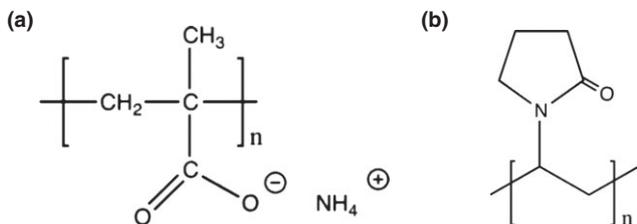


Fig. 1. Structure of (a) Dolapix[®] CE64 poly(methacrylic acid) ammonium salt (PMAA-NH₄) and (b) polyvinylpyrrolidone (1-ethenyl-2-pyrrolidinone homopolymer) used in fabrication of depletion-stabilized alumina suspensions.

thermal, or chemical agents. In addition, high ceramic concentrations (>50 vol%) are achievable, allowing for the fabrication of green bodies with higher densities resulting in higher attainable densities in pressureless sintered samples.²³

The role and effect of dispersants and polymer chains on the viscoelasticity of alumina suspensions has been previously examined^{4,5,12,13,16–21,24,25} as well as with charged polymers such as polysaccharides, natural gums, carbopol, etc.^{26–31} However, extensive characterization using nonadsorbed PVP of different molecular weights as a polymer carrier has yet to be investigated. Because PVP is a water-soluble and environmentally friendly polymer with a neutral character at pH values above the IEP of alumina,^{19,32} it is possible to obtain suspensions in which rheological behavior that can be controlled by simple variations of polymer content and molecular weight, while attaining high ceramic concentrations because of the stable nature of the polymer in the suspension. In addition, the low cost of alumina and PVP makes this system an ideal model suspension for studying a depletion-interactions approach and its effects on ceramic forming where control of rheology is of essential importance.

In this study, highly loaded aqueous alumina suspensions were fabricated using PVP and an anionic dispersant (Dolapix[®] CE-64). Through parallel plate rheometry, the objective was to characterize the effect of ceramic powder content and varying polymer average molecular weight and concentration on the rheological response of the suspensions. The interparticle interactions governing the suspensions were also approximated through application of Derjaguin–Landau–Verwey–Overbeek (DLVO), steric, and depletion models. The interaction potential estimations were then matched with experimental observations. This study allows for the understanding of how the rheological response of stable suspensions with polymers that are nonadsorbed to the inorganic powder can be manipulated.

II. Experimental Procedure

(1) Materials

The suspensions used for this work were fabricated using deionized (DI) water and A-16 SG alumina (Almatis, New Milford, CT) with an average particle size of $0.48 \pm 0.13 \mu\text{m}$ determined using a Beckman Coulter LS 230 particle size analyzer (Brea, CA) and BET surface area of $7.8 \pm 0.22 \text{ m}^2/\text{g}$ found using a TriStar 3000 gas adsorption analyzer (Micromeritics Instrument Corporation, Norcross, GA). In addition, an anionic dispersant (Dolapix[®] CE64 from Zschimmer & Schwarz, Milledgeville, GA) was used. Dolapix[®] CE64, as previously investigated by Dakskobler *et al.*,^{11–13} is a poly(methacrylic acid) ammonium salt [PMAA-NH₄, chemical structure shown in Fig. 1(a)], which is a cation-exchange deflocculating agent used to obtain excellent flowability for suspensions with high solid loadings.³³ It modifies the electrical double-layer and makes the particles more negatively charged. According to spectroscopy studies performed by Dakskobler and Kosmač, Dolapix[®] CE64 has an average molecular weight of 320 g/mol.¹² It has been observed by previous investigators that alumina suspensions containing

30–50 vol% of the ceramic require additions of Dolapix[®] CE64 of ~0.6 vol% to be stabilized at pHs <9.^{34–36} Finally, polyvinylpyrrolidone (PVP, 1-ethenyl-2-pyrrolidinone homopolymer; Sigma-Aldrich, St. Louis, MO) with average molecular weights of 10 000, 55 000, 360 000, and 1 300 000 g/mol was used as a rheological modifier. Its structure is shown in Fig. 1(b), and its content was varied from 0 to 5.1 vol%.

(2) Suspension Formulation and Characterization

In an initial step, a slurry was mixed using DI water, dispersant, and alumina powder. The ceramic powder was added incrementally by ball milling in Nalgene bottles with alumina milling media (U.S. Stoneware, East Palestine, OH) for 24 h. To attain high alumina concentrations, additional dispersant was added throughout this step as needed to allow for adequate dispersion of the powders. Simultaneously, a separate solution comprised of DI water and PVP was magnetically stirred for 24–48 h. Once the ceramic slurry and the polymer solution were homogeneous, they were combined together through additional ball milling over a 24 h period.

To isolate the effect of PVP alone on the flow properties of the alumina-PVP suspensions, a series of four polymer solutions comprised of 12.1 vol% PVP with average molecular weights of 10 000, 55 000, 360 000, and 1 300 000 g/mol, respectively, in water were also prepared by magnetic stirring. The PVP content in these four solutions was selected to correspond to 5.1 vol% PVP in an alumina-PVP suspension. In addition, the pH of a solution of PVP with molecular weight of 360 000 g/mol and Dolapix[®] CE64 in water at concentrations identical to the alumina suspension with 5.1 vol% PVP was modified to 9.5 using ammonium hydroxide to determine if PVP and PMAA could together cause an alternate adsorption effect.

Table I lists suspensions fabricated without PVP, where the amount of alumina was varied from 30 to 54.7 vol%. To analyze the effect of PVP concentration, average molecular weight, and molecular weight distribution on rheological behavior, suspensions were fabricated with compositions shown in Table II. For suspensions with only 1 300 000 and/or 55 000 g/mol PVP (suspensions 1A through 15A in Table II), P_r is defined as the vol% of 55 000 g/mol PVP divided by the total sum of the vol% of 1 300 000 and 55 000 g/mol PVP. The alumina concentration was kept in a narrow range from 53.4 to 55.7 vol% for these suspensions. Suspension compositions were observed to be stable at pH > IEP with dispersant concentrations of ~3.7–3.9 vol%. For the type of compositions in this investigation the dispersant did not considerably affect the effective particle size while maintaining a stable configuration of the powders.^{2,15,22,34–36}

The effect of PVP additions on the pH of the system was studied in selected suspensions (3A, 6A, 8A, 10A, and 13A) from Table II. An Oakton pH 5 meter (Vernon Hills, IL) previously calibrated with electrolytic buffer solutions at pHs of 4, 7, and 10 was used to obtain pH values of polymer-water solutions and ceramic slurries before and after adding the PVP-DI water solution to the suspensions. The electrokinetic potential (ζ in mV) of alumina powder surfaces was measured in dilute solutions of alumina and DI water with Dolapix[®] CE64 using a Malvern Nano ZS Zetasizer

Table I. Compositions of A-16 SG Alumina Suspensions Fabricated Without PVP and with Increasing Inorganic Content (30–54.7 vol% Alumina)

Suspension	Al ₂ O ₃ (vol%)	H ₂ O (vol%)	Dolapix [®] CE-64 (vol%)
1	54.7	41.3	4.0
2	50.0	45.5	4.5
3	40.0	54.7	5.3
4	30.0	63.7	6.3

Table II. Compositions and Calculated Curve Fit Parameters from the Herschel–Bulkley Model used in Flow Curves ($R = 0.99$) of A-16 SG Alumina Suspensions Fabricated with PVP Contents of 1, 2.6, and 5.1 vol% PVP as well as PVP Solutions Without Alumina or Dispersant. P_r Represents the Ratio of the Lowest Molecular Weight PVP to the Total Amount of PVP in the Formulation

Suspension	Al ₂ O ₃ (vol%)	Dolapix® CE-64 (vol%)	1.3 × 10 ⁶ g/mol PVP (vol%)	55 × 10 ³ g/mol PVP (vol%)	Total polymer (vol%)	P_r	σ_y (Pa)	k (Pa·s ^{<i>n</i>})	n
1	54.7	4.0	–	–	–	–	18.5 ± 4.1	2.5 ± 1.5	0.59 ± 0.11
1A	55.7	3.9	–	1.00	1.0	1	74.9 ± 3.2	12.2 ± 1.5	0.51 ± 0.02
2A	55.7	3.9	0.25	0.75	1.0	0.75	81.3 ± 2.0	9.9 ± 0.9	0.55 ± 0.02
3A	55.7	3.9	0.50	0.50	1.0	0.5	54.8 ± 3.1	7.8 ± 0.8	0.52 ± 0.01
4A	55.7	3.9	0.75	0.25	1.0	0.25	80.6 ± 1.2	6.9 ± 0.5	0.58 ± 0.01
5A	55.7	3.9	1.00	–	1.0	0	58.4 ± 0.6	5.3 ± 0.2	0.59 ± 0.01
6A	54.8	3.8	–	2.60	2.6	1	81.1 ± 2.1	8.2 ± 0.8	0.60 ± 0.02
7A	54.8	3.8	0.65	1.95	2.6	0.75	114.7 ± 2.5	9.6 ± 0.9	0.62 ± 0.02
8A	54.8	3.8	1.30	1.30	2.6	0.5	93.6 ± 1.6	7.5 ± 0.5	0.66 ± 0.01
9A	54.8	3.8	1.95	0.65	2.6	0.25	174.1 ± 2.8	7.6 ± 0.5	0.84 ± 0.01
10A	54.8	3.8	2.60	–	2.6	0	165.7 ± 2.9	7.8 ± 0.5	0.87 ± 0.01
11A	53.4	3.7	–	5.10	5.1	1	177.5 ± 6.1	17.8 ± 2.1	0.65 ± 0.02
12A	53.4	3.7	1.30	3.80	5.1	0.75	163.8 ± 3.3	14.6 ± 0.8	0.76 ± 0.01
13A	53.4	3.7	2.55	2.55	5.1	0.5	150.0 ± 1.0	11.6 ± 0.5	0.77 ± 0.01
14A	53.4	3.7	3.80	1.30	5.1	0.25	169.3 ± 35.8	93.6 ± 13.8	0.60 ± 0.03
15A	53.4	3.7	5.10	–	5.1	0	161.0 ± 84.1	127.8 ± 35.9	0.56 ± 0.05
16A [†]	53.4	3.7	–	–	5.1	–	54.1 ± 1.3	8.7 ± 0.6	0.52 ± 0.01
17A [‡]	53.4	3.7	–	–	5.1	–	149.1 ± 18.5	13.8 ± 4.3	0.78 ± 0.06
1P [†]	–	–	–	–	12.1	–	0.067 ± 0.15	8.9 × 10 ^{–4} ± 4.5 × 10 ^{–3}	1.1 ± 0.81
2P	–	–	–	12.1	12.1	1	0.14 ± 0.4	3 × 10 ^{–3} ± 1.4 × 10 ^{–2}	1.1 ± 0.74
3P [‡]	–	–	–	–	12.1	–	0 ± 0.27	3.3 × 10 ^{–1} ± 2.3 × 10 ^{–2}	0.95 ± 0.01
4P	–	–	12.1	–	12.1	0	1.3 ± 0.33	1.2 ± 0.04	0.84 ± 5.3 × 10 ^{–3}

