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STABILIZATION OF AQUEOUS $BaTiO_3$ SUSPENSION WITH POLYACRYLIC ACID

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Abstract

Colloid stability of aqueous $BaTiO_3$ suspensions with polyacrylic acid (PAA) has been studied at alkaline pH. Zeta potential studies showed that the particle surfaces are positively charged, while adsorption of PAA gives negative surface charge at high pH. Adsorption isotherms and sedimentation experiments indicated that colloid stability is related to the surface coverage with PAA on $BaTiO_3$ surface.

1. Introduction

Slip casting is used to consolidate ceramic powders at high green density into sophisticate shapes. One of the most important factors to obtain high green density is to well disperse a powder in a solvent, e.g. water in most cases. In general, suspensions can be dispersed by electrostatic, steric, electrosteric stabilization mechanisms. Ceserano, et al. [1] has shown that slip cast green density increased as the surface coverage with PMMA increased when PMMA was ionized. They suggested a combination of electrostatic and steric stabilization is responsible for their stable suspensions.

The dispersion of $BaTiO_3$ in pure water is found to be difficult Bzdawka and Haworth [2] Mizuta, Parish, and Bowen [3-4]. Kahn [5] and Shiraki et al. [6] showed that $NaPO_4$ is one of the few ionic dispersants effective for $BaTiO_3$ stabilization. But $NaPO_4$ leaves Na and P dopants in the specimen. We have shown [7] that high colloid stability of aqueous $BaTiO_3$ suspensions was achieved with polyacrylic acid (PAA). The suspension stability is related to the dissociation of PAA as a function of pH. The stabilization is believed to be due to the surface adsorption of negatively charged polyelectrolyte. High sediment density and high slip cast density were obtained in alkaline solution of ionized PAA.

In this study we will focus on the effect of PAA on suspensions at pH 10.5. The colloid stability is measured by sediment density as a function of PAA concentration. Zeta potential measurements were performed, and adsorption isotherms measured at pH 10.5. Finally, ceramic slip casting results are presented and explained with these colloidal stabilization ideas.

2. Experimental Procedures

The powder used in this study [Criceram (Courbevoie, France, Batch No. VPP 20)] is nonstoichiometric with 1.8 % excess Ba. The reported BET surface area was 2.5 m^2 gm^{-1}. The particle size distribution was measured by a Horiba Capa#700 using PAA/NH_40H solution as a dispersant. The median particle size was 0.75 μm with standard deviation of 0.5 μm. Polyacrylic acid was obtained from Aldrich Chemie (Steiheim, Germany). The reported average molecular weight was 5,000.

For sedimentation density and adsorption isotherm experiments, suspensions, 14 vol% and 6.23 vol% respectively, of $BaTiO_3$ were prepared with various concentrations of PAA. The pH of the suspension was adjusted, by KOH solution for adsorption and NH_4OH for sedimentation, and tried several times so that the final pH remained at pH 10.5. KOH was used instead of NH_4OH to regulate the solution pH in adsorption experiments because NH_4OH tends to give noise during final titration analysis of PAA. After mixing, the samples were ultrasonicated for 10 min in an ultrasonic bath. In the sedimentation experiments, the volume of the settled particles in the test tube was measured until no more change in sedimentation volume occurred, which normally took 2-3 weeks. In the adsorption experiments, the samples were thermostated at 25°C and vibrated at a speed of 200rpm. After one day, the suspension was centrifuged. A portion of the supernatant was then titrated using an automatic pH titration apparatus operated in the first-derivative mode to determine the PAA concentration in solution. The amount of PAA adsorbed was calculated based on mass balance of PAA.

Zeta potential information was obtained by using the Pen-Kem Acoustophoresis System 7000, which measures the particle mobility in concentrated ceramic dispersions.

For slip casting, solutions of 0.5 wt% PAA were prepared at pH 10.5 using a 5% NH_4OH solution to adjust the pH. $BaTiO_3$ powder was weighted and mixed with PAA solution to give specific solution/solid ratios between 0.15 to 0.22 (ml PAA solution/.gm $BaTiO_3$). The suspensions were then ultrasonicated 1 minute and mechanically shaken 1 minute. Suspension degasing was performed for 1 minute using a water ejector for the vacuum. The suspension were then poured into a mold which consisted of a flat plaster of Paris base and a silicon rubber plate with seven ø15 mm holes. The cast specimens were then removed from the mold after 1 hr. The density of slip-cast green compact was measured by isopropanol displacement method after drying one day in ambient atmosphere.

