

Dispersion Properties of BaTiO₃ Colloids with Amphoteric Polyelectrolytes

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An amphoteric water-soluble copolymer, i.e., poly(acrylamide/ (α -N,N-dimethyl-N-acryloyloxyethyl) ammonium ethanate) (PAAM/DAAE), was evaluated as a novel dispersant for aqueous BaTiO₃ (BT) slurries. The dispersing property of this copolymer was examined by means of rheology, sedimentation, particle size, green density, zeta potential, and leached Ba²⁺ concentration measurements. The results indicate that PAAM/DAAE could reduce the viscosity of slurries greatly, cause BT particle sizes to shift to smaller values, and make green compacts more consolidated. Compared with a commercial dispersant, ammonium salt of poly(methacrylic acid) (PMAA-NH₄), it is as effective or even better in preparing stabilized suspensions. More importantly, PAAM/DAAE could lessen the leached Ba²⁺ concentration. This is related to the adsorption behavior of this copolymer onto BT particles, and the interaction between the adsorbed dispersant and dissolved barium ions.

I. Introduction

Barium titanate (BT) is a widely used material in making electronic devices such as multilayer capacitors, communications filters, and piezoelectric sensors.^{1,2} The electric properties of the final devices clearly depend on the microstructural characteristics. In turn, the microstructural characteristics are dependent on the manufacturing processes. Tape casting is a common wet process in preparing BT green tapes or thin films. To produce these ceramic green tapes with a uniform microstructure and high packing density, the preparation of well-dispersed slurries is prerequisite. Traditionally, organic solvents are used to disperse the powder. Nowadays, the preparation of aqueous-based suspensions has been given more attention because of safety, economic, and environmental reasons.^{2–4}

In preparing well-dispersed aqueous slurries, dispersing agents are usually incorporated into the system. The mechanism of these dispersants is that, after being adsorbed on ceramic particles, they will create electrostatic, steric, or electrosteric forces.^{5–8} This results in the dissociation of the agglomerates into primary particles with a significant decrease in viscosity, thus achieving a stable cloudy state of suspensions.

Among commercial dispersants, acrylic acid-based polyelectrolytes are often used for BT and other ceramic powders.^{1,3,7,9–15} For example, Cesarano III and co-workers^{5,6} showed that alumina suspensions could be stabilized with a sufficient amount of sodium salt of poly(methacrylic acid), ammonium salt of poly(methacrylic acid) (PMAA-NH₄), or polyacrylic acid (PAA). Chen *et al.*⁷ and Jean and Wang⁴ found that either PAA or

PMAA-NH₄ could stabilize BT slurries under certain pH conditions. de Laat and van den Heuvel⁹ reported that the molecular weight fraction of adsorbed PAA salts onto BT particles depended on the molecular weight distribution of dispersants. Shih and Hon¹³ studied the stability of colloidal silicon nitride suspensions with PAA-NH₄, and concluded that conformation of the polymer chain and the electrostatic interactions were the major factors in determining the stability of the slurries. Bertrand *et al.*¹⁴ also reported that the stabilization of alumina slurries by ammonium salt of PAA was mainly electrosteric.

Although good results using acrylic acid-based dispersants have been reported, some aspects can still be improved. Specifically for BT powder, the resulting slurries were suggested to be processed in basic conditions because of the substantial amount of Ba²⁺ leached out from the particles to the solutions at pH < 7.^{2,11} However, the adsorption of acrylic acid-based polyelectrolytes on BT particles was found to decrease with increasing pH, because the polymers were more negatively dissociated.¹⁴ Usually, more adsorption or greater surface coverage of dispersants is preferred, which generates larger electrostatic, steric, or electrosteric forces. Additionally, the added dispersant molecules are expected to enhance Ba²⁺ leaching because of their interactions with barium ions.¹⁶ This would cause a change in the Ba/Ti ratio on the particle surface, thus resulting in exaggerated grain growth in the later sintering process, and a low sintered density.^{2,17,18} Therefore, new and more effective dispersants should be developed.

In this study, we evaluated an amphoteric water-soluble copolymer as a dispersant for BT powder. This copolymer is poly(acrylamide/ (α -N,N-dimethyl-N-acryloyloxyethyl) ammonium ethanate) (PAAM/DAAE). The dispersing effects of PAAM/DAAE on viscosity, sedimentation height, and particle size of BT suspensions were examined. In addition, the concentration of Ba²⁺ leached from the particles was also measured. The results were compared with those of a commercial dispersant, PMAA-NH₄.

