

GT2005-68491

TAILORED RHEOLOGICAL BEHAVIOR OF MULLITE AND BSAS SUSPENSIONS USING A CATIONIC POLYELECTROLYTE

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ABSTRACT

The effects of a cationic polyelectrolyte, polyethylenimine, on the rheological behavior of aqueous mullite and celsian phase, barium strontium aluminosilicate (BSAS) suspensions have been studied to optimize a dip-coating process. The surface of the ceramic particles was characterized in aqueous media using zeta potential measurements. The ionization behavior and hydrodynamic radius of polyethylenimine in aqueous media was characterized by potentiometric titration and dynamic light scattering measurements, respectively. The rheological behavior of concentrated ceramic suspensions containing polyethylenimine was characterized by stress viscometry and elastic modulus measurements. Polyethylenimine imparts repulsive, electrosteric interactions between mullite and BSAS particles in aqueous suspension, resulting in shear thinning flow behavior, linear elastic moduli, and yield stress values that are minimized for suspensions with a critical PEI concentration of 0.2 mg PEI per m² of mullite and 0.4 mg PEI per m² of BSAS, respectively. The elastic moduli and yield stress of mullite and BSAS suspensions were nearly identical at equivalent fractions of their critical PEI concentration. Uniform coatings were obtained upon dipping SiC, Si₃N₄, and Si-metal substrates into shear-thinning suspensions containing PEI at 81-88% of the critical concentration. Dense mullite coatings were demonstrated on SiC substrates after sintering at 1400°C.

INTRODUCTION

Aluminosilicate-based ceramic materials have been studied for high temperature protective coatings because of their excellent thermal shock properties, low thermal conductivity, and thermal expansion match with silicon-based (nonoxide) substrates, e.g. SiC, SiC-SiC composites, and Si₃N₄. These substrate materials exhibit significant fatigue strength and chemical stability in dry air environments, but are susceptible to formation of a fast-growing silica scale that undergoes volatilization and corrosion in high temperature environments containing water vapor and alkali salts, e.g., K₂SO₄ and

Na₂SO₄. This limits the applicability of these materials for extended service in many high temperature, steam-based energy conversion and combustion systems.[1-3] In addition, the deleterious effects of steam and alkali salts are compounded by erosion in high velocity systems such as turbine engines. As a result, development of protective oxide coatings is paramount for extended life cycles of silicon-based ceramic components in actual operating conditions.

Stoichiometric mullite, i.e., 3Al₂O₃·2SiO₂, is perhaps the most widely characterized coating material in high temperature steam and alkali salt environments, although its effectiveness remains a topic of current debate. Diverse results are reported for coatings of varying thickness, density, and uniformity formed by various processing methods. For example, several studies indicate inadequate resistance of plasma-sprayed mullite layers (~ 100-200 μm) to high temperature steam (both high and low gas velocity).[4-8] Tsarenko *et al.* [9] also report that dense, uniform, and thin mullite coatings (0.1 μm) deposited by chemical vapor deposition (CVD) provide no protection from low velocity, high temperature steam. On the other hand, recent results by Haynes *et al.* [10] show that dense CVD mullite layers of increased thickness (~2 μm) provide significant protection in low velocity steam, although poor performance was observed in high velocity conditions.

Efforts are currently underway to identify new coating materials to address the limitations of the mullite system. For example, a doped aluminosilicate, celsian-phase barium strontium aluminosilicate (BSAS), has been identified and is currently being evaluated as a protective coating for high temperature structural ceramics.[4-6,11] This material is believed to provide better protection from corrosion in high temperature steam than mullite due to its lower silica activity.[5] However, it is difficult to directly compare the efficacy of diverse coating materials due to broad variations in coating quality that can arise during processing. Consequently, a concerted effort must be made to separate processing variables from baseline material properties. Protective coatings must be thin, dense, uniform, adherent, and formed

reproducibly on silicon-based ceramic components of complex geometry.

