

## Study of processing adsorption mechanism of amphoteric polyelectrolyte in BaTiO<sub>3</sub> colloids suspension

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An amphoteric dispersant, copolymer ( $\alpha$ -N,N-dimethyl-N-acryloyloxyethyl) ammonium ethanateacrylamide (PAAM/DAAE), was used for the dispersion of BaTiO<sub>3</sub> (BT) colloids in an aqueous solution, and compared to a commercial acrylic-based polymeric dispersant, ammonium salt of polymethylacrylic acid (PMAA-NH<sub>4</sub>). Several properties, including surface potential, sedimentation height ratio, green density, and Ba<sup>2+</sup> dissolution from the particle surface were studied. Due to the branch structure of PAAM/DAAE and more importantly the amphoteric functional groups of PAAM/DAAE, the macromolecules adsorbed on BT in much higher concentration (up to 7 mg/g) and limited the dissolution of Ba<sup>2+</sup> ions from the BT surface. Strong steric repulsion between BT particles with PAAM/DAAE resulted in a good dispersion of fine particles and greater packing density in the green state than that of PMAA-NH<sub>4</sub>. The adsorption mechanism and interactions among BT, dispersants, and H<sub>2</sub>O are reported.

**Key words:** dispersant, colloid, adsorption, Ba<sup>2+</sup> dissolution,  $\zeta$ -potential, PAAM/DAAE.

### Introduction

Recent development of barium titania (BaTiO<sub>3</sub>, BT), materials by aqueous tape casting, has gained industrial interest, mainly due to the environmental needs of reducing organic wastage and possibly lowering production costs. In our previous report [1], one amphoteric polyelectrolyte was synthesized to use for ceramic powder dispersion. The details of the colloidal processing and dispersion mechanisms have not yet been reported.

It has been documented that, when BaTiO<sub>3</sub> is milled in deionized water, Ba<sup>2+</sup> ions are leached out from the powder. That would result in a Ti-rich surface on the BT powder. It is also found that the amount of Ba<sup>2+</sup> leaching is dependent upon the pH of the solution [1-3]. The reactions of BaTiO<sub>3</sub> in H<sub>2</sub>O are [4]:



The dissolution of Ba<sup>2+</sup> ions not only changes the Ba/Ti ratio on the powder surface, but also affects the pH value of the solution. An important consequence is also expected that leached Ba<sup>2+</sup> ions would re-deposit on the powder surface in the drying stage, resulting in exaggerated grain growth and lower sintered density in sintering stage [5].

A polyelectrolyte has the ability to modify the inter-particle forces through the adsorption of the polymer in solution. Polyelectrolytes adsorbed on the surface of particles can stabilize colloidal suspensions through steric or electrosteric effects [6-8]. When the polymeric chain is highly charged, especially for short polyelectrolytes, the polymer will be stretched and adsorbed in a flat manner conforming to the surface of the particle [9]. Since the polymer concentration needed for stabilization might change with pH [10], the dispersive effect of polymer concentration [11] could be described by a stability map.

Dispersants based on carboxylic acid units, such as, ammonium salts of polymethacrylic acid (PMAA) and polyacrylic acid (PAA) [12] are known to be effective [13, 14] in stabilizing concentrated suspensions of different ceramic oxides, as well as Al<sub>2</sub>O<sub>3</sub> [15], and BT aqueous suspensions [16]. Additionally, an anionic polyelectrolyte is reported to be more effective as a dispersant for aqueous BaTiO<sub>3</sub> suspension than a cationic counterpart [17].

In this report, we use two different dispersants to disperse BaTiO<sub>3</sub> powder in aqueous slurries and study the adsorption mechanisms of the dispersants onto BaTiO<sub>3</sub> powder. One is an amphoteric dispersant which was synthesized in previously referenced work [1]. Another is an anionic dispersant, i.e. PMAA-NH<sub>4</sub>, known as Darven-C, which is chosen because it has been used to disperse BaTiO<sub>3</sub> powder and has been shown to stabilize BaTiO<sub>3</sub> aqueous slurry.

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## Experimental Procedure

### Raw Materials

The BaTiO<sub>3</sub> powder used in this study was synthesized by a precipitation method (Degussa Uden, Japan Co. Ltd) with a Ba:Ti ratio of 0.995. The powder had an average particle size of 0.68 μm and a specific area of 0.64 m<sup>2</sup>/g. An PMAA-NH<sub>4</sub> (a commercial polymeric dispersant\*) is an anionic dispersant used to disperse ceramic powders. The anionic functional group is -COO<sup>-</sup>. An amphoteric dispersant, a copolymer PAAM/DAAE [(α-N,N-dimethyl-N-acryloyloxyethyl) ammonium ethanate-acrylamide], shows two kinds of functional groups. The anionic functional group is -COO<sup>-</sup>, which is same as PMAA-NH<sub>4</sub>. The cationic functional group is -N<sup>+</sup>R<sub>3</sub>. Due to the cationic functional group, the dispersive behaviors of BT aqueous slurries with PMAA-NH<sub>4</sub> or PAAM/DAAE would be different.