II. Experimental Procedures

(1) Materials

A high-purity BT (Prosperity Dielectrics, Taoyuan, Taiwan) was used. The powder shows a Ba/Ti ratio of 1.00, a median size (d_{50}) of 0.9 μ m, and a BET-specific surface area of 2.45 m²/g. Table I lists the characteristics of BT powder. Two dispersants were used. One is PAAM/DAAE, which was prepared from acrylamide (AAM) and DAAE through free radical polymerization. The detailed preparation procedure of PAAM/DAAE can be found elsewhere.¹⁹ The prepared PAAM/DAAE polymer has a fixed AAM/DAAE molar ratio of 10/1, and a weight-average molecular weight (Mw) of 3.0×10^5 and a number-average molecular weight (Mn) of 6.0×10^4 . The other is a commercial dispersant, PMAA-NH₄ with Mw = 1.0×10^4 and Mn = 1.6×10^3 , which was used for comparison. The molecular weights of PAAM/DAAE and PMAA-NH₄ polymers were

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Table I. Basic Properties of BaTiO₃ Powder

Ba/Ti	1/1
Purity (%)	99.76
SrO (%)	0.0667
Nb ₂ O ₅ (%)	0.008
Al ₂ O ₃ (%)	0.0428
SiO ₂ (%)	0.0152
d ₅₀ (μm)	0.9
Moisture (%)	0.16
Ignition loss (%)	0.23
Compressed Density (g/cm ³)	3.269
BET-specific surface area (m ² /g)	2.45

measured by the gel permeation chromatography (GPC) mentioned below. Figure 1 shows the chemical structures of these two polymers.

(2) GPC Measurements

The molecular weight of dispersants was determined using a GPC that contains a Jasco liquid chromatography equipped with three coupled columns (Shodex OHpak KB802.5, KB804 and KB806, SHOWA DENKO K.K., Tokyo, Japan), a pump (Jasco PU-980, Tokyo, Japan), and an RI detector (Jasco RI-930). The samples were analyzed using a 0.1M KCl/methanol (80/20) aqueous solution as eluent, at a flow rate of 1 mL/min. Monodispersed polystyrene sulfonates of different Mw (1.8 × 10³, 8.0 × 10³, 3.5 × 10⁴, 1.0 × 10⁵, 1.3 × 10⁶) were used as calibration standards.

(3) Preparations of BT Suspensions

Aqueous suspensions containing either 22.7 mass% (= 5 vol%) or 60 mass% BT powder were prepared. They contained dispersant of 0–32 mg/g BT. The suspensions were milled and mixed in a ceramic jar with a fixed amount of 3T-TZP zirconia balls (i.e., turbo-mixed) for 24 h. The 24 h time period of milling is believed to be long enough to reach a homogeneously dispersed state. In this study, deionized and distilled water was used and the pH value of the prepared suspensions was adjusted to 12 by the addition of either HCl_(aq) or NaOH_(aq). Unless specified otherwise, the pH value of suspensions was controlled at 12.

(4) Viscosity Measurements

The viscosity of 60 mass% BT aqueous suspensions with or without dispersants present was determined by a viscometer (Brookfield DV-II, Brookfield Engineering Labs., Middleboro, MA) using either #1 or #4 spindle at a rotation speed of 60 rpm.

(5) Sedimentation Tests

5 vol% (= 22.7 mass%) BT aqueous suspensions with or without dispersants present were prepared and poured into 200 mL

graduated cylinders. The initial height of the suspension in the graduated cylinder was measured as H_0 . These graduated cylinders were kept still for 30 days, and the height of the cloudy suspensions at different settled time was measured as H_t .

(6) Zeta Potential Measurements

5 vol% BT aqueous suspensions with or without dispersants present were prepared at various pH values. After being turbo-mixed and centrifuged, a small amount of supernatant was taken and the zeta potential of the remaining powders in the supernatant was measured by a zeta meter. (Model 501, Pen Kem, Bedford Hills, NY)

(7) Particle Size Measurements

5 vol% BT aqueous suspensions with or without dispersants present were prepared. After being turbo-mixed, a small amount of slurry was taken. The particle size of powder in samples was determined by using a particle size analyzer (Malvern Mastersizer 2000, Worcestershire, U.K.).

