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. 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 the safety, economic, and environmental reasons.

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. 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. For example, Cesaran III and co-workers 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. and Jean and Wang found that either PAA or PMAA-NH₄ could stabilize BT slurries under certain pH conditions. de Laat and van den Heuvel reported that the molecular weight fraction of adsorbed PAA salts onto BT particles depended on the molecular weight distribution of dispersants. Shih and Hon 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. 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. 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. 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. 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. 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 (d₅₀) of 0.9 μm, 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. 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 × 10⁴ and a number-average molecular weight (Mn) of 6.0 × 10³. The other is a commercial dispersant, PMAA-NH₄ with Mw = 1.0 × 10⁴ and Mn = 1.6 × 10³, which was used for comparison. The molecular weights of PAAM/DAAE and PMAA-NH₄ polymers were

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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 0.1 M KCl/methanol (80:20) aqueous solution as eluent, at a flow rate of 1 mL/min. Monodispersed polystyrene sulfonates of different Mw 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 or NaOH. 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 Masterizer 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) **Ba$^{2+}$ Concentration Measurements**

Aqueous solutions containing 100 ppm Ba$^{2+}$ ions and various amount of dispersants were prepared. The Ba$^{2+}$ 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 Ba$^{2+}$ 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-NH$_4$ 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-NH$_4$ 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 or PMAA-NH$_4$ are 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-NH$_4$ concentration, and then reaches a minimum value. The amount of PMAA-NH$_4$ required to achieve the lowest viscosity is about 1.5 mg/g BT, which is much higher than PAAM/DAAE.
less than that of PAAM/DAAE required. Furthermore, the minimum viscosity of the suspensions with PMAA-NH$_4$ 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 ($H_f/H_0$) is 28%. The sedimentation behavior of BT suspensions with 6.4 mg/g PAAM/DAAE is similar to that without dispersants present, but the $H_f/H_0$ 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% BT suspensions with the addition of PMAA-NH$_4$. Compared with the suspension without dispersant, the PMAA-NH$_4$ 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-NH$_4$ 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-NH$_4$ 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
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 difference. 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 TiO₂.²² 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-
NH₄⁺ because it contains longer side chains and has higher molecular weight.

It is well understood that the function of dispersants is dispersing and stabilizing particles, and reducing greatly the viscosity of slurries. However, the resulting viscosity of slurries should not be too low to cause a fast sedimentation of particles, and aggregate each other; otherwise, poor compact density and sintered properties may be resulted.¹¹ As the BT suspension with PAAM/DAAE was more viscous than that with PMAA-NH₄ the former was found to remain turbid longer and more stable in the sedimentation tests. Consequently, compacts with PAAM/DAAE showed higher packing density and lower porosity than those with the other dispersant.

Besides, the trend of leached Ba²⁺ concentration varies with different dispersants in the BT suspensions. The Ba²⁺ concentration was found to decrease with the increase of PAAM/DAAE content, but to increase with increasing PMAA-NH₄ content. The difference of the trend is related to the adsorption behaviors of these two chemicals onto BT particles.

As shown in Fig. 1, the PMAA-NH₄ molecule contains COONH₄ functional groups, which change to anionic (COO⁻) groups when dissociated in an aqueous solution. Figure 9 shows the percent dissociation of dispersant molecules as a function of pH. The percent dissociation is defined as the percentage of the number of COO⁻ to the total number of functional groups in the molecule. The PMAA-NH₄ molecule was found to be unassociated at pH < 2. It starts to dissociate at pH > 2, and becomes more dissociated at a higher pH value. At pH > 11, PMAA-NH₄ molecules are dissociated completely. This result agrees well with that reported previously.⁴

For PAAM/DAAE, only the carboxyl functional group in the structural unit dissociates in an aqueous solution, as is shown in the following equation. That is, the dissociated PAAM/DAAE molecule contains not only anionic (COO⁻) groups but also cationic (–N⁺) groups.