3. Result and Discussion

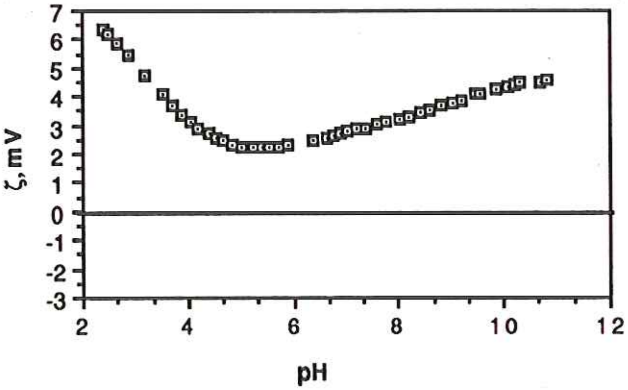

Fig. 1 Zeta potential of Criceram $BaTiO_3$ as a function of pH.

Surface Potential of $BaTiO_3$ Figure 1 shows the zeta potential plotted versus pH for Criceram $BaTiO_3$ powder. There is no isoelectric point between pH 2-11 for suspension without PAA. In general, the zeta potential of oxide powders is expected to be positive in acidic solution and negative in alkali solution by passing through an isoelectric point. Some investigators, Gherardi and Matijevic [8] and Anderson, et al. [9] measured the zeta potential by micro-electrophoresis of several $BaTiO_3$ powders. The isoelectric point (IEP), these authors measured for stoichiometric $BaTiO_3$ was pH≈8.5. However, Barringer [10] measured zeta potentials for TiO_2 with Ba ion present in the solution. By increasing of $BaCl_2$ concentration in basic solution, the zeta potential of TiO_2 becomes more positive. Finally, at $[Ba^{2+}]=10^{-3}M$ the shape of the curve is similar to Fig 1 suggesting that the barium ion in the solution acts as a potential-determining ion. Anderson, et al.[9] studied the surface chemistry of $BaTiO_3$ in aqueous solution and found that barium dissolves and re-deposits on the particle surface. The Criceram $BaTiO_3$ powder has an excess 1.8 % barium. Upon titrating back and forth during our experiments, barium ions dissolve in the low pH region then re-deposit on the $BaTiO_3$ surface at high pH. Acidic supernatants of Criceram suspensions show a white precipitate, i.e., $BaSO_4$, when H_2SO_4 is added.

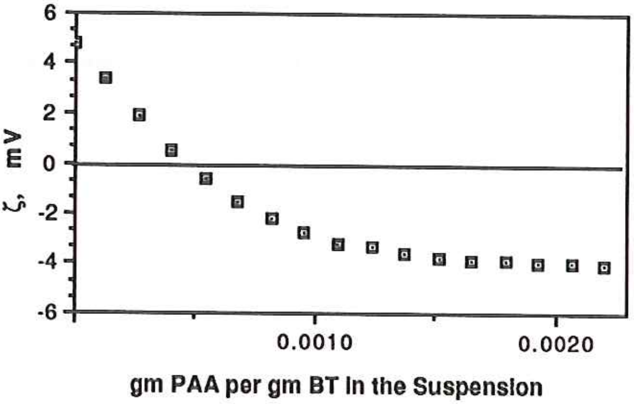

Fig. 2 Zeta potential as a function of PAA addition.at 5 wt% solid content, pH 10.5.

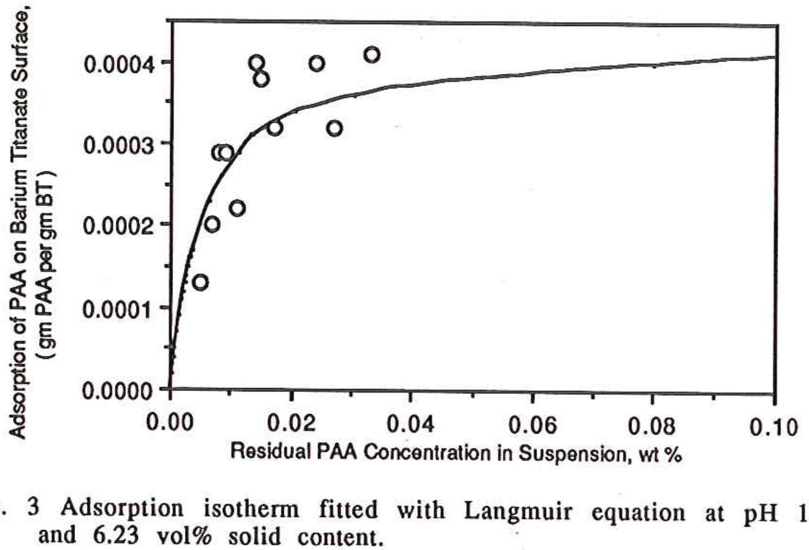

Fig. 3 Adsorption isotherm fitted with Langmuir equation at pH 10.5 and 6.23 vol% solid content.

Adsorption of PAA on $BaTiO_3$ Surface Fig. 2 shows the ζ potential of $BaTiO_3$ as a function of PAA addition. The pH of the added solution was always adjusted so that the pH of the final suspension remained at pH 10.5. From these results, zeta potential changed from positive to negative at 0.0005 gmPAA/gm $BaTiO_3$.