Colloidal processing of ceramic suspensions offers a low cost alternative processing approach for reliably producing ceramic coatings on complex-shaped components via a simple dip coating process. This approach has been demonstrated in many multi-disciplinary areas including other types of coatings (paints, glazes), fabrication of monolithic components (slip casting, rapid prototyping, and gelcasting), pharmaceuticals, cosmetics, and food processing. Control of suspension rheological behavior is essential for producing quality coatings and can be accomplished by tailoring interparticle (surface) forces.[12,13] In aqueous-based suspensions, long-range attractive van der Waals forces are ubiquitous and must be balanced by repulsive forces to tailor the desired degree of suspension stability. For example, ionizable polymeric dispersants, or polyelectrolytes, are commonly used to modify the surface of particles to impart repulsive electrosteric interparticle forces.[14,15]

In this study, the rheological behavior of aqueous mullite and BSAS suspensions were characterized in the presence of polyethylenimine (PEI). PEI is a branched, cationic polyelectrolyte with one protonizable amine group (NH) per monomer unit (C_2H_5N). Zeta potential measurements were carried out to understand the surface behavior of the ceramic particles in aqueous media. Potentiometric titrations and dynamic light scattering measurements were performed to understand the protonization behavior and determine the size of PEI in aqueous media. The rheological behavior of concentrated mullite and BSAS suspensions was characterized by stress viscometry and oscillatory shear measurements. Finally, SiC, Si_3N_4 (AS800), and silicon substrates were dipped into suspensions of varying rheological behavior and the quality of the resultant coatings was characterized.

NOMENCLATURE

- A_s , BET surface area of colloidal particles
- G'_0 , linear elastic modulus
- R_H , hydrodynamic radius of polyelectrolyte in solution
- α , fraction of protonated amine groups
- δ , adsorbed polyelectrolyte layer thickness
- η_{rel} , relative suspension viscosity
- η_{sol} , solution viscosity
- η_{susp} , suspension viscosity (in the high shear limit)
- ϕ , volume fraction of solids in suspension
- ϕ_{eff} , effective volume fraction of solids in suspension
- ϕ_{max} , maximum volume fraction of solids in suspension
- ρ , density of colloidal particles
- τ_Y , yield stress

EXPERIMENTAL PROCEDURE

The ceramic powders used were mullite (MULCR®, Baikowski International Corporation, Charlotte, NC) and celsian-phase, barium strontium aluminosilicate (United Technologies Research Center, East Hartford, CT), which were both phase pure as determined by X-ray diffraction (XGEN-4000, Scintag USA, Sunnyvale, CA). The mullite and BSAS powders were attritor milled to an average particle size (D_{50}) of

1.2 μm and 1.3 μm , respectively, determined using laser diffraction (LA-700, Horiba Instruments Incorporated, Irvine, CA) and a surface area of 26.0 m^2/g and 19.9 m^2/g , respectively, determined using BET analysis (Autosorb-1, Quantachrome Instruments, Boynton Beach, FL). Polyethylenimine (Polysciences, Warrington, PA) was implemented as a rheological modifier in this study. This species had an average molecular weight of 10,000 g/mol and thus, a degree of polymerization of ~ 196 .

Zeta potential measurements were carried out on the mullite and BSAS in dilute aqueous suspension using capillary electrophoresis (Zetasizer 3000HS, Malvern Instruments Ltd., Worcestershire, UK). Dilute suspensions with solids volume fraction (ϕ) of $\sim 10^{-5}$ were prepared by combining the appropriate amount of ceramic powder to deionized water with added KNO_3 (0.01 M) as a background electrolyte. The suspension pH was adjusted over a broad range (2-11) using stock solutions of 1 M HNO_3 and 1 M NH_4OH . Dilute suspensions were ultrasonically treated (60 Hz) for 2 min to break up soft agglomerates and mixed for 24 hours to achieve equilibrium. The pH was measured and adjusted as needed prior to measurement.