As shown in Fig. 9, the PAAM/DAAE molecule will not dissociate and contains only positive charges (–N⁺) at pH < 3. It begins to dissociate at a higher pH value, and the percent dissociation increases with pH. At pH > 9.2, PAAM/DAAE molecules are totally dissociated, and become amphoteric because they contain both –N⁺ and COO⁻ functional groups. Although the dissociation behaviors of these two dispersants appear to be similar, their dissociation degrees at a given pH value differ slightly, for these two chemicals have different molecular weights and contain different functional groups in the structure.

Figure 10 shows the amount of these two dispersants adsorbed onto BT particles as a function of the initial dispersant concentration at pH = 12. In general, the amount adsorbed increases quickly with the initial dispersant concentration, and then reaches a plateau. The value at the plateau accounts for the amount of polymers required for the formation of a monolayer on the particle surface. For PMAA-NH₄, the value is about 0.19 mg/g BT, which agrees with Jean and Wang’s results.⁴ The adsorbed amount at the plateau for PAAM/DAAE is much greater, i.e., about 6.6 mg/g BT. The reason for the difference in adsorbed amount of polymers is attributed to the different chemical natures of these two dispersants. At pH = 12, the surface charges of particles are negative, which is difficult for the adsorption of negatively charged PMAA-NH₄ molecules onto the particle surface when they are completely dissociated. On the contrary, PAAM/DAAE molecules become amphoteric in a basic solution. Their cationic groups (–N⁺) would favor themselves to be adsorbed onto the BT surface. In addition, the amide functional group (–CONH₂) in the structural unit could also interact with the particle surface by hydrogen bonding and could enhance the adsorption.

Furthermore, the adsorption of PMAA-NH₄ molecules onto BT particles would be in a relatively flat conformation, as it was reported that polyacrylate molecules become stretched and expanded when they are totally dissociated.⁵ In contrast, the adsorbed PAAM/DAAE molecules would be more coiled in the structure, and the adsorbed layer is thicker. Accordingly, the adsorbed amount of PAAM/DAAE is much more than that of PMAA-NH₄.

Separately, both dissociated dispersants containing anionic (–COO⁻) group could interact with Ba²⁺ ions, as reported elsewhere.⁴ The interactions between dispersants and barium ions are also indicated in Fig. 11, which shows the measured Ba²⁺ concentration as a function of dispersant concentration in aqueous solutions. Initially, aqueous solutions containing 100 ppm Ba²⁺ ions were prepared. Then, various amounts of dispersants were added. The Ba²⁺ concentration in solutions with various amount of dispersants was measured by ICP-AES. As shown in Fig. 11, the incorporated dispersant causes a decrease in meas-
Therefore, addition of PAAM/DAAE causes a decrease in the measured Ba$^{2+}$ concentration in the resulting solutions. The more the difference between the initial and the measured Ba$^{2+}$ 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 [Ba$^{2+}$] in the PAAM/DAAE solution was lower than that in the PMAA-NH$_4$ solution.

When PMAA-NH$_4$ is added into the suspensions, it will promote the leaching of barium ions from the particles because of the interactions between −COO$^-$ groups and Ba$^{2+}$ ions. As a result, [Ba$^{2+}$] in the slurries with PMAA-NH$_4$ was observed from Fig. 6 to be slightly higher than that without any dispersant present. Although PAAM/DAAE can also enhance the dissolution of Ba$^{2+}$ from the powder, an appreciated fraction of released Ba$^{2+}$ 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-NH$_4$ (0.19 mg/g BT). Therefore, addition of PAAM/DAAE causes a decrease in the leached Ba$^{2+}$ concentration in the resulting suspensions. It is further noted that the leached [Ba$^{2+}$] 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 [Ba$^{2+}$] 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 help the particle sizes to shift to smaller values. As a result, denser and more consolidated green compacts were formed. Compared with PMAA-NH$_4$, 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 Ba$^{2+}$ ions redeposited and interacted with the adsorbed polymer on the particle surface, PAAM/DAAE were found to reduce Ba$^{2+}$ dissolution from BT powder in suspensions.

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