The difference in volume fraction for each suspension equals the amount of DI water used. The coefficient of determination $R^2 > 0.99$ for all values calculated using the Herschel–Bulkley model.

[†]PVP with molecular weight of 10×10^3 g/mol was used.

[‡]PVP with molecular weight of 360×10^3 g/mol was used.

Table III. Compositions of A-16 SG Alumina Suspensions with Inorganic Contents Between ~45–50 vol%, and PVP Concentrations Ranging Between 7.4 and 8.2 vol% with Calculated Fit Parameters from the Herschel–Bulkley Model from the Flow Curves of Fig. 6 ($R \sim 0.99$). P_r was Constant at 0.5

Suspension	Al ₂ O ₃ (vol%)	H ₂ O (vol%)	Dolapix® CE-64 (vol%)	1.3 × 10 ⁶ (g/mol) PVP (vol%)	55 × 10 ³ (g/mol) PVP (vol%)	Total polymer (vol%)	σ_y (Pa)	k (Pa·s ^{<i>n</i>})	n
1B	50.1	39.0	3.5	3.7	3.7	7.4	198.8 ± 2.2	32.6 ± 0.8	0.61 ± 0.01
2B	48.8	40.0	3.6	3.8	3.8	7.6	194.7 ± 2.9	25.9 ± 1.0	0.63 ± 0.01
3B	47.5	41.0	3.7	3.9	3.9	7.8	151.5 ± 4.5	35.1 ± 2.0	0.54 ± 0.01
4B	46.1	42.1	3.8	4.0	4.0	8.0	156.0 ± 1.6	18.4 ± 0.6	0.62 ± 0.01
5B	44.6	43.3	3.9	4.1	4.1	8.2	109.0 ± 2.7	21.7 ± 1.1	0.57 ± 0.01

(Westborough, MA). The pH of the solution was adjusted using ammonium hydroxide additions and monitored using the previously mentioned Oakton pH 5 meter. Finally, the compositions listed in Table III were used to study the effect of increasing alumina phase concentration (from ~45 to ~50 vol%) in the presence of 7.4–8.2 vol% PVP with a constant $P_r = 0.5$.

The rheological response of the suspensions as well as of aqueous polymer solutions were analyzed using a TA Instruments ARG2 rheometer (New Castle, DE) with a 40 mm parallel plate geometry, a gap of 500 μm at 25°C, and a moisture trap to avoid temperature gradients and drying of the material during testing. Parallel plate rheometry allows for characterizing highly loaded particulate suspensions at high rates without material interrupting the flow under the gap of the geometry.^{2,22} Similarly, other studies have previously applied parallel plate rheometry to investigate the rheological response of highly loaded alumina suspensions.^{26,29} In this study, parallel plate rheometry was selected over cone and plate rheometry as the gap provided by a cone and plate geometry would not allow the instrument to run at

a wide range of shear rates.^{2,37} The alumina–PVP suspensions and PVP solutions were presheared at the maximum shear rate (100 s^{–1}) for 5 min and stabilized for 1 min before ramping continuously to 100 s^{–1} and back to 0 s^{–1}. Oscillation stress sweeps were run at a frequency of 1 Hz from 0.1 to 1000 Pa, and frequency sweeps were performed at an oscillation stress of 1 Pa (in the linear viscoelastic region) from 0.01 to 100 Hz. To evaluate the thixotropy of the alumina–PVP suspensions, three consecutive hysteresis loops were measured up to three different maximum shear rates in decreasing order (600, 100, and 10 s^{–1}).

Flow curves were fitted using the least-squares method to the Herschel–Bulkley model² that is typically used for yield-pseudoplastic materials given as:

$$\sigma = \sigma_y + k\dot{\gamma}^n \quad (1)$$

where σ (Pa) is stress and σ_y (Pa) represents the shear yield stress. The second component of the equation consists of a power law where $\dot{\gamma}$ is the shear rate (1/s) applied to the material as well as the consistency or apparent viscosity, k (Pa s^{*n*}),

and flow index of the material, n , which ranges from 0 to 1. For values of $n < 1$, the behavior of the suspension can be considered yield pseudoplastic. If $n = 1$, the mixture is a Bingham-type fluid.² The calculated shear yield stress of the suspensions presented in this study was determined by extrapolating the fit to the axis limits. The correlation factor, R , obtained from the fitting parameters of Eq. (1) was always ~ 0.99 .

III. Results and Discussion

(1) Polymer-Dispersant Interactions with Alumina

The pH of the alumina/DI water slurries with Dolapix[®] CE64 changed negligibly from 9.50 ± 0.01 to 9.50 ± 0.05 after adding PVP. Thus, the inherent pH of the suspension was always greater than the pH at the IEP of ~ 8.7 as reported previously,^{11–13} implying a negatively charged surface on the alumina particles in this study. The zeta potential was determined to be -72 mV at a pH of 9.44 ± 0.06 , which was comparable to the pH of the suspensions investigated.

The implication of these results is twofold. First, the pH of the alumina/DI water/Dolapix[®] CE64 system is such that the ceramic surfaces experience highly repulsive interactions allowing for high solid loadings.^{12,38} Second, PVP chains act as a neutral agent in the alumina/DI water/Dolapix[®] CE64 system, but can dramatically alter the rheological response by situating themselves between the powder particles, suggesting that depletion interactions may be occurring.^{19,32} Due to PVP additions in the suspensions, a significantly higher powder loading (>50 vol% solids) was attainable in the ceramic-PVP suspensions. It was speculated that depletion interactions might play a role in the unique flow properties of the alumina suspensions examined here. Further discussion of this conclusion is described in subsequent sections.

(2) Rheological Behavior of Alumina|DI Water|Dolapix[®] CE64|PVP Suspensions

(A) *Effect of Powder Loading and PVP Addition:* The effect of increasing inorganic content on the rheological behavior of alumina suspensions without polymer is presented in Fig. 2 for the shear-rate range studied (0 – 100 s⁻¹).

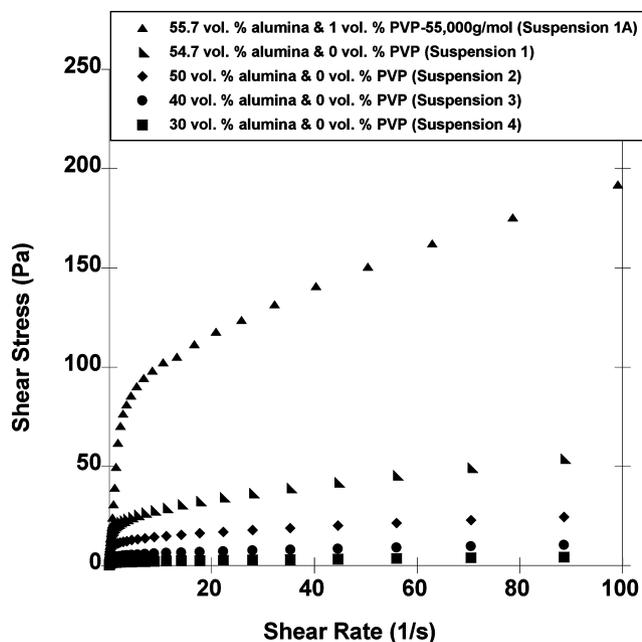


Fig. 2. Flow curves of alumina suspensions using Dolapix[®] CE64 as dispersant. Specimens 1–4 from Table I do not include PVP in the formulation. Specimen 1A from Table II contains PVP. A drastic change in flow behavior can be observed with increasing ceramic concentration and addition of PVP.