Potentiometric titrations were conducted on dilute PEI solutions (50 mg PEI/mL solution, initial pH 11.0) to measure the pH as a function of titrant addition. The titrant species was a 1 M HNO_3 solution, which was dosed into a continuously stirred sample in regular aliquots. The pH response was measured using a standard silver-silver chloride electrode. Data analysis was conducted, as outlined by Arnold and Overbeek [16] and by Hunter [17], to determine the protonization behavior of amine groups as a function of pH. In addition, dynamic light scattering (Zetasizer 3000HS, Malvern Instruments Ltd., Worcestershire, UK) was conducted at neutral pH to measure the average size of PEI. To ensure that the solutions were free from particulate contaminants they were passed through a 0.45 μm filter into dust-free cuvettes and capped. Data analysis was carried out using the CONTIN algorithm by Provencher.[18]

Rheological measurements were carried out on mullite and BSAS suspensions of varying composition using a controlled-stress rheometer (Rheometric Scientific SR5, TA Instruments, New Castle, DE) fitted with a concentric cylinder geometry. Concentrated suspensions ($\phi = 0.20-0.45$) were formulated by mixing an appropriate amount of ceramic powder into aqueous solutions of pH 7 and varying PEI concentration. The suspensions were ultrasonically treated for 5 min to break up soft agglomerates and stirred for 24 hours to achieve equilibrium. The suspensions were injected into the sample cup, presheared at a stress of 200 Pa for 5 min, and allowed to equilibrate for 15 min prior to measurement. Furthermore, a specially designed solvent trap was used to minimize the evaporation of water. In this way, variations in sample handling were minimized to ensure reproducibility of the data. Stress viscometry measurements were carried out by logarithmically ramping an applied shear stress from 0.15 to 1000 Pa. A delay time (i.e., the time between two consecutive data acquisition events) of 1 min was used. After repeating the preshear procedure mentioned above, elastic modulus measurements were carried out by logarithmically ramping an oscillatory shear stress from 0.025 to 1000 Pa at a constant frequency of 1 Hz. All rheological measurements were

performed at a constant temperature of 25°C, maintained by a controlled temperature bath.

Substrates of varying composition, including SiC (Hexaloy, Carborundum Co., Niagara Falls, NY), Si₃N₄ (AS800, Honeywell Ceramic Components, Torrance, California), and metallic silicon, were dipped into concentrated mullite suspensions ($\phi = 0.45$) of varying PEI concentration. The substrates were plunged at rate of 1.5 mm/s, submerged for 1 min, and withdrawn at a rate of 1.5 mm/s. Coated substrates were dried under ambient conditions.

RESULTS AND DISCUSSION

Mullite, BSAS, and PEI Characterization

Zeta potential measurements were carried out on dilute mullite and BSAS suspensions ($\phi = 10^{-5}$) of varying pH and the results are shown in Fig. 1. The isoelectric point (IEP) of mullite was observed at pH 3.8 (Fig. 1a). This value is lower than the range typically reported for mullite (7-8) and closer to the range typically reported for pure silica (pH 1.5-3.0).[19] This finding is in agreement with recent work by Zhou, *et al.* [20] that suggest a thin, silica film forms on the surface of mullite particles after equilibration is achieved in aqueous media. The isoelectric point of BSAS (Fig. 1b) was also observed in acidic conditions, i.e., pH 3. Such measurements are the first to be reported for BSAS. Negative zeta potential values were measured at pH values greater than the IEP; thus, the mullite and BSAS surfaces were negative over a broad pH range.

The protonization behavior of polyethylenimine in dilute solution depended strongly on solution pH. The fraction of protonated amine groups, α , where $\alpha = [\text{NH}_2^+]/([\text{NH}] + [\text{NH}_2^+])$, is shown as a function of pH in Fig. 2. At pH 11, there were no protonated groups ($\alpha = 0$). α increased with decreasing pH until complete protonization ($\alpha = 1$) was achieved at pH 5.5. As the PEI molecule undergoes protonization, repulsive electrostatic interactions between like-charged (positive) segments induce conformational changes that increase the size in solution. At pH 7, the protonated fraction was 0.8 and the size, i.e., the hydrodynamic radius (R_H), was $2.1 \text{ nm} \pm 0.25 \text{ nm}$ as determined by dynamic light scattering.