(8) Green Density Measurements

Compacts were made from gravitational settlement and consolidation of 60 mass% BT suspensions with or without the presence of dispersants. The density of green compacts was determined by the Archimedes method.

(9) Ba²⁺ Concentration Measurements

Aqueous solutions containing 100 ppm Ba²⁺ ions and various amount of dispersants were prepared. The Ba²⁺ concentration in solutions was measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (JOBIN YVON JY24, Longjumeau, France).

Separately, 5 vol% BT aqueous suspensions with or without dispersants present were prepared. After being turbo-mixed and centrifuged, a small amount of supernatant was taken and the Ba²⁺ concentration in the supernatant was also measured by ICP-AES.

(10) Determination of Dissociation of Dispersants

The percent dissociation of either PAAM/DAAE or PMAA-NH₄ in aqueous solutions at various pH values was determined by a titration method reported elsewhere.⁵

(11) Adsorption Measurements of Dispersants

5 vol% BT aqueous suspensions with different concentrations of either PAAM/DAAE or PMAA-NH₄ were prepared at pH = 12. These suspensions were turbo-mixed and centrifuged to obtain supernatants. The residual dispersant concentration in the supernatants was analyzed and determined by a titration procedure mentioned above. The amount of dispersant adsorbed on BT was calculated from the difference in dispersant concentration before and after adsorption.

III. Results

(1) Rheological Behavior

The viscosity measurement is an appropriate way to evaluate the degree of dispersion for concentrated suspensions. Figure 2 shows the effect of dispersant concentration on the viscosity of 60 mass% BT suspensions. The viscosity of suspensions without dispersant is about 1800 cps. The value becomes less when PAAM/DAAE is incorporated. When PAAM/DAAE concentration is increased, the viscosity of suspensions first decreases, and then reaches a plateau. The critical dispersant concentration is about 9 mg/g BT, which approaches the lowest viscosity, i.e., 400 cps. In contrast, the viscosity of suspensions is decreased rather sharply with PMAA-NH₄ concentration, and then reaches a minimum value. The amount of PMAA-NH₄ required to achieve the lowest viscosity is about 1.5 mg/g BT, which is much

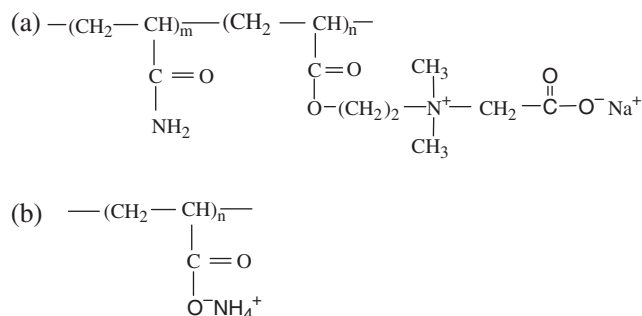


Fig. 1. Chemical structures of (a) poly(acrylamide)/(α -N,N-dimethyl-N-acryloyloxyethyl) ammonium ethanate and (b) ammonium salt of poly(methacrylic acid).

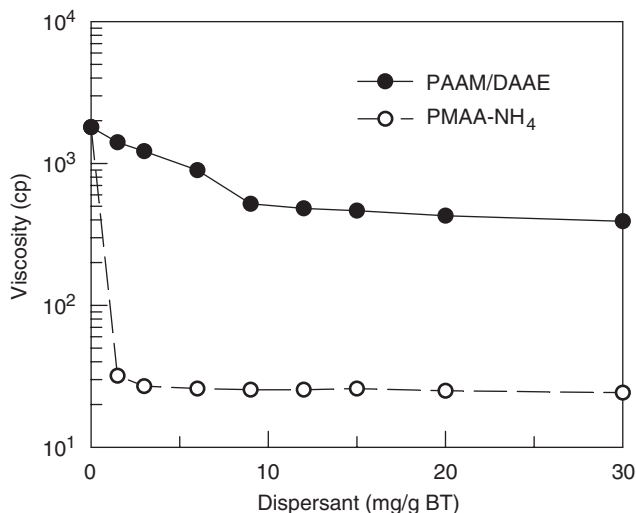


Fig. 2. Effect of dispersant concentration on the viscosity of 60 mass% barium titanate (BT) suspensions.

less than that of PAAM/DAAE required. Furthermore, the minimum viscosity of the suspensions with PMAA-NH₄ is about 24 cps, which is lower than that with PAAM/DAAE.