Suspensions 1 through 4 in Fig. 2 contain no PVP, but possess alumina concentrations ranging from 30 to 54.7 vol%. The rheological response changes from Newtonian for suspensions containing 30 vol% alumina to a shear thinning behavior for suspensions with 40 vol% alumina and above. In addition, for each suspension composition an increase in yield stress is observed with increasing alumina content. The mechanism explaining these rheological changes is the reduction in the interaction volume between particles as the number of particles is increased and is due to higher electrostatic repulsion forces.^{22,39} Generally, aqueous alumina suspensions containing dispersant and organic additives with low ceramic concentrations (<30 vol%) follow a Newtonian flow behavior.^{30,31,40} At higher alumina concentrations (~ 50 vol%), stronger particle interactions generate a pseudoplastic or yield-pseudoplastic behavior,^{2,30,31,41–43} which can be modeled by the Herschel-Bulkley model in Eq. (1).^{2,22}

Figure 2 also indicates that the addition of 1 vol% PVP to a suspension with 55.7 vol% Al₂O₃ (suspension 1A) greatly influences flow behavior compared to a composition with a similar alumina content but without PVP (suspension 1). For example, an approximate three-fold increase in yield stress was observed in suspension 1A compared to suspension 1. Suspension 1A also demonstrated Herschel–Bulkley flow behavior as all PVP-containing suspensions did in this study.

(B) *Effect of PVP Concentration and Average Molecular Weight:* A more complex behavior is observed for suspensions in which the PVP content varies in terms of concentration and average molecular weight after being added to an alumina slurry. Figure 3(a) shows flow curves of compositions containing PVP of the same average molecular

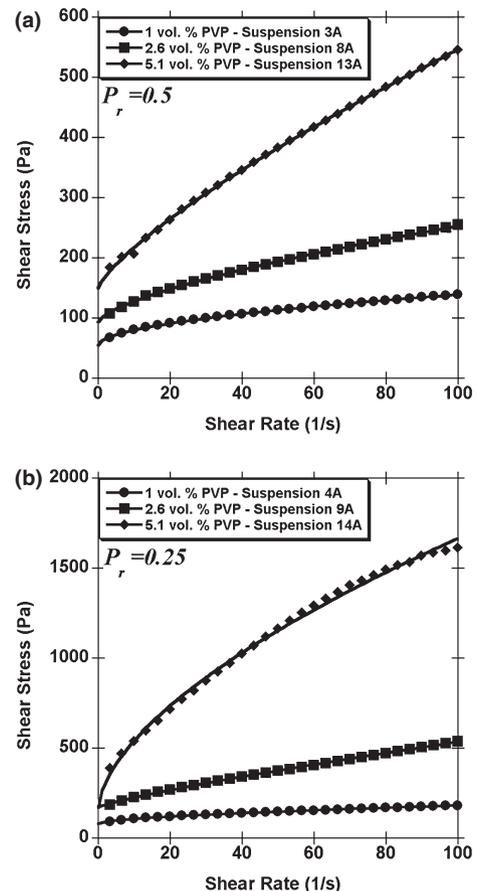


Fig. 3. Flow behavior measurements of alumina suspensions containing PVP. Increasing polymer content and average molecular weight in both cases for (a) $P_r = 0.5$ and (b) $P_r = 0.25$ causes an increase in the yield stress (σ_y), and the consistency (k) of the suspensions. The black continuous lines are curve fits to the Herschel–Bulkley fluid model ($R \sim 0.99$).

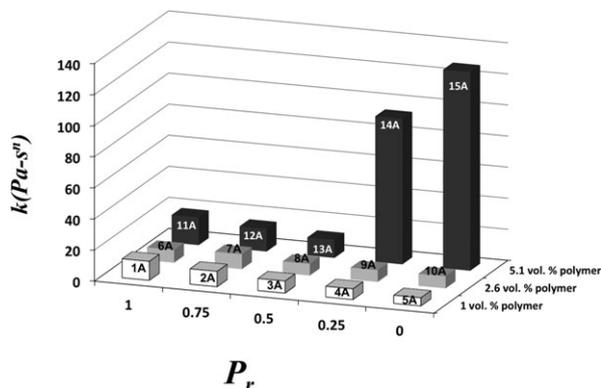


Fig. 4. Comparison of the consistency (k) values obtained from curve fits of the flow curves of specimens 1A–17A to the Herschel–Bulkley model. See Table II for compositions and for the summary of all the parameters calculated from the Herschel–Bulkley model. A drastic increase in consistency is observed for compositions with $P_r = 0.25$ and $P_r = 0$ containing 5.1 vol% PVP due to the effect of higher concentrations of 1 300 000 g/mol PVP.

weight ($P_r = 0.5$), but varying concentration (1, 2.6, and 5.1 vol%). Similarly, Fig. 3(b) depicts the flow response of suspensions with varying PVP concentrations, but with higher average molecular weight ($P_r = 0.25$). In both cases, good agreement with the Herschel–Bulkley model [Eq. (1)] was observed (correlation factor, $R \sim 0.99$). Table II summarizes the parameters obtained from fitting the Herschel–Bulkley model to the compositions presented in Figs. 3(a) and (b) as well as the rest of the compositions in Table II.

An increase in yield stress and flow index with increasing polymer amount is depicted in Figs. 3(a) and (b). For example, the yield strength increased from 54.8 to 150.0 Pa when the amount of PVP was increased from 1 to 5.1 vol% for $P_r = 0.5$. Increasing the yield strength of a formed green body can be beneficial for postforming handling. For identical conditions, the flow index increased from 0.52 to 0.77, indicating less shear thinning for the suspension containing more PVP. Similar trends were noted for suspensions of identical PVP volume additions but with a higher average molecular weight as shown in Fig. 3(b).

The effect of increasing the average molecular weight of the PVP on the flow behavior is evident by comparing Figs. 3(a) and (b). In addition to an increase in yield strength for $P_r = 0.25$ suspensions compared to $P_r = 0.5$ suspensions with identical PVP loading, a large change in consistency, k , was noted. Consistency values for suspension 1A through 15A, representing values of P_r from 0 to 1, are plotted in Fig. 4. Of particular interest are suspensions 14A and 15A, each containing 5.1 total vol% polymer and a large fraction of 1 300 000 g/mol PVP, where dramatic increases in k are observed compared to the other suspensions. Physically, suspensions 14A and 15A were considerably more viscous than the other formulations shown in Table II.

To further investigate the effect of the molecular weight, suspensions were fabricated with the same amount of PVP (5.1 vol%), but with four different average molecular weights (10 000, 55 000, 360 000, and 1 300 000 g/mol) corresponding to compositions 16A, 1A, 17A, and 15A, respectively, as listed in Table II. The flow responses of these compositions are plotted in Fig. 5. An increase in consistency and yield stress is observed for the suspensions with molecular weights of 55 000 and 360,000 g/mol with respect to the suspension containing the lowest molecular weight PVP, but this increment is noticeably higher for the suspension containing the 1 300 000 g/mol PVP.

The flow behavior in Fig. 5 suggests that consistency rises slowly (or is relatively constant) at low to moderate molecular weights, but that above some critical molecular weight, it increases dramatically as observed in suspensions 14A and

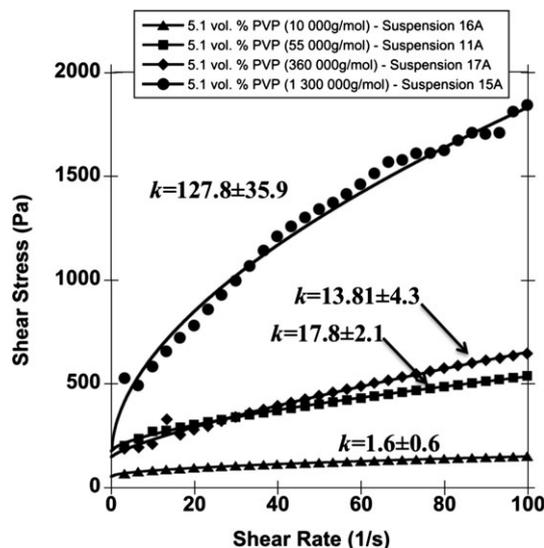


Fig. 5. Flow behavior of alumina suspensions containing 5.1 vol% PVP of 10 000, 55 000, 360 000, and 1 300 000 g/mol average molecular weights (suspensions listed in Table II). The black continuous lines are curve fits to the Herschel–Bulkley fluid model ($R \sim 0.99$). Increasing average molecular weight directly affects the consistency (k) and yield stress (σ_y) of the suspensions. Parameters calculated using the Herschel–Bulkley model are listed in Table II.

15A. At this point, the flow index decreased for the two suspensions. The increase in consistency noted in Figs. 4 and 5 and simultaneous decrease in flow index as indicated in Table II for suspensions with high average molecular weights could be attributed to the following: the effect of bridging between particles and PVP chains or PVP and PMAA chains, entanglements between adjacent polymer chains, and/or an increase in the radius of gyration of the polymer.

The effect of the polymer solutions on the suspension were further examined as well. Table II shows the parameters obtained from fitting the Herschel–Bulkley model to solutions comprised of water and PVP with varying average molecular weights without alumina or dispersant. These PVP solutions acted more Newtonian than yield pseudoplastic, although the PVP solution with molecular weight of 1 300 000 g/mol was more shear thinning than the other three solutions of lower molecular weights. The lack of yield point and more Newtonian flow pattern of the PVP solutions do not wholly explain the more complicated flow properties exhibited by the alumina suspensions with PVP additions as described above. This suggests that a solute effect cannot entirely explain the rheology of the suspension and that another interaction mechanism is dominating. In addition, the PVP-Dolapix® CE64 solution at a pH of 9.5 in water exhibited no qualitative change in viscosity compared with the PVP-water solution suggesting that PVP and PMAA did not synergistically cause adsorption. The combination of the two polymers alone did not directly affect the flow properties of the highly loaded alumina suspensions.