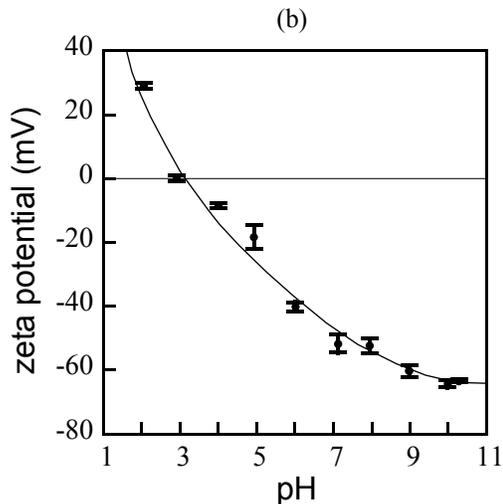
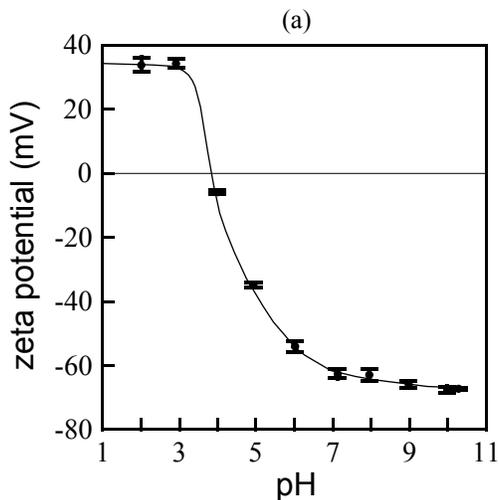


Figure 1. Zeta potential as a function of pH for dilute (a) mullite and (b) BSAS suspensions ($\phi = 10^{-5}$). The symbols and error bars reflect the average and standard deviation, respectively, of ten individual measurements. Note, the solid lines merely guide the eye.

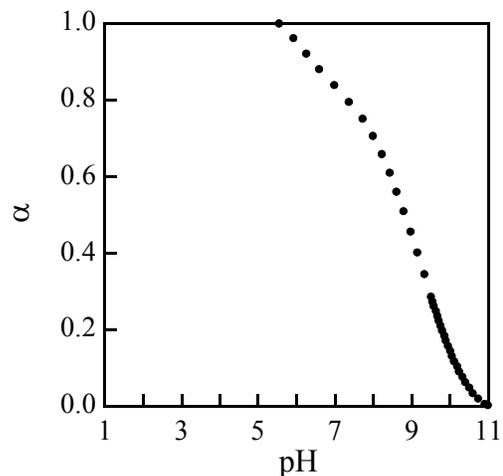


Figure 2. Protonated fraction of amine groups (α) as a function of pH for PEI in dilute solution. Note, $\alpha = [\text{NH}_2^+]/([\text{NH}] + [\text{NH}_2^+])$.

Comparing the zeta potential behavior of the ceramic particles and the protonization behavior of the PEI in aqueous solution, it is apparent that the surfaces of the ceramic particles are oppositely charged from PEI over a broad pH range, i.e. 3.8-11 and 3-11 for mullite and BSAS, respectively. Such conditions are favorable for adsorption of PEI onto the particle surfaces. Furthermore, at pH 7, where the concentrated suspensions were formulated, the adsorbed PEI layer (or adlayer) is highly charged and thus, possesses an extended conformation. As a result, repulsive electrosteric interactions are experienced between the PEI layers on adjacent ceramic particles. Such interactions have dramatic impact on the rheological behavior of concentrated ceramic suspensions, as reported below.