(2) Sedimentation

The sedimentation observation and measurement is another way of examining the colloidal stability. A good dispersant will enable suspensions to maintain a cloudy state. Figure 3 shows the sedimentation behavior of 5 vol% BT suspensions with various amounts of PAAM/DAAE. For suspensions without any dispersants present, two distinct layers were observed after sedimentation of 1 day. These two layers are a clear aqueous layer on the top and a sediment layer. The relative height of the sediment layer (H_t/H_0) is 28%. The sedimentation behavior of BT suspensions with 6.4 mg/g PAAM/DAAE is similar to that without dispersants present, but the H_t/H_0 value is lower. When the PAAM/DAAE concentration is 13 mg/g BT or more, the resulting suspensions become more stable and remain cloudy even having settled for 30 days. In addition, a clear aqueous layer forms gradually above the cloudy layer and becomes thicker in suspensions along with elapsed time or decreasing polymer content. Figure 4 shows the sedimentation behavior of 5 vol%

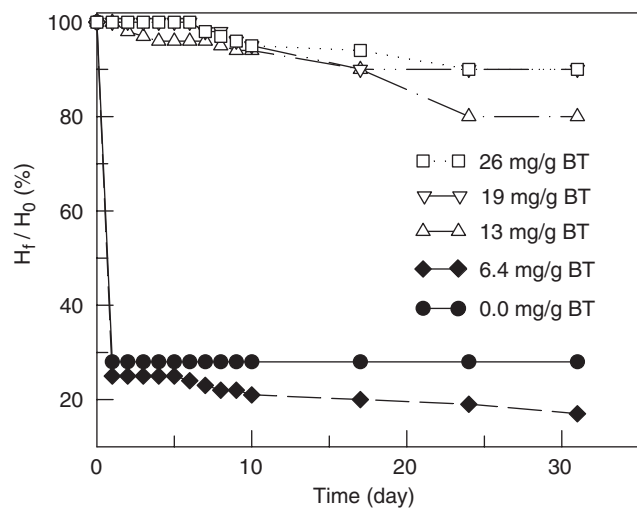


Fig. 3. Sedimentation behavior of 5 vol% barium titanate (BT) suspensions with various amounts of poly(acrylamide/α-N,N-dimethyl-N-acryloyloxyethyl) ammonium ethanate). (Blank symbols (turbid layer); filled symbols (sediment layer)).

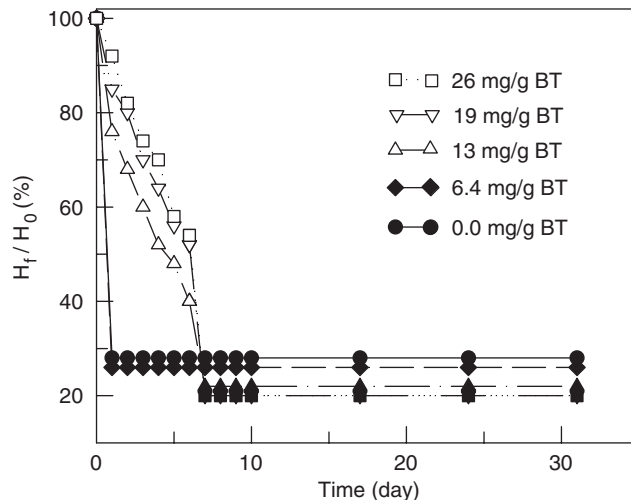


Fig. 4. Sedimentation behavior of 5 vol% barium titanate (BT) suspensions with various amounts of ammonium salt of poly(methacrylic acid). (Blank symbols (turbid layer); filled symbols (sediment layer)).

BT suspensions with the addition of PMAA-NH₄. Compared with the suspension without dispersant, the PMAA-NH₄ suspension shows similar settling behavior when the polymer concentration is 6.4 mg/g BT. If the amount of the polymer increases to 13 mg/g BT or more, three layers, i.e., a clear layer, a cloudy layer, and a sediment layer, were found in the settling period from 7 to 17 days. When the settling time is more than 17 days, all PMAA-NH₄ suspensions become unstable and separate into two layers (a clear layer and a sediment layer).