Adsorption isotherms for pH 10.5 are shown in Fig. 3. The adsorption data were fitted with Langmuir isotherm equation,

$$\Gamma = \frac{\Gamma_o KC}{1 + KC}$$

where Γ is the amount adsorbed, Γ_o the amount adsorbed at the plateau, C the concentration of residual adsobate species in solution and K is a constant. The fitted values of Γ_o and K are 0.00043 gmPAA/gm$BaTiO_3$ and 182.15wt%$^{-1}$ respectively. By combining the ζ potential measurements and adsorption isotherm, one can conclude that the adsorption of PAA onto $BaTiO_3$ surface gives negative charges, which consist of ionized PAA carboxylic acid groups on the particle surface.

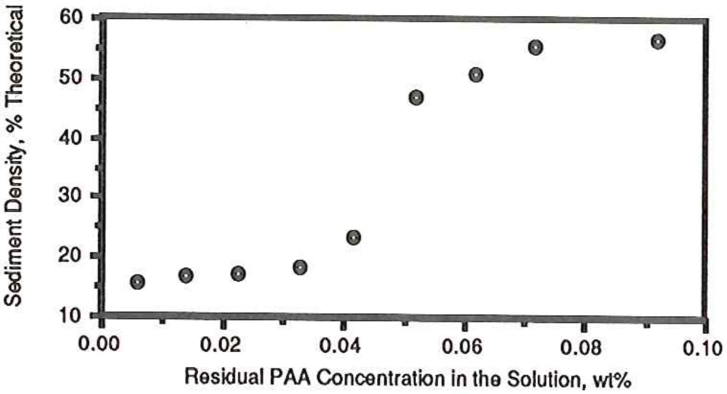

Fig. 4 Sediment density as a function of residual PAA concentration in the suspension at 14 vol% solid content.

Effect of PAA on Stability of Aqueous $BaTiO_3$ Solution

Sediment density experiments, Fig. 4, shows sediment densities were measured as a function of residual PAA concentration. The sediment density increases as the residual PAA concentration in the suspension increases. The residual PAA concentration given in this plot are calculated based on the Langmuir equation using the Γ_o and K values given above. It is believed that the suspension is stabilized by surface adsorption of negatively charged polyelectrolyte. Due to polymer adsorption and its negative charge on the $BaTiO_3$ surface, we believe the stabilization mechanism is electrosteric as claimed by Aksay [1].

Slip Casting of $BaTiO_3$ Suspension In Fig. 5, slip-cast green density of $BaTiO_3$ is plotted against the initial PAA/$BaTiO_3$ in the suspension. The green density increases rapidly as the amount of PAA increases, then reaches a maximum, 59 % theoretical, before decreasing slightly. The amount of PAA required to stabilize the concentrated suspension is much more than that for monolayer coverage in Fig. 3. The kinetics of PAA adsorption are slow, the time constant of adsorption is about 34 hours at pH 10.5. Normally, it takes 5-10 minutes to disperse and slip cast the suspension, while much longer time was used for adsorption (2 day) and sedimentation experiments (2-3 weeks). After optimizing other factors, such as amount of solid to liquid ratio, outgasing time, etc., we obtained a green slip cast density 62 % of theoretical which is larger than that (58%) obtained by isostatic pressing at 242 MPa.

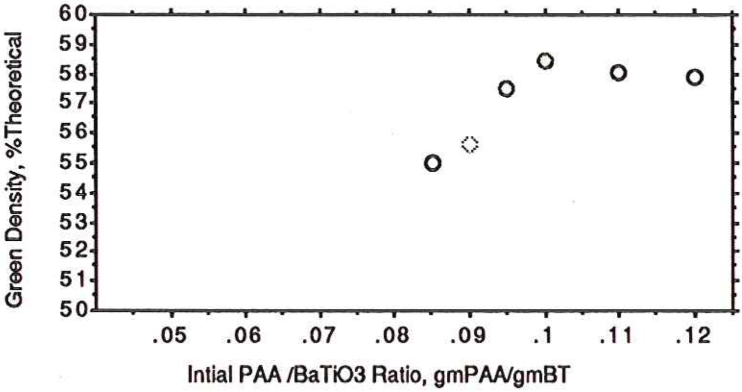

Fig. 5 Slip cast green density as a function of initial PAA/ $BaTiO_3$ ratio in the suspension. Cast at 40-50 vol% solid content and pH 10.5.

4. Conclusion

In concentrated suspension, the surface of Criceram $BaTiO_3$ is always positively charged due to Ba^{2+} dissolution and adsorption. The adsorption of PAA gives negative surface charge at pH 10.5 due to ionized carboxylic groups in the polymer adsorbed on the particle surface. At pH 10.5, more adsorption of PAA onto particle surface gives higher degree of colloid stability (i.e. higher sediment density) and higher slip cast green density. Green density of 62 % theoretical value can be achieved with PAA adsorption compared to 58% obatined by isostatic pressing at 242 MPa.

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