Figure 6 presents the flow behavior for suspensions with alumina content >44.6 vol% and PVP content of 7.4–8.2 vol% PVP. These suspension compositions (1B through 5B) are presented in Table III, along with the Herschel–Bulkley fluid model fitting parameters. Yield strength was noted to increase with powder loading. Meanwhile, the consistency did not show considerable change, and the flow index values were typical of a pseudoplastic suspension (~ 0.6). This result shows that it is possible to modify the yield stress of the suspension at high ceramic loadings, but the consistency and the flow index of the material will stay within the same range of values. Consequently, only a gradual shift of the flow curves is possible with increasing powder content between ~ 45 and 50 vol% inorganics.

(C) *Thixotropy Investigations of Alumina/Dolapix[®] CE64/PVP Aqueous Suspensions*: Suspensions that are thixotropic require a finite time period to achieve an equilibrium viscosity. For example, at a constant shear rate a thixotropic fluid might demonstrate a continuing decrease in viscosity over several seconds or longer and then may take a finite amount of time to achieve its final viscosity after shear is removed.² In terms of ceramic forming, thixotropic suspensions are generally undesired as it implies that the viscosity will increase slowly over time after the stress is removed. The time interval required to increase the viscosity as well as develop the yield point could allow a formed part to self-flow or slump, affecting its final dimensions.

Thixotropic characteristics, if any, of the current suspensions were evaluated by sequentially ramping and unraming the suspension using shear rates from 0 to 600 s⁻¹, from 0 to 100 s⁻¹, and finally from 0 to 10 s⁻¹ and back to 0 s⁻¹. Thixotropy will be apparent if a different viscosity is measured between the ramped and unramped portion of the data at the same shear rate. This difference could arise due to several reasons, including the active breakup of a network of colloidal particles or particles bridged by dispersant or polymer.^{2,21,22,30} Furthermore, viscosity hysteresis will be observed if there is a finite time frame for reforming the original network that has been disturbed by shear.

Figures 7(a) and (b) for specimens 6A and 15A, respectively, show the viscosity versus shear rate for the tests conducted. After each maximum shear rate was reached, the path of the ramp upon reduction in the shear rate followed was the same as the positive ramp regardless of the average molecular weight and the PVP concentration. Although thixotropic behavior would be intuitively expected from the sharp increase in consistency data for samples 14A and 15A presented in Fig. 4, the data highlighted in Figs. 7(a) and (b) indicated that the viscosity of the suspensions was not time-dependent. Thus, thixotropy was not apparent in Figs. 7(a) and (b), nor was thixotropy observed in suspensions 1A through 15A. Thus, there is likely little to no bridging across powders to form network structures. In addition, with depletion interactions the neutral polymer, by virtue of its manifestation in the interstitial volume, may interrupt the inherent network formation of a colloidal powder. For either reason described above, the lack of network formation prevented thixotropy from being

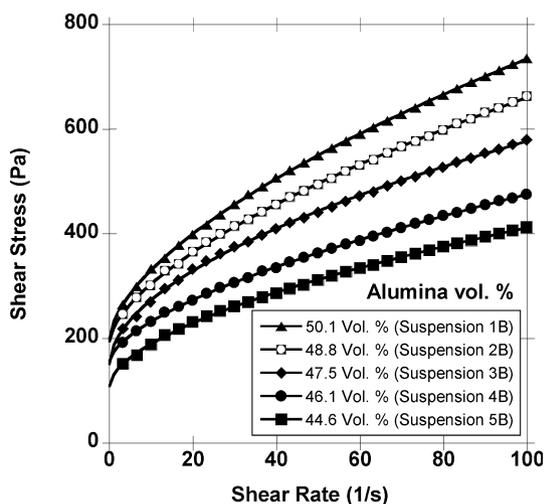


Fig. 6. Flow behavior of alumina suspensions from Table III. A gradual increase in shear stress can be observed with increasing powder content in suspensions containing inorganics at loads between ~45 and ~50 vol%. A general increase in shear stress can be observed for the shear stress range studied. The black continuous lines are curve fits to the Herschel-Bulkley fluid model ($R \sim 0.99$).

observed experimentally suggesting depletion interactions were at play.^{10,21}

(D) *Stress and Frequency Response of Alumina/Dolapix[®] CE64/PVP Aqueous Suspensions*: The viscoelastic response of the suspensions was first evaluated in terms of an oscillatory stress. Figures 8(a) and (b) depict the storage modulus, G' , of four of the compositions in Table II at an oscillation frequency of 1 Hz. These compositions were chosen to show the effects of PVP loading and average molecular weight. In both Figs. 8(a) and (b) the linear viscoelastic regime exists at ranges <10 Pa. As expected G' increased as more PVP was added or as the average molecular weight of PVP was increased. In all cases at stresses >10 Pa, the storage modulus took a precipitous drop.

Based on the results presented in Figs. 8(a) and (b), frequency sweeps at 10⁻¹ Hz through 10² Hz were performed at an oscillation stress inside the linear viscoelastic region (1 Pa) to simplify the complex modulus response. Figure 9(a) shows the storage (G') and loss (G'') modulus for suspensions with constant average molecular weight ($P_r = 0.5$) and polymer contents of 1 and 5.1 vol% PVP, typical of all formulations studied. As shown in Fig. 9(a), a small increase in both G' and G'' was observed for both suspension formulations as test frequency was increased. For some suspensions tested near 100 Hz there was a decline in G' that might have indicated the onset of crossover into a more liquid-like regime. However, further testing at rates greater than 100 Hz would be needed to verify this. In addition, over the frequency ranges measured, G' was always greater than G'' , indicating that the solid properties of the suspension dominate over these frequency ranges. The G' and G'' response of suspensions with the same PVP content but different molecular weight are presented in Fig. 9(b). G' and G'' increased with increasing average molecular weight, and G' was greater than G'' for all frequencies.

The behavior described above corresponds to a nearly frequency independent solid-like response from the materials, which is typical of an elastic material that can recover stored energy. In this case, the weak interaction of the polymer with the dispersant and the alumina generate a colloidal structure with a response that is mostly dependent on the polymer configuration, but not on the adsorption to the ceramic pow-

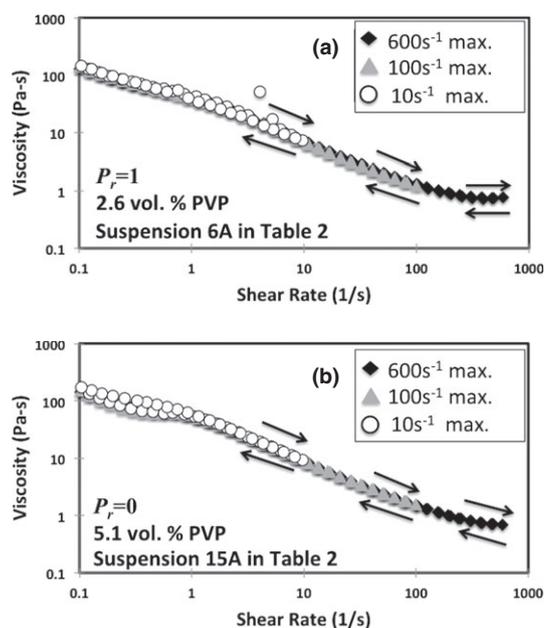


Fig. 7. Multiple experimental hysteresis loops performed on (a) suspension 6A and (b) suspension 15A from Table II. The resultant loops are very narrow as the response of the suspensions is not thixotropic (i.e., no time dependence).

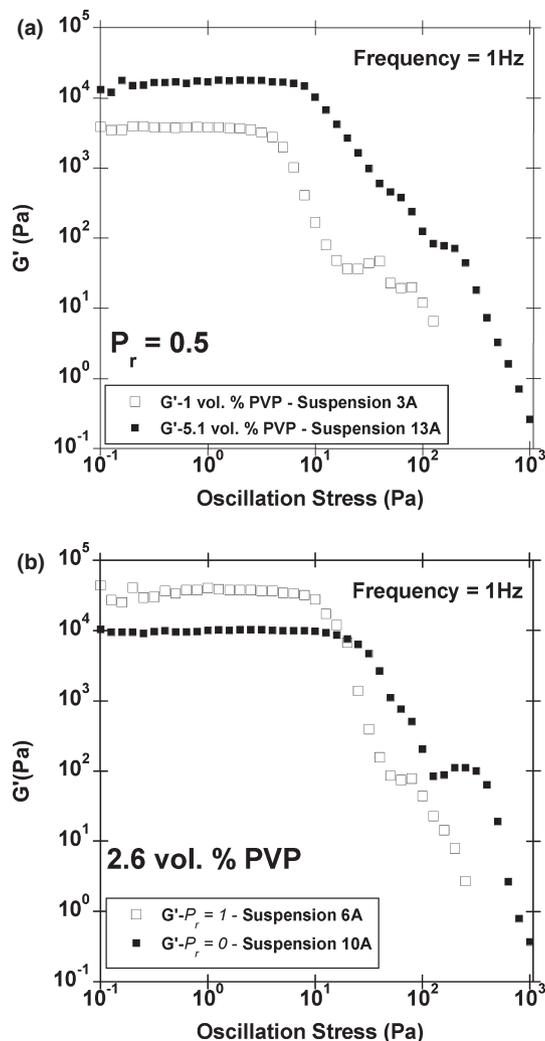


Fig. 8. Oscillation stress sweep on alumina (a) suspensions 3A and 13A (Table II) and (b) suspensions 6A and 10A (Table II) showing a linear viscoelastic region < 10 Pa. In both cases, the range of the linear viscoelastic region is independent of polymer concentration and molecular weight.

der or the dispersant.^{5,29,39,44–46} These types of yield-pseudo-plastic suspensions with frequency independent responses can be manipulated by selecting the type, molecular weight, and concentration of polymer to obtain the desired rheological response, which can be tailored to different ceramic fabrication processes. In addition, the frequency independent response of the suspensions affords a robust processing window over a large forming speed range.