### Experimental methods

#### Standard Procedure for BT Slurry Preparation

Different amounts of PMAA-NH<sub>4</sub> or PAAM/DAAE, based on the mass of the powder, were added into deionized water and shaken for about 30 s. The pH value of this solution was measured (assigned as "pH<sub>0</sub>"), and then BT powder was added to the solution. After 24 hr of turbo-mixing, the slurry was poured into a test tube and the pH value of this suspension was measured (assigned as "pH<sub>i</sub>"). After sedimentation or centrifugation, the value of pH of the supernatant was measured as pH<sub>f</sub>.

#### Zeta Potential

For ζ-potential measurement, the suspension was prepared by mixing 300 ppm BT powder in deionized water at different pH values with dispersant. The acidity was adjusted by using NaOH or HCl solutions. In addition, the ionic strength of the aqueous solutions was controlled via the addition of NaCl. Before the test, the suspension was treated by ultrasonic vibration for 10 min. After aging for 24 hr, the ζ-potential of the powder in suspension was measured again to determine the ζ-potential at equilibrium by a zeta-meter (Model 501, Lazer Zee Meter, Pen Kem, NY, US). An average of five measurements for each sample was made.

#### Dissolution of Ba ions

Inductively Coupled Plasma Spectroscopy (ICP, JY24, JOBIN YVON, French) was used to measure the Ba<sup>2+</sup> concentration of the supernatant of the BT slurry. In order to obtain a clean solution (supernatant), the solid particles have to be separated from the aqueous BT slurries with various dispersant additions. The slurries for the test were centrifuged (HERMLE Z380, Germany)

at 5000 rpm for 13 min. The centrifuging time depends on the clarity of the BT supernatant to avoid the residual BT particles that would affect the concentration measurement of Ba ion in the solutions. An average of at least three measurements for each sample was made. Standard solutions of Ba<sup>2+</sup> in various concentrations for the ICP calibration were diluted from 1000 ppm standard solution (reagent grade, MERCK).

#### Adsorption of Dispersant

The amount of the two dispersants adsorbed on BT surfaces was measured by Gel Penetration Chromatography (GPC, a pump of JASCO 9U-980, with a detector of JASCO RI-930, Japan) with three columns (OHpeak KB-806M, OHpeak KB-805, and OHpeak KB-802.5.) For the GPC measurements, 0.08 M KCl solution was prepared as a mobile phase and the polymer standards were injected into the KCl solution to get a calibration curve. The residual amount of dispersant in the supernatant of the BT slurry with the pH value adjusted to 12 was measured by GPC. The amount of dispersants adsorbed onto BT surfaces was obtained by a mass balance with the residual amount in the supernatant.

#### Sedimentation test and green density measurement

The solid loading for the sedimentation test was kept at 3 vol%. The BT slurries was prepared by using the previously described procedure. After 24 hr of turbo-mixing, the slurry was poured into a test tube and the height of the suspension in the tube was measured as H<sub>0</sub>. These glass tubes were then kept still for 40 days. After sedimentation, the value of pH and the height of the sediment were measured as pH<sub>f</sub> and H<sub>f</sub>. We could estimate and compare the dispersive properties of the dispersant by the ratio of sedimentation (H<sub>f</sub>/H<sub>0</sub>) and the acidity conditions of the solution.

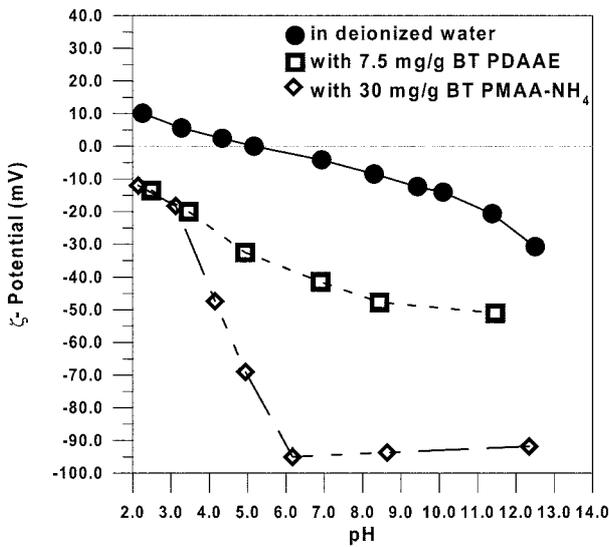
Following a similar slurry preparation procedure, the particle size of the BT slurries was determined by a particle size analyzer (Mastersizer 2000, Malvern, UK). After 40 days, we could get the BT sediments from the bottom of the glass tubes in the sedimentation test. To evaluate the properties of BT sediments, the apparent density (D<sub>a</sub>) and bulk density (D<sub>b</sub>) of these sediments were determined by Archimedes method after a drying procedure (40°C held for one day, 60°C for one day, and 105°C for one day).