Rheological Behavior

Stress viscometry measurements were carried out on concentrated mullite and BSAS suspensions ($\phi = 0.45$, pH 7) of varying PEI concentration. The apparent viscosity is plotted as a function of applied shear stress in Fig. 3. The degree of shear thinning decreased with increasing PEI concentration until nearly Newtonian flow behavior was observed at a critical PEI concentration of 0.2 mg PEI per m² of mullite and 0.4 mg PEI per m² of BSAS. Above the critical PEI concentration of each system, the apparent viscosity increased and shear-thinning flow behavior intensified with increasing PEI concentration. Such effects typically stem from an increasing fraction of polymer that does not adsorb to the ceramic particles, but is dissolved in the solution medium.[21,22]

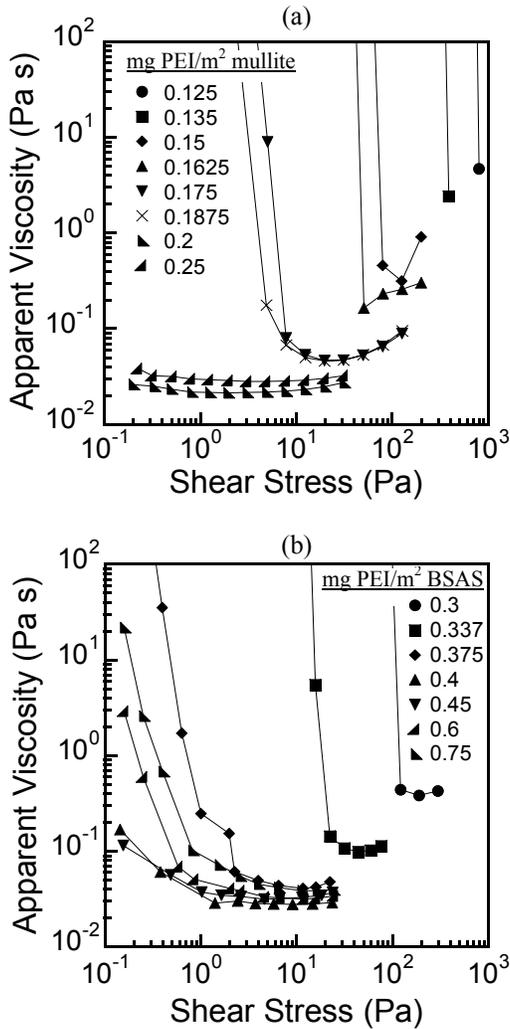


Figure 3. Apparent viscosity as a function of shear stress for (a) mullite and (b) BSAS suspensions ($\phi = 0.45$, pH 7) of varying PEI concentration. Note, the solid lines merely guide the eye.

Elastic shear modulus measurements were also carried out as a function of applied shear stress on mullite and BSAS

suspensions of varying PEI concentration and the results are plotted in Fig. 4. Solid-like behavior, indicative of particle flocculation into a continuous network, was observed at all PEI concentrations. The strength of the particle network, or gel, was quantified by the linear elastic modulus, G'_0 , observed at low shear stress, and the yield stress, τ_y , observed when the particle network is broken down and the elastic modulus decreases sharply. Both G'_0 and τ_y varied with the PEI concentration over several orders of magnitude. At the critical PEI concentration, G'_0 and τ_y were minimal ($G'_0 \sim 1$ Pa, $\tau_y \sim 0.02$ Pa), suggesting that the particles flocculate into very weak attractive minima. Interestingly, the G'_0 and τ_y behavior of mullite and BSAS suspensions was nearly identical at equivalent fractions of their critical PEI concentration (Fig. 5). Thus, these elastic properties can be easily adjusted to characteristic requirements for a wide range of forming processes by scaling the PEI addition relative to the critical concentration of each system.