(E) Correlating Rheological Observations with Modeled Potential Interactions of Alumina/Dolapix® CE64/PVP Aqueous Suspensions: From the rheological observations previously described, bridging flocculation cannot be fully ruled out, although it is not likely to be the sole culprit behind the dramatic increase in yield stress and consistency that has been observed in the alumina-PVP suspensions. This conclusion was based on discussion in Section I and results in Section III in which adsorption of PVP to the particle surface for a pH of ~ 9.5 was negligible. In addition, the solution of PVP with Dolapix® CE64 did not exhibit high viscosity to suggest that the two polymers interacted to cause an adsorption effect that would result in bridging. Entanglement does occur between adjacent polymer molecules up to some critical molecular weight. Above this value, an increase in molecular weight does not significantly affect the number of entanglements between adjacent chains. It is possible that the order-of-magnitude increase in consistency between the

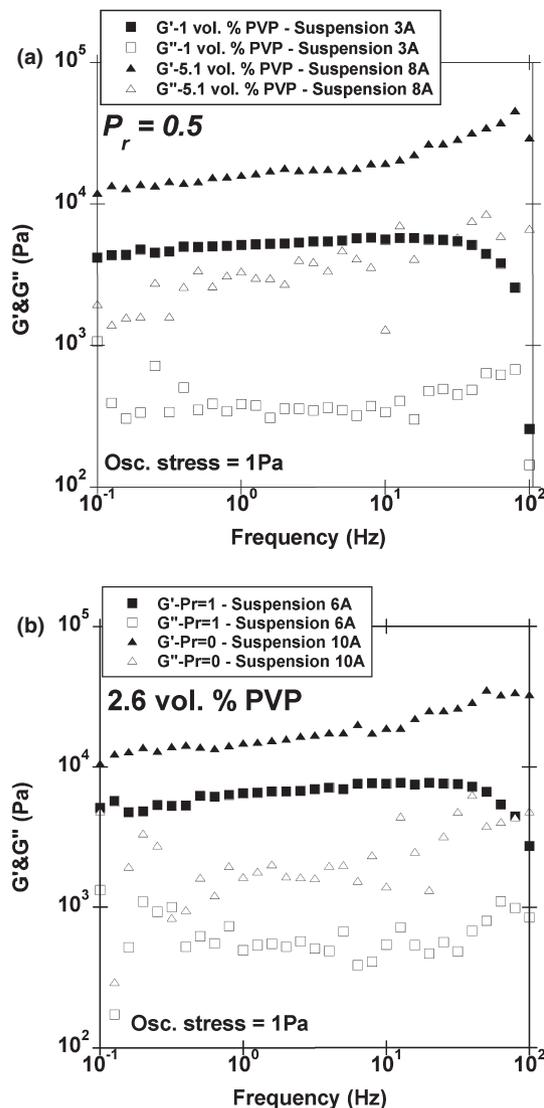


Fig. 9. Frequency sweep of alumina (a) suspensions 3A and 13A (Table II) and (b) suspensions 6A and 10A (Table II). Frequency independent behavior can be observed ($G' > G''$ for the frequencies observed). An increase in G' and G'' can be observed with increasing polymer content and average molecular weight as in Figs. 9(a) and (b), respectively.

10 000 g/mol PVP suspension and the 55 000 g/mol PVP suspension represents this transition between polymer chains moving independently and dependently with respect to one another. However, entanglement of polymers does not explain the dramatic increase in consistency for polymers with molecular weights above 55 000 g/mol. In other words, because entanglement would be expected for the suspensions containing 55 000, 360 000, and 1 300 000 g/mol polymer, differences in flow behavior cannot be attributed to this phenomenon.

In depletion interactions, the polymer chains are segregated to the interstitial volume between powders, because they do not adsorb on their surface. It has been established that the radius of gyration (R_g) of a polymer scales with molecular weight.⁴⁷ Furthermore, for a good solvent as is the case for water dissolving PVP, the volume that the polymer occupies can be described as a sphere with an R_g that increases as the number of repeats (or molecular weight) to the 0.6 power ($N^{3/5}$).^{47,48} There is a limit to the interstitial volume that is available between the particles, and it is reduced as powder volume is increased.⁴⁹ This becomes important in highly loaded suspensions such as those studied currently. Alternatively, as molecular weight increases, a

single polymer chain eventually occupies a large enough volume such that it approaches the interstitial volume available between the particles.^{50,51} Thus, the coiled polymer molecules will be forced into interaction with the particles. However, at higher molecular weights, interactions between particle and polymer can distort the spherical random coil representing the thermodynamic ground state of the polymer and affect flow of the polymer around the powders. Such chain distortions, interparticle forces, and/or resistance to easy flow between particles will be visible in rheological data.^{10,21,52}

To correlate the underlying interparticle interactions with the rheological observations presented in previous sections, a qualitative assessment of the colloidal interactions in the alumina-PVP system was performed. As the total potential energy can reveal the interparticle interactions that determine the overall stability of a colloidal system, the total interaction potential energy, V_{tot} , was treated as the sum of the long-range van der Waals attractive potential energy, V_{vdw} , the repulsive steric potential energy term, V_{steric} , the repulsive electrostatic double-layer interaction energy, V_{elect} , and the depletion potential energy, V_{dep} (refer to Appendix for the qualitative calculations considered in this study). This approach has been previously applied to complex, dilute systems containing free polymer, and the model has been observed to qualitatively match experimental observations.^{53,54} Although the suspensions evaluated in this study were concentrated, the current assessment allowed for a qualitative appraisal of the interparticle forces governing the rheological behavior of the overall system.

The total potential energy curve for the suspension without neutral PVP is shown in Fig. 10. At close interparticle spacings, the V_{steric} and V_{elect} terms dominated causing an overall repulsive interaction until the particle spacing was greater than four nanometers resulting in the formation of a potential minimum. Although the minimum of attraction was somewhat shallow, its presence suggested that the dispersed alumina system was weakly flocculated.²¹ However, in accordance with stability criteria described by Russel,⁵² where stable colloidal suspensions exhibited $\epsilon_0 \psi_0^2 a / k_B T \gg 1$ or $\frac{1}{2} - \chi > 0$, with ϵ_0 being the dielectric constant, ψ_0 approximated by the zeta potential, a representing the radius of the alumina particles, k_B as the Boltzmann constant, T being temperature, and χ as the Flory-Huggins polymer/solvent interaction parameter, the suspensions without PVP were considered to be stable. It was important to include both V_{steric} and V_{elect} in the determination of the total potential curve as Dolapix[®] CE64 was a low molecular weight dispersant that caused a

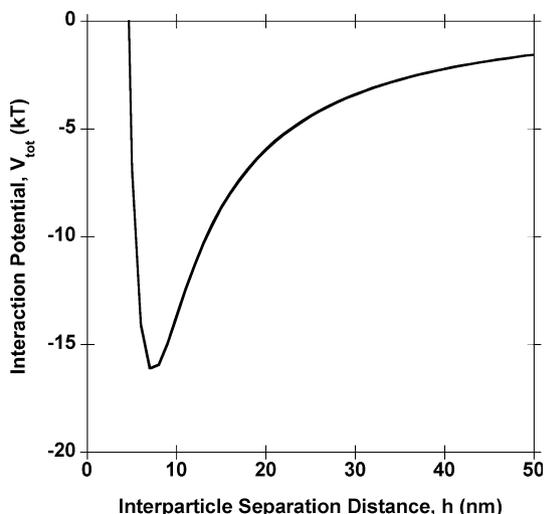


Fig. 10. Total interaction potential curve for alumina-Dolapix[®] CE64 suspensions without PVP additions exhibits a shallow potential minimum indicating weak flocculation of the suspension.

thin adsorbed layer (calculated to be <1 nm) to form, which modified the surface charge of the particles thus enhancing stability.^{11–13} Without consideration of both terms, the attractive van der Waals potential would have inaccurately dominated potential interactions suggesting instability of the suspension.

By accounting for the repulsive steric, electrostatic, and attractive van der Waals terms, the depletion component was calculated by treating the neutral PVP as the depletant in solution. The total potential minimum including V_{dep} with depletant volume fractions approximated as 0.01, 0.026, and 0.051 qualitatively decreased with increasing PVP content for each of the four molecular weights investigated. However, it was observed that with increasing molecular weight the magnitude of both the depth and height of the depletion potential curves decreased, which contradicted current theoretical predictions that depletion interactions would be enhanced with increasing molecular weight.^{8,55} The increase in the depth of the total potential energy minimum with increasing volume fraction implied that PVP slightly enhanced the attractive potential interactions. This qualitative observation corresponded to the rheological behavior of the alumina-PVP suspensions where yield stress increased with increasing PVP content as highlighted in Fig. 3. Because increasing yield stress is indicative of stronger attractive interactions in a colloidal system,² this enhanced flocculation may possibly be attributed to a depletion flocculation mechanism with the introduction of PVP. Although secondary minima were present, the magnitudes of the depletion forces that were estimated, as shown in Fig. 11, were too small to justify the marked difference in flow stresses observed in the rheological data of Fig. 3. It is clear that the calculated depletion interactions considered here have a minimal effect on the overall stability or instability of the system suggesting that other interparticle interactions, such as polymer chain overlap, free volume restrictions or interpenetration of the adlayer on particle surfaces, are influencing the system.