(3) Particle Size

Figure 5 shows the effect of dispersant concentration on the particle size of powder in 5 vol% BT suspensions. For suspensions without dispersants, the d_{10} , d_{50} , and d_{90} values are 1.1, 2.5, and 4.9 μm, respectively. They shifted to smaller values when dispersants were incorporated in the suspensions. Furthermore, these values were found to decrease with the dispersant concentration initially, and then reach plateaus. For the PAAM/DAAE suspension, the plateaus occur at a dispersant concentration of about 13 mg/g BT; the approached values are 0.56, 1.5, and 3.1 μm, respectively. For the PMAA-NH₄ suspension, the plateaus occur at a dispersant concentration of 6.4 mg/g BT or below; the resulting d_{10} , d_{50} , and d_{90} values are 0.57, 1.1, and

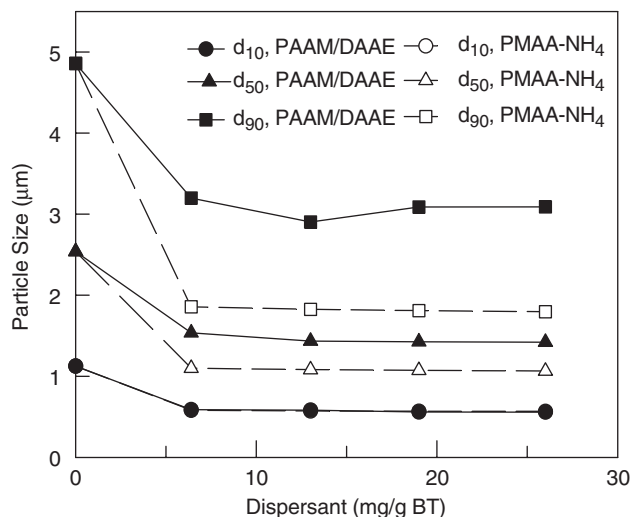


Fig. 5. Effect of dispersant concentration on the particle size of powder in 5 vol% barium titanate (BT) suspensions.

1.8 μm, respectively. Clearly, the suspensions incorporated with PAAM/DAAE require greater amount of dispersant and contain BT powder with a slightly larger particle size than those incorporated with PMAA-NH₄.

(4) Ba²⁺ Dissolution

When BT powder was milled in deionized water, Ba²⁺ ions were expected to leach out from the powder. The amount of leached Ba²⁺ ions is a function of pH value, solid loading, and the addition of dispersant of BT slurries. Controlling the dissolution of BT in aqueous suspensions is essential to avoid composition deviation, exaggerated grain growth, and degradation of sintered properties. Figure 6 shows the effect of dispersant concentration on Ba²⁺ dissolution concentration of 5 vol% BT suspensions. The dissolved [Ba²⁺] was found to increase or decrease with dispersant content, depending on which dispersant was incorporated. In other words, the suspension with PAAM/DAAE contains lower Ba²⁺ concentration than that without. The more the polymer incorporated, the less Ba²⁺ is leached. The leached [Ba²⁺] reaches a minimum value when the dispersant concentration is about 13 mg/g BT. In contrast, PMAA-NH₄ causes the opposite effect on the leaching of Ba²⁺ from BT powder.

(5) Green Compact Density

The relative green density of BT compact obtained from gravitational sedimentation and consolidation of the suspension is shown in Fig. 7. For compacts without any dispersant incorporated, the green density is 45.4% theoretical density. The green density was found to exhibit higher values when dispersants were incorporated in the solutions. Along with increasing dispersant content, the values also increase. Furthermore, compacts with PAAM/DAAE show slightly higher green density than those with PMAA-NH₄, when the dispersant concentration is 5 mg/g BT or more.

IV. Discussion

From the above results, it is clear that addition of PAAM/DAAE could reduce the viscosity, and maintain a cloudy state in the BT suspension. It could also cause the particle sizes to shift to smaller values. These evidences indicate that PAAM/DAAE can disperse powder and stabilize BT slurries with less agglomeration.