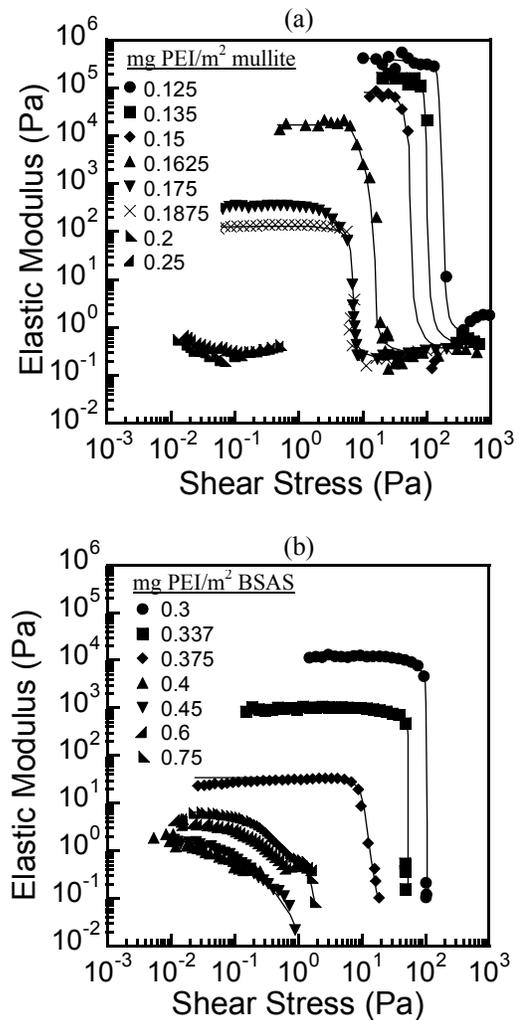


Figure 4. Elastic shear modulus as a function of shear stress for (a) mullite and (b) BSAS suspensions ($\phi = 0.45$, pH 7) of varying PEI concentration. Note, the solid lines merely guide the eye.

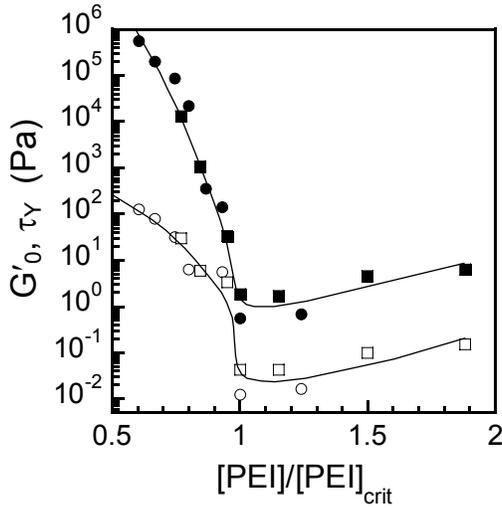


Figure 5. The linear elastic shear modulus, G'_0 , (closed symbols) and yield stress, τ_Y , (open symbols) plotted as a function of $[\text{PEI}]/[\text{PEI}]_{\text{crit}}$ where $[\text{PEI}]$ is the PEI concentration and $[\text{PEI}]_{\text{crit}}$ is the critical PEI concentration. Note, $[\text{PEI}]_{\text{crit}}$ was 0.2 mg PEI per m^2 of mullite and 0.4 mg PEI per m^2 of BSAS. The data for mullite and BSAS is represented by circles and squares, respectively. The solid lines merely guide the eye.

The relative viscosity (η_{rel}) of mullite and BSAS suspensions are plotted in Fig. 6 as a function of the effective colloids volume fraction (ϕ_{eff}), where $\eta_{\text{rel}} = \eta_{\text{susp}}/\eta_{\text{sol}}$, η_{susp} is the apparent suspension viscosity measured in the high shear limit, and η_{sol} is the solution viscosity. ϕ_{eff} was determined using the following relationship:[23]

$$\phi_{\text{eff}} = \phi(1 + \delta A_s \rho_s) \quad (1)$$

where δ is the thickness of the adsorbed dispersant layer (or adlayer), A_s is the specific surface area of the ceramic powder, and ρ_s is the powder density. Eq. (1) accounts for excluded volume effects arising from adsorbed dispersant species, which become significant when the surface area of the ceramic particles is large, as is the case for the mullite and BSAS particles in this study. ϕ_{eff} was estimated using the experimental value of the hydrodynamic radius, assuming $\delta \approx R_H$. The estimated ϕ_{eff} values exhibit excellent agreement with the predicted behavior determined by the Krieger-Dougherty relationship:[24]