Although the qualitative estimation of interparticle interactions without depletion considerations reflected the rheological behavior exhibited by the suspensions without PVP, depletion interactions calculated using current predictions did not account for the discrepancies observed in yield stress values with increasing PVP content. This can likely be

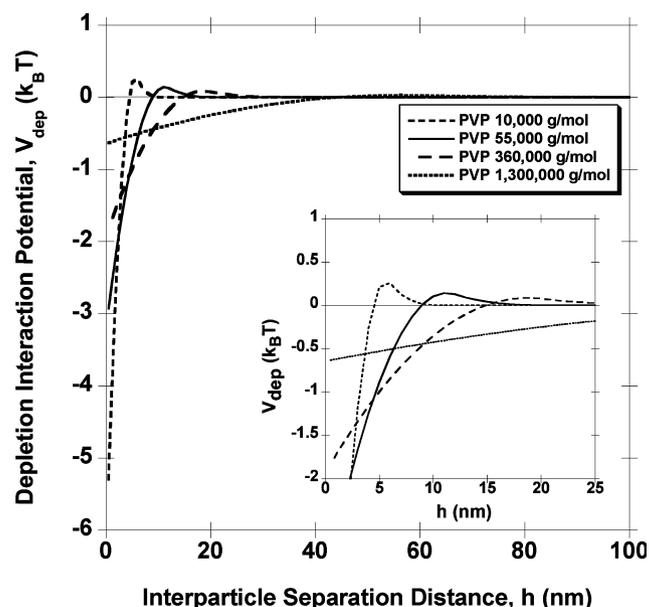


Fig. 11. Depletion interaction potential curves for alumina-Dolapix[®] CE64 suspensions with 5.1 vol% PVP of varying molecular weights. (Inset depicts same curves at shorter interparticle separations.)

ascribed to the fact that the current model does not fully reconcile the subtleties of conformation effects and free volume restrictions on depletion interactions in more complex concentrated suspensions of high molecular weight free polymer and with high solids loading.⁵⁶ Further analysis is required to identify the exact interparticle interactions of these highly loaded alumina suspensions in which a minimal amount of neutral polymer is necessary to dramatically alter the rheological response.

IV. Summary and Conclusions

The rheological behavior of highly loaded alumina (>50 vol%) aqueous suspensions was studied for formulations in which Dolapix[®] CE64 was used as a dispersant, and PVP with different average molecular weights was added as a response modifier. Stable suspensions were fabricated with pH \approx 9.5, and PVP additions of 1, 2.6, and 5.1 vol% with different average molecular weights allowing for a yield-pseudoplastic flow behavior. Parallel plate rheometry was used to examine the effect of alumina loading, polymer amount, and average molecular weight of the polymer on the flow, stress, and oscillatory response of the suspensions fabricated.

In suspensions with inorganic content higher than 50 vol%, adding PVP had a strong effect on the flow behavior. PVP greatly increased the yield stress of the formulations at low shear rates as well as increased the shear stress for the range studied. The flow curves measured from the specimens were fit to the Herschel–Bulkley fluid model with good agreement for all cases. At alumina concentrations between 45 and 50 vol%, a general increase in shear stress was observed as a result of the reduction in interaction volume between particles suggesting weak flocculation. It was found that for suspensions containing PVP, it was possible to increase the yield stress by increasing polymer content and average molecular weight. The consistency, k , of the formulations showed a drastic increase for higher polymer contents (5.1 vol% PVP) and higher average molecular weights ($P_r > 0.25$). This was proposed to be due to the PVP gyration volume being greater than the interstitial volume between powders.

The aqueous alumina/Dolapix[®] CE64/PVP suspensions fabricated in this study demonstrated very narrow viscosity versus shear rate hysteresis loops, which is an indication of non-thixotropic behavior. Oscillatory response measurements performed in the linear viscoelastic region of the suspensions (<10 Pa) showed that the formulations were frequency independent and had a highly elastic and solid-like behavior ($G' \gg G''$ for all frequencies tested). This was attributed to the high alumina concentration and the weak interaction of PVP with the dispersant and the alumina. Both non-thixotropic and frequency independent behavior along with the neutral character of PVP at the pH of the suspensions suggested that depletion interactions might have affected the overall interparticle interactions, as PVP minimally interacted with the dispersant (Dolapix[®] CE64) and the surface of the alumina.

Through qualitative consideration of interparticle forces, the potential interaction plot captured overall experimental observations. By incorporating the depletion interaction model presented by Mao *et al.*,⁵⁷ it was determined that the depletion component negligibly affected the colloidal stability of the suspensions examined suggesting that other interactions were at play, such as PVP chain overlap, polymer conformation restrictions or interpenetration of the adsorbed PMAA layer on the alumina particle surfaces. Current depletion calculation methods cannot yet capture such fine polymer dynamic details particularly in suspensions with high depletant concentrations and solid loadings. Although simple suspensions with lower solid loadings lend themselves to the study and direct observation of depletion interactions, high loadings are more suitable for practical applications in ceramics processing in which high loadings are most desirable. To better understand highly loaded sus-

pensions with a neutral polymer species, a model that accounts for such system conditions is needed. Depletion interactions may offer a simple approach to manipulate the response of ceramic colloids that can be adapted to a number of ceramic fabrication methods that require near-net morphologies.

In conclusion, the exact mechanism dictating the unique rheological response of these highly loaded alumina suspensions with minimal polymer carrier cannot be resolved without additional study. However, the minimal addition of polymer in a highly loaded suspension allowed for the introduction of a slight, controlled degree of weak flocculation indicated by the increase in yield stress. This ability to tailor rheological properties with a minimal amount of a neutral polymer carrier will no doubt prove useful in the development of novel ceramic processing methods.

Appendix

To qualitatively ascertain the interparticle potentials of the alumina-PVP suspension evaluated in this study, total interaction potential energy, V_{tot} , was calculated by considering four major components:

$$V_{\text{tot}} = V_{\text{vdw}} + V_{\text{steric}} + V_{\text{elect}} + V_{\text{dep}} \quad (2)$$

where V_{vdw} was the long-range van der Waals attractive potential energy, V_{steric} represented the repulsive steric potential energy term that resulted from the adsorbed PMAA from the dispersant interacting with particle surfaces, V_{elect} was the repulsive electrostatic double-layer potential energy originating from interactions among particles with similar surface charges, and V_{dep} was the depletion potential energy arising due to the nonadsorbing PVP in solution. The V_{vdw} interaction potential for equal-sized spherical particles is given by the Hamaker expression:

$$V_{\text{vdw}} = -\frac{A}{6} \left(\frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln \left(\frac{s^2 - 4}{s^2} \right) \right) \quad (3)$$

where A is the non-retarded Hamaker constant, $s = \frac{2a+h}{a}$, h is the spacing between the surfaces of the alumina particles, and a is the radius of the alumina particles.⁵⁸ For this study, the Hamaker constant, $A = 3.67 \times 10^{-20}$ J, for alumina interacting across water at 298 K was used.⁵⁹

The V_{steric} potential energy term was determined using the approach developed by Vincent *et al.*⁶⁰ for adsorbed polymer layers on spherical particles. The steric potential contribution is dependent on particle spacing with respect to the adlayer thickness, δ , and can be subdivided into three domains of interaction: the noninteractional domain, the interpenetration domain, and the interpenetration-plus-compressional domain.⁶¹ In the first domain, the adsorbed polymer layers do not interact at separation distances $h \geq 2\delta$, and $V_{\text{steric}} = 0$. The interpenetration domain applies when steric layers begin to interact at $\delta \geq h \geq 2\delta$. This steric mixing component assuming that the adsorbed polymers behave as a pseudo-homopolymer is given by $V_{\text{s,mix}}$:

$$V_{\text{s,mix}} = \frac{32\pi a k_B T (\phi_2^a)^2}{5v_1 \delta^4} \left(\frac{1}{2} - \chi \right) \left(\delta - \frac{h}{2} \right)^6 \quad (4)$$

where k_B is the Boltzmann constant, T is temperature, v_1 is the molar volume of the solvent, χ is the Flory–Huggins polymer/solvent interaction parameter, and ϕ_2^a is the average volume fraction of segments in an adsorbed layer determined to be 0.28 for this system using equations set forth by van den Boomgaard *et al.*⁶² The interpenetration-plus-compressional domain occurs at very low interparticle spacings of

$0 \geq h \geq \delta$. Assuming that the adsorbed polymer segment density is homogeneous, the steric potential, V_{steric} , is comprised of the sum of two terms accounting for a mixing component, $V_{\text{s,mix}}$, and elastic compression of the polymer chains, $V_{\text{s,el}}$:

$$V_{\text{s,mix}} = \frac{4\pi a \delta^2 k_B T}{v_1} (\phi_2^a)^2 \left(\frac{1}{2} - \chi \right) \left[\frac{h}{2\delta} - \frac{1}{4} - \ln \frac{h}{\delta} \right] \quad (5)$$

$$V_{\text{s,el}} = \frac{2\pi a \delta^2 k_B T \rho_2 \phi_2^a}{M_2^a} \left\{ \frac{h}{\delta} \ln \left[\frac{h}{\delta} \left(\frac{3-h/\delta}{2} \right)^2 \right] - 6 \ln \left[\frac{3-h/\delta}{2} \right] + 3 \left(1 - \frac{h}{\delta} \right) \right\} \quad (6)$$

where ρ_2 is the density and M_2^a is the molecular weight of the adsorbed polymer.⁶⁰