Compared with PMAA-NH₄, PAAM/DAAE requires a greater amount to reach a minimum viscosity and the approached value is higher. Two factors account for this differ-

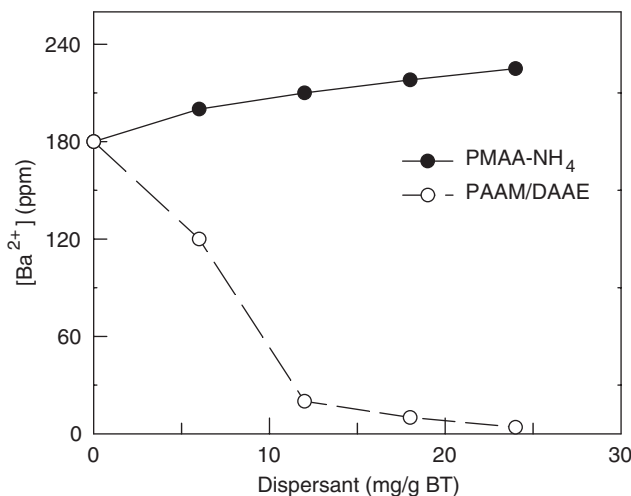


Fig. 6. Effect of dispersant concentration on Ba²⁺ dissolution concentration of 5 vol% barium titanate (BT) suspensions.

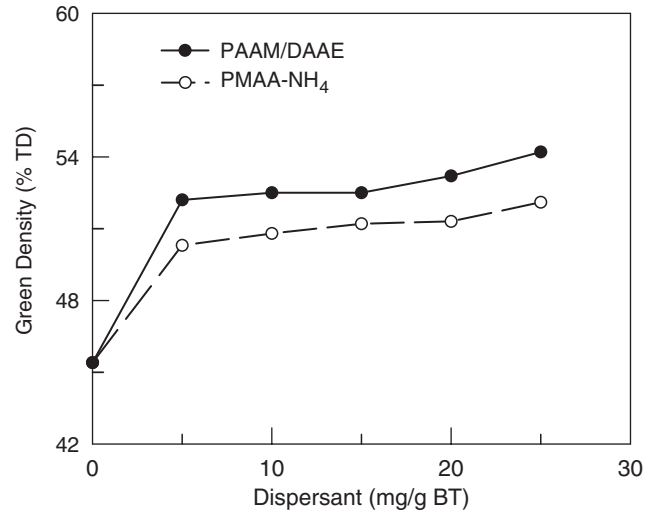


Fig. 7. Effect of dispersant concentration on the relative green density of barium titanate (BT) compact.

ence. First, the viscosity of PAAM/DAAE aqueous solution itself is higher, because this polymer has greater molecular weight than PMAA-NH₄. Second, these two chemicals induce different dispersion actions. As shown in Fig. 1, PMAA-NH₄ molecules are anionic polyelectrolytes, which would mainly cause electrostatic repulsions when adsorbed onto BT particles. PAAM/DAAE molecules also cause electrostatic repulsions when adsorbed onto particles; the effect should be less because they are amphoteric.

Figure 8 shows the zeta potential of particles in 5 vol% BT suspensions with or without dispersants as a function of pH. The surface charge or zeta potential of particles is positive at low pH values, and becomes negative at high pH values. The isoelectric point occurs at about pH = 5.6, which is below the reported value for unmilled, stoichiometric BT powder, i.e., pH = 8.5.²⁰ Instead, this value is close to that of TiO₂, i.e., pH = 4–6.²¹ The shift of the isoelectric point is because of the growth of a surface layer depleted in Ba and enriched in TiO₂.^{2,22} When dispersant is present in suspensions, the zeta potential decreases and the isoelectric point shifts to a lower value. Furthermore, suspensions with PMAA-NH₄ show greater change in the zeta potential than those with PAAM/DAAE. This confirms that PAAM/DAAE generates less electrostatic repulsions than the commercial one. Nevertheless, PAAM/DAAE is expected to produce more steric effect than PMAA-