$$\eta_{\text{rel}} = \left(1 - \frac{\phi}{\phi_{\text{max}}}\right)^{-k\phi_{\text{max}}} \quad (2)$$

where ϕ is the colloid volume fraction and is given by ϕ_{eff} for dispersant-stabilized suspensions, ϕ_{max} is 0.6, and k is a constant that depends on the shape of the colloids (note, a value of 2.5 was assumed that corresponds to spherical particles).[25,26]

This agreement suggests that the measured value of R_H for PEI in dilute solution represents a reasonable approximation for the adlayer thickness on mullite or BSAS particles. The excluded volume effects arising from this thin layer limits the maximum solids loading that can be achieved for high surface area ceramic powders. The theoretical limit was determined to be 51.4 vol% and 53.0 vol% for mullite and BSAS, respectively, calculated by setting $\phi_{\text{eff}} = \phi_{\text{max}} = 0.6$ in Eq. (1) and solving for ϕ .

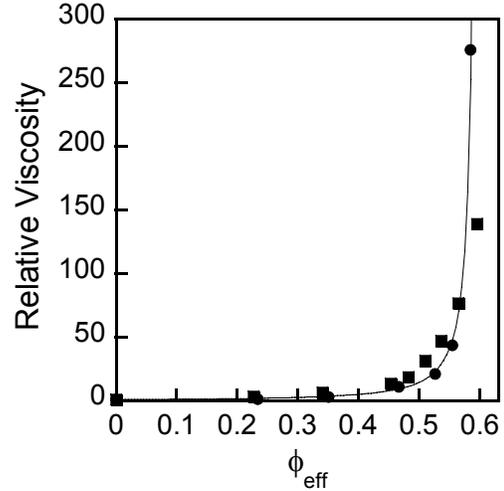


Figure 6. Relative (high shear) viscosity as a function of the effective solids volume fraction for mullite and BSAS suspensions stabilized with PEI. The data for mullite and BSAS is represented by circles and squares, respectively. The solid line corresponds to theoretical behavior predicted by the Krieger-Doherty model, where $\phi_{\text{max}} = 0.6$ and $k = 2.5$.

Coating Characterization

SiC, Si_3N_4 , and Si-metal substrates were dipped into concentrated mullite suspensions of varying PEI concentration, dried under ambient conditions, and photographed. As shown in Fig. 7, the quality of the resulting coatings was relatively independent of the type of substrate, but a strong function of the suspension rheological behavior. Uniform coatings were obtained from dipping into shear thinning suspensions that contained PEI at 81-88% of the critical concentration. Mullite suspensions containing less PEI resulted in thick, uneven coatings. Such defects stem from a particle gel network that is too strong, i.e., a linear elastic modulus and yield stress greater than ~ 5 kPa and 20 Pa, respectively. On the other hand, mullite suspensions containing higher PEI concentrations have a particle network that is too weak, with linear elastic modulus and yield stress less than ~ 300 Pa and 4 Pa, respectively. The force due to gravity exceeds the yield stress of such suspensions; thus, the coating does not maintain a uniform shape, but drips off of the substrate before the drying process is complete. Furthermore, entrained air bubbles were stabilized in these suspensions and eventually became pores in the coatings after drying.