The electrostatic component, V_{elect} , was calculated using an approximation for a 1:1 electrolyte to determine the electrostatic potential between two spheres of equal size,

$$V_{\text{elect}} = 4.61 \times 10^{-11} a \tan h^2 (ze\psi_0/4k_B T) e^{-\kappa h} \quad (7)$$

with valency $z = 1$, elementary charge e , ψ_0 approximated by the zeta potential and $1/\kappa$ being the Debye length.⁴⁷ This numerical approximation was selected over the more frequently applied Debye-Hückel approximation for low surface potentials⁶³ due to the high surface potential ($ze\psi_0/2k_B T > 1$)⁵³ observed in the suspensions of alumina particles with adsorbed PMAA-NH₄ in water as determined by zeta potential analysis [refer to Section III (I)]. The Debye length was found to be 0.743 nm assuming PMAA-NH₄ to be a 1:1 electrolyte⁶⁴ and that complete dissociation of PMAA-NH₄ occurred at the pH of the suspension, pH ~ 9.5 , as previously observed for basic alumina-Dolapix® CE64 solutions.¹¹

This study adopted the approach taken by Ogden and Lewis⁵⁴ to approximate depletion interactions by applying the model set forth by Mao *et al.*⁵⁷ The model calculates the depletion potential between large spheres in dilute solutions of small, equally sized spheres with radius, a_{dep} , and of volume fraction, ϕ_{dep} , as

$$\frac{V_{\text{dep}}(\lambda)}{k_B T} = 0, \quad h \geq 2a_{\text{dep}} \quad (8)$$

$$\frac{V_{\text{dep}}(\lambda)}{k_B T} = \frac{a(\phi_{\text{dep}})^2}{10a_{\text{dep}}} (12 - 45\lambda + 60\lambda^2 - 30\lambda^3 + 3\lambda^5), \quad (9)$$

$$4a_{\text{dep}} > h \geq 2a_{\text{dep}}$$

$$\frac{V_{\text{dep}}(\lambda)}{k_B T} = -\frac{3a\phi_{\text{dep}}}{2a_{\text{dep}}} \lambda^2 + \frac{a(\phi_{\text{dep}})^2}{10a_{\text{dep}}} (12 - 45\lambda - 60\lambda^2), \quad h < 2a_{\text{dep}} \quad (10)$$

where $\lambda = h - 2a_{\text{dep}}/2a_{\text{dep}}$. The caveat of applying this set of equations is that it is only valid when particles are considered hard spheres (i.e., the steric effect of the adsorbing polymer on the particle surfaces is neglected) with the adsorbed polymer species modeled as monodispersed spheres. These assumptions can only be represented by a dilute solution, that is when ϕ_{dep} is given by the excluded volume fraction, $\phi_{\text{dep}} = n_b \pi (2a_{\text{dep}})^3 / 6$ with n_b corresponding to the bulk density of the free polymer in the suspension, and ϕ_{dep} is less than the critical concentration for the dilute-semidilute transition, ϕ^* .^{54,57} Above ϕ^* the nonadsorbing polymer coils

begin to overlap resulting in more complex interactions with the particles and surrounding coils affecting the overall achievable polymer conformations as well as the free volume they may occupy.⁶⁵ Furthermore, the high solid loadings (>50 vol%) used in the alumina-PVP suspensions further complicated the behavior of the neutral polymer when compared with previous studies at much lower solid contents (<20 vol%).⁵⁴ Conformations of neutral polymer chains in solution were likely further restricted by the small interparticle spacings making it difficult to isolate the precise effect of the nonadsorbing phase on the stability of the system. These factors greatly influenced the overall value of ϕ_{dep} and thus the magnitude of the depletion potential calculated using Eqs (8)–(10). The depletant volume fractions were estimated in this study to be 0.01, 0.026, and 0.051, and as a result, the magnitudes at different PVP contents described in Section III (I) serve merely as a basic qualitative assessment of the depletion interactions occurring in the suspension.

Acknowledgments

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References

- F. Harbach and H. Nienburg, "Homogeneous Functional Ceramic Components Through Electrophoretic Deposition From Stable Colloidal Suspensions-I. Basic Concepts and Application to Zirconia," *J. Am. Ceram. Soc.*, **18** [6] 675–83 (1998).
- R. G. Larson, *The Structure and Rheology of Complex Fluids*. Oxford University Press, New York, 1999.
- J. S. Reed, "Common Raw Materials/Industrial Inorganic Chemicals," pp. 40–9 in *Principles of Ceramics Processing*. Wiley Interscience, New York, NY, 1995.
- D. Hotza and P. Greil, "Review: Aqueous Tape Casting of Ceramic Powders," *Mater. Sci. Eng., A*, **202**, 206–17 (1995).
- W. M. Sigmund, N. S. Bell, and L. Bergström, "Novel Powder-Processing Methods for Advanced Ceramics," *J. Am. Ceram. Soc.*, **83** [7] 1557–74 (2000).
- P. Somasundaran, *Encyclopedia of Surface And Colloid Science*. Vol. 7, 2006.
- A. L. Ogden and J. A. Lewis, "Effect of Nonadsorbed Polymer on the Stability of Weakly Flocculated Suspensions," *Langmuir*, **12**, 3413–34 (1996).
- R. I. Feigin and D. H. Napper, "Depletion Stabilization and Depletion Flocculation," *J. Colloid Interface Sci.*, **75** [2] 525–41 (1980).
- R. I. Feigin and D. H. Napper, "Stabilization of Colloids by Free Polymer," *J. Colloid Interface Sci.*, **74** [2] 567–71 (1980).
- R. G. Horn, "Surface Forces and Their Action in Ceramic Materials," *J. Am. Ceram. Soc.*, **73** [5] 1117–35 (1990).
- A. Daksobler, K. Kočevar, and T. Kosmač, "Short Range Repulsive Potential Developed by the Addition of Mg(II) Ions to Aqueous Alumina Slurries," *J. Eur. Ceram. Soc.*, **21**, 2361–8 (2001).
- A. Daksobler and T. Kosmač, "Weakly Flocculated Aqueous Alumina Suspensions Prepared by the Addition of Mg(II) Ions," *J. Am. Ceram. Soc.*, **83** [3] 666–8 (2000).
- A. Daksobler and T. Kosmač, "Destabilization of an Alkaline Aqueous Alumina Suspension by the Addition of Magnesium Acetate," *Colloids Surf. A*, **195**, 197–203 (2001).
- I. Ganesh, G. Sundararajan, S. M. Olhero, P. M. C. Torres, and J. M. F. Ferreira, "A Novel Colloidal Processing Route to Alumina Ceramics," *Ceram. Int.*, **36** [4] 1357–64 (2010).
- G. Tari, J. M. F. Ferreira, A. T. Fonseca, and O. Lyckfeldt, "Influence of Particle Size Distribution on Colloidal Processing of Alumina," *J. Eur. Ceram. Soc.*, **18** [3] 249–53 (1998).
- R. Bury, B. Desmazières, and C. Treiner, "Interactions Between Poly(Vinylpyrrolidone) and Ionic Surfactants at Various Solid/Water Interfaces: A Calorimetric Investigation," *Colloids Surf. A*, **127**, 113–24 (1997).
- K. Ishiduki and K. Esumi, "Adsorption of Poly(Acrylic Acid) and Poly(Vinylpyrrolidone) on Alumina From Their Mixtures in Aqueous Solution," *J. Colloid Interface Sci.*, **185**, 274–7 (1997).
- K. Esumi, M. Litaka, and K. Torigoe, "Kinetics of Simultaneous Adsorption of Poly(Vinylpyrrolidone) and Sodium Dodecyl Sulfate on Alumina Particles," *J. Colloid Interface Sci.*, **282**, 71–5 (2000).
- I. Száraz and W. Forlsing, "PVP and Azelaic Acid Adsorption on γ -Alumina Studied by FT-IR Spectroscopy," *Vib. Spectrosc.*, **29**, 15–20 (2002).
- M. Pattanaik and S. K. Bhattacharya, "Adsorption Behavior of Polyvinyl Pyrrolidone on Oxide Surfaces," *Mater. Lett.*, **44**, 352–60 (2000).
- J. A. Lewis, "Colloidal Processing of Ceramics," *J. Am. Ceram. Soc.*, **83** [10] 2341–59 (2000).