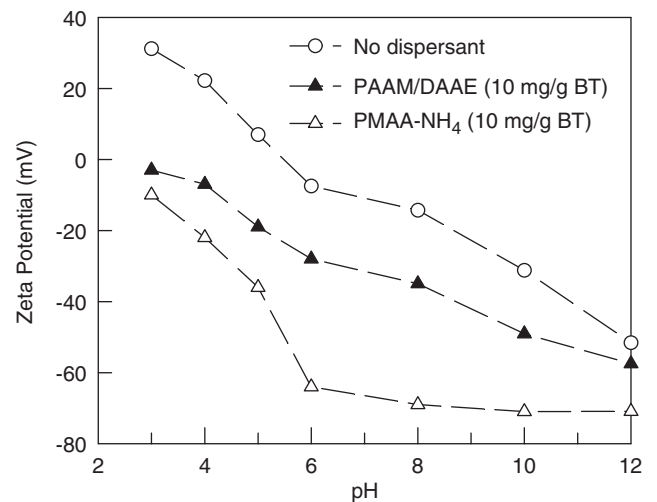


Fig. 8. The zeta potential of powder in 5 vol% barium titanate (BT) suspensions with or without a dispersant as a function of pH.

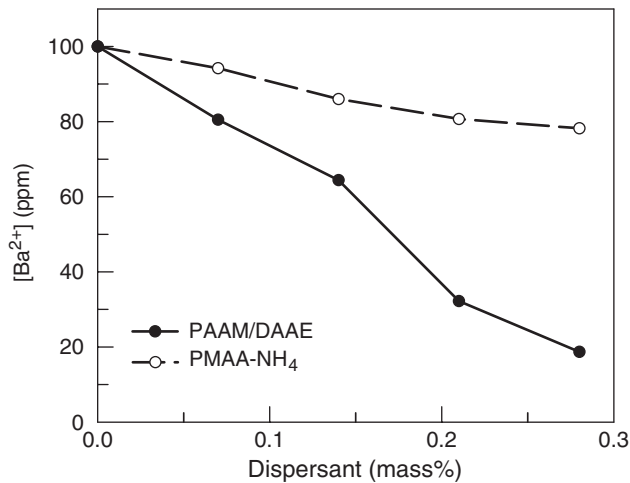


Fig. 11. Effect of dispersant concentration on measured Ba²⁺ concentration in aqueous solutions.

ured [Ba²⁺] in the resulting solutions. The more the difference between the initial and the measured Ba²⁺ concentration, the more the interactions between the dispersant and metal ions. It appears that PAAM/DAAE interacts with barium ions more strongly, for the measured [Ba²⁺] in the PAAM/DAAE solution was lower than that in the PMAA-NH₄ solution.

When PMAA-NH₄ is added into the suspensions, it will promote the leaching of barium ions from the particles because of the interactions between -COO⁻ groups and Ba²⁺ ions. As a result, [Ba²⁺] in the slurries with PMAA-NH₄ was observed from Fig. 6 to be slightly higher than that without any dispersant present. Although PAAM/DAAE can also enhance the dissolution of Ba²⁺ from the powder, an appreciated fraction of released Ba²⁺ ions would redeposit and chemically link with the adsorbed polymer on the particle surface. This is because PAAM/DAAE has stronger interactions with barium ions and the adsorbed amount of this polymer at the plateau (6.6 mg/g BT) is much higher than that of PMAA-NH₄ (0.19 mg/g BT). Therefore, addition of PAAM/DAAE causes a decrease in the leached Ba²⁺ concentration in the resulting suspensions. It is further noted that the leached [Ba²⁺] in Fig. 6 approaches a constant value, which corresponds to the adsorbed amount of PAAM/DAAE at the plateau in Fig. 10, because both cases occur at the same dispersant concentration, i.e., about 13 mg/g BT. This suggests that the adsorption of PAAM/DAAE is a key factor in reducing the leached [Ba²⁺] in BT slurries.

V. Conclusions

An amphoteric water-soluble copolymer, PAAM/DAAE, was evaluated as a dispersing agent for aqueous BT suspensions. Incorporation of PAAM/DAAE could reduce the viscosity and stabilize the resulting slurries. It could also help the particle sizes to shift to smaller values. As a result, denser and more consolidated green compacts were formed. Compared with PMAA-NH₄, the copolymer is as effective or even better. This is because PAAM/DAAE contains cationic groups (-N⁺), which would

favor themselves to be adsorbed onto the BT surface. As the leached Ba²⁺ ions redeposited and interacted with the adsorbed polymer on the particle surface, PAAM/DAAE were found to reduce Ba²⁺ dissolution from BT powder in suspensions.

Acknowledgments

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