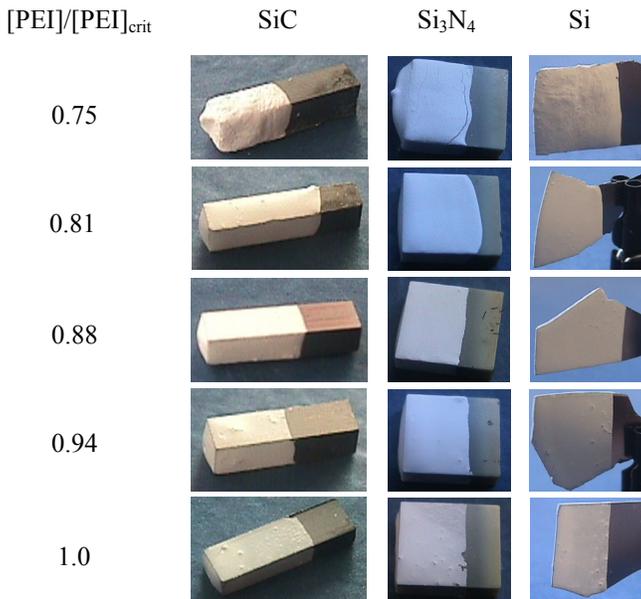


Figure 7. Mullite coatings on SiC, Si₃N₄, and Si-metal substrates. The coatings were formed by dipping into mullite suspensions ($\phi = 0.45$) of varying PEI concentration.

By reducing the solids volume fraction to 0.25 and utilizing colloidal processing techniques to mimic the rheological behavior discussed above, uniform layers of $\sim 20 \mu\text{m}$ thickness were formed by the dip-coating process. A mullite coating on SiC, densified by heat treating at 1400°C for 2 h, is demonstrated in Fig. 8. The formation of a wide variety of coatings on SiC and Si₃N₄ is a topic of ongoing research.

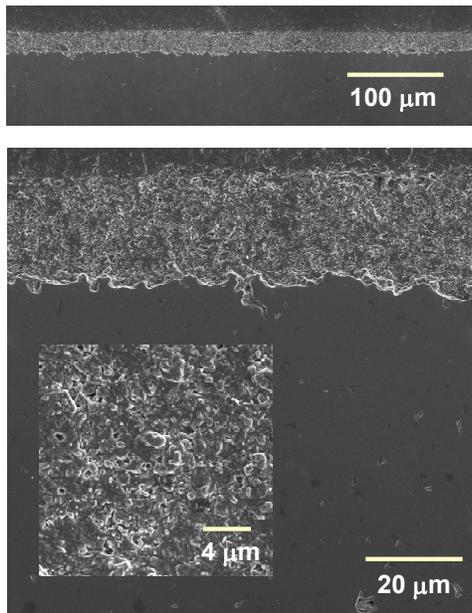


Figure 8. SEM micrographs of a mullite layer on a SiC substrate. The layer was formed by dipping the substrate into a mullite suspension of 0.25 volume fraction solids.

CONCLUSIONS

The rheological behavior of aqueous mullite and BSAS suspensions was demonstrated to be controlled by a cationic polyelectrolyte, polyethylenimine. Such species were an effective electrosteric dispersant for concentrated mullite and BSAS suspensions, and can be used to form slurries with a wide range of rheological properties tailored for forming processes such as dip coating. Suspension flow behavior, elastic modulus, and yield stress varied widely with PEI addition, but were minimized at critical PEI concentrations of $0.2 \text{ mg PEI per m}^2$ of mullite and $0.4 \text{ mg PEI per m}^2$ of BSAS. The elastic properties of mullite and BSAS suspensions were nearly identical at equivalent fractions of their respective critical PEI concentrations. A maximum (theoretical) solids loading of 51.4 vol% and 53.0 vol% was predicted for mullite and BSAS suspensions, respectively, because of excluded volume effects arising from the adsorbed PEI layer. Uniform mullite coatings were obtained upon dipping SiC, Si₃N₄, and Si-metal substrates into shear-thinning suspensions containing PEI at 81-88% of the critical concentration. Dense mullite coatings of $\sim 20 \mu\text{m}$ thickness were demonstrated on SiC substrates after sintering at 1400°C .

ACKNOWLEDGMENTS

This research was sponsored by the U.S. Department of Energy, Office of Distributed Energy. The Oak Ridge National Laboratory is operated by UT-Battelle LLC for the U.S. Department of Energy under contract DE-AC05-00OR22725. The authors would like to thank H.- T. Lin, Matt Ferber, Karren More, and Ted Besmann for fruitful discussions.

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