- ²²R. J. Hunter, *Introduction to Modern Colloid Science*. Oxford Science Publications, New York, 2003.
- ²³A. Krell, P. Blank, H. Ma, T. Hutzler, and M. Nebelung, "Processing of High-Density Submicrometer Al₂O₃ for New Applications," *J. Am. Ceram. Soc.*, **86** [4] 546–53 (2003).
- ²⁴S. Blackburn and D. I. Wilson, "Shaping Ceramics by Plastic Processing," *J. Eur. Ceram. Soc.*, **28**, 1341–51 (2008).
- ²⁵R. Janssen, S. Scheppokat, and N. Claussen, "Tailor-Made Ceramic-Based Components—Advantages by Reactive Processing and Advanced Shaping Techniques," *J. Eur. Ceram. Soc.*, **28**, 1369–79 (2008).
- ²⁶C. H. Schilling, M. Sikora, P. Tomasik, C. Li, and V. Garcia, "Rheology of Alumina–Nanoparticle Suspensions: Effects of Lower Saccharides and Sugar Alcohols," *J. Eur. Ceram. Soc.*, **22** [6] 917–21 (2002).
- ²⁷N. E. Kiratzis and P. F. Luckham, "The Rheology of Aqueous Alumina Suspensions in the Presence of Hydroxyethylcellulose as Binder," *J. Eur. Ceram. Soc.*, **19** [15] 2605–12 (1999).
- ²⁸C. H. Schilling, P. Tomasik, C. Li, and M. Sikora, "Protein Plasticizers for Aqueous Suspensions of Micrometric- and Nanometric-Alumina Powder," *Mater. Sci. Eng., A*, **336** [1–2] 219–24 (2002).
- ²⁹L. B. Garrido and A. N. Califano, "Effect of an Excess Polyelectrolyte on Viscoelastic Properties of Suspensions of Alumina and Zircon Mixtures," *Colloids Surf. A*, **302**, 24–30 (2007).
- ³⁰M. Pradhan and P. Bhargava, "Influence of Sucrose Addition on the Rheology of Alumina Slurries Dispersed With Polyacrylate Dispersant," *J. Am. Ceram. Soc.*, **88** [4] 833–8 (2005).
- ³¹J. C. Kim, K. H. Auh, and C. H. Schilling, "Effects of Polysaccharides on the Rheology of Alumina Slurries," *J. Eur. Ceram. Soc.*, **20**, 259–66 (2000).
- ³²C. Maltesh, P. Somasundaran, R. A. Kulkarni, and S. Gundiah, "Polymer-Polymer Complexation in Dilute Aqueous Solutions: Poly(Acrylic Acid)-Poly(Ethylene Oxide) and Poly(Acrylic Acid)-Poly(Vinylpyrrolidone)," *Langmuir*, **7**, 2108–11 (1991).
- ³³Zschimmer & Schwarz, "Dolapix CE 64", in Technical Data Sheet. 2012.
- ³⁴R. Moreno, A. Salomoni, and I. Stamenkovic, "Influence of Slip Rheology on Pressure Casting of Alumina," *J. Eur. Ceram. Soc.*, **17** [2–3] 327–31 (1997).
- ³⁵S. Novak and K. König, "Fabrication of Alumina Parts by Electrophoretic Deposition From Ethanol and Aqueous Suspensions," *Ceram. Int.*, **35** [7] 2823–9 (2009).
- ³⁶S. Novak, G. Dražić, and S. Macek, "A Study of Ceramic-Suspension Solidification Using Complex-Impedance Spectroscopy," *J. Eur. Ceram. Soc.*, **21** [10–11] 2081–4 (2001).
- ³⁷B. G. Liptak, *Instrument Engineers' Handbook*. 4th edn, CRC Press, Boca Raton, Florida, 2003.
- ³⁸S. Gaydardzhiev and P. Ay, "Characterization of Aqueous Suspensions of Fumed Aluminum Oxide in the Presence of Two Dolapix Surfactants," *J. Mater. Sci.*, **41**, 5257–62 (2006).
- ³⁹M. S. Subbanna, Pradip, and S. G. Malghan, "Shear Yield Stress of Flocculated Alumina-Zirconia Mixed Suspensions: Effect of Solid Loading, Composition and Particle Size Distribution," *Chem. Eng. Sci.*, **17** [530] 3073–19 (1998).
- ⁴⁰C. J. Martinez and J. A. Lewis, "Rheological, Structural, and Stress Evolution of Al₂O₃: Latex Tape-Cast Layers," *J. Am. Ceram. Soc.*, **85** [10] 2406–16 (2002).
- ⁴¹K. Prabhakaran, S. Ananthakumar, and C. Pavithran, "Gel Casting of Alumina Using Boehmite as a Binder," *J. Eur. Ceram. Soc.*, **19**, 2875–81 (1999).
- ⁴²M. J. Edirisinghe, H. M. Shaw, and K. L. Tomkins, "Flow Behavior of Ceramic Injection Moulding Suspensions," *Ceram. Int.*, **18**, 193–200 (1992).
- ⁴³T. Lemke, F. Bagusat, K. Köhnke, K. Huseman, and H. J. Mögel, "Time Dependent Viscosity of Concentrated Alumina Suspensions," *Colloids Surf. A*, **150**, 283–7 (1999).
- ⁴⁴K. Esumi, "Adsorption of Polymer and Surfactant From Their Binary Mixtures on Alumina," pp. 138–52. in *Surfactant Adsorption and Surface Solubilization*, Vol. **615**. ACS Symposium Series. American Chemical Society, 1996.
- ⁴⁵M. S. Ali, M. Suhail, G. Ghosh, M. Kammil, and Kabir-ud-Din, "Interactions Between Cationic Gemini/Conventional Surfactants With Polyvinylpyrrolidone: Specific Conductivity and Dynamic Light Scattering Studies," *Colloids Surf. A*, **350**, 51–6 (2009).
- ⁴⁶H. M. Wyss, E. V. Tervoort, and L. J. Gauckler, "Mechanics and Microstructures of Concentrated Particle Gels," *J. Am. Ceram. Soc.*, **88** [9] 2337–48 (2005).
- ⁴⁷J. Israelachvili, *Intermolecular and Surface Forces*. pp. 450, 2nd edn. Academic Press, Oxford, UK, 1991.
- ⁴⁸P. J. Flory, *Statistical Mechanics of Chain Molecules*. Hanser Gardner Pubs, Long Beach, CA, 1989.
- ⁴⁹R. J. Flatt and P. Bowen, "Yodel: A Yield Stress Model for Suspensions," *J. Am. Ceram. Soc.*, **89** [4] 1244–56 (2006).
- ⁵⁰E. Tarassova, V. Aseyev, H. Tenhu, and S. Klenin, "Poly(Vinyl Pyrrolidone)-C70 Complexes in Aqueous Solutions," *Polymer*, **44** [17] 4863–70 (2003).
- ⁵¹J. K. Armstrong, R. B. Wenby, H. J. Meiselman, and T. C. Fisher, "The Hydrodynamic Radii of Macromolecules and Their Effect on Red Blood Cell Aggregation," *Biophys. J.*, **87** [6] 4259–70 (2004).
- ⁵²W. B. Russel, "Review of the Role of Colloidal Forces in the Rheology of Suspensions," *J. Rheol.*, **24** [3] 287–317 (1980).
- ⁵³J. E. Seebergh and J. C. Berg, "Depletion Flocculation of Aqueous, Electrosterically-Stabilized Latex Dispersions," *Langmuir*, **10** [2] 454–63 (1994).
- ⁵⁴A. L. Ogden and J. A. Lewis, "Effect of Nonadsorbed Polymer on the Stability of Weakly Flocculated Suspensions," *Langmuir*, **12** [14] 3413–24 (1996).
- ⁵⁵T. Kuhl, Y. Guo, J. L. Alderfer, A. D. Berman, D. Leckband, J. Israelachvili, and S. W. Hui, "Direct Measurement of Polyethylene Glycol Induced Depletion Attraction Between Lipid Bilayers," *Langmuir*, **12** [12] 3003–14 (1996).
- ⁵⁶P. Jenkins and M. Snowden, "Depletion Flocculation in Colloidal Dispersions," *Adv. Colloid Interface Sci.*, **68** [0] 57–96 (1996).
- ⁵⁷Y. Mao, M. E. Cates, and H. N. W. Lekkerkerker, "Depletion Force in Colloidal Systems," *Phys. A*, **222** [1–4] 10–24 (1995).
- ⁵⁸R. J. Hunter, *Foundations of Colloid Science*. Vol. 2, Oxford University Press, Oxford, 2001.
- ⁵⁹L. Bergström, "Hamaker Constants of Inorganic Materials," *Adv. Colloid Interface Sci.*, **70** [0] 125–69 (1997).
- ⁶⁰B. Vincent, J. Edwards, S. Emmett, and A. Jones, "Depletion Flocculation in Dispersions of Sterically-Stabilised Particles ("Soft Spheres")," *Colloids Surf.*, **18** [2–4] 261–81 (1986).
- ⁶¹D. H. Napper, *Polymeric Stabilization of Colloidal Dispersions*. Academic Press Inc., New York, 1983.
- ⁶²T. van den Boomgaard, T. A. King, T. F. Tadros, H. Tang, and B. Vincent, "The Influence of Temperature on the Adsorption and Adsorbed Layer Thickness of Various Molecular Weight Fractions of Poly(Vinyl Alcohol) on Polystyrene Latex Particles," *J. Colloid Interface Sci.*, **66** [1] 68–76 (1978).
- ⁶³R. Hogg, T. W. Healy, and D. W. Fuerstenau, "Mutual Coagulation of Colloidal Dispersions," *Trans. Faraday Soc.*, **62** [0] 1638–51 (1966).
- ⁶⁴J. Cesarano III and I. A. Aksay, "Processing of Highly Concentrated Aqueous Alpha-Alumina Suspensions Stabilized With Polyelectrolytes," *J. Am. Ceram. Soc.*, **71** [12] 1062–7 (1988).
- ⁶⁵B. Vincent, P. F. Luckham, and F. A. Waite, "The Effect of Free Polymer on the Stability of Sterically Stabilized Dispersions," *J. Colloid Interface Sci.*, **73** [2] 508–21 (1980). □