## Results

### Surface Potential and Dissolution of BaTiO<sub>3</sub>

In order to study the effects of PAAM/DAAE or PMAA-NH<sub>4</sub> on the surface chemistry of BT colloids, the z-potential of the BT was measured and is shown in Fig. 1. The absolute potential with the addition of either PAAM/DAAE or PMAA-NH<sub>4</sub> is larger than that without dispersant in deionized water, and the iso-

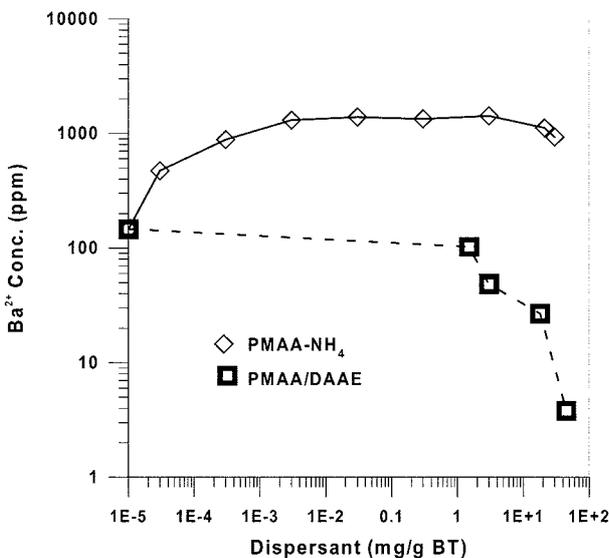
\*commercial name is Darvan-C (R.T. Vanderbilt Co., Norwalk, CT).



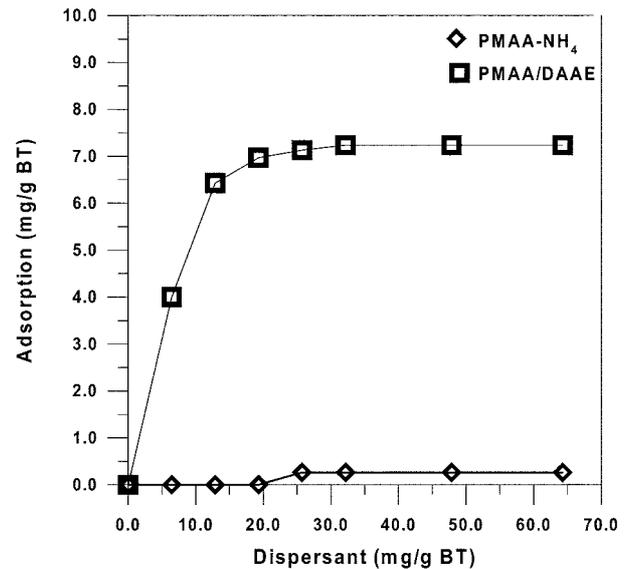
**Fig. 1.**  $\zeta$ -potential of BT powder in a concentration of 300 ppm in aqueous solution with different dispersants. The test solution contained either PAAM/DAAE in 7.5 mg/g BT or PMAA-NH<sub>4</sub> in 30 mg/g with respect to BT powders.

electric point (iep) could not be observed in the previous two cases for the pH range of the solutions investigated. In addition, the absolute surface potential of the BT with PAAM/DAAE, in the range of 40-50 mV, is lower than that with PMAA-NH<sub>4</sub> (90-100 mV).

It has been reported that the dissolution of BaTiO<sub>3</sub> is a function of pH value, solid loading, and the addition of dispersant to the BT slurry [2, 3, 9, 11-13, 16-19]. Controlling the dissolution of BaTiO<sub>3</sub> in aqueous suspensions is the main task to avoid composition deviation, exaggerated grain growth, and degradation of dielectric properties. In this study, the concentration of Ba ions in the supernatant was measured and is shown in Fig. 2. The Ba<sup>2+</sup> dissolution concentration decreases



**Fig. 2.** Ba<sup>2+</sup> ion dissolution of 3 vol% BT suspension with dispersants at room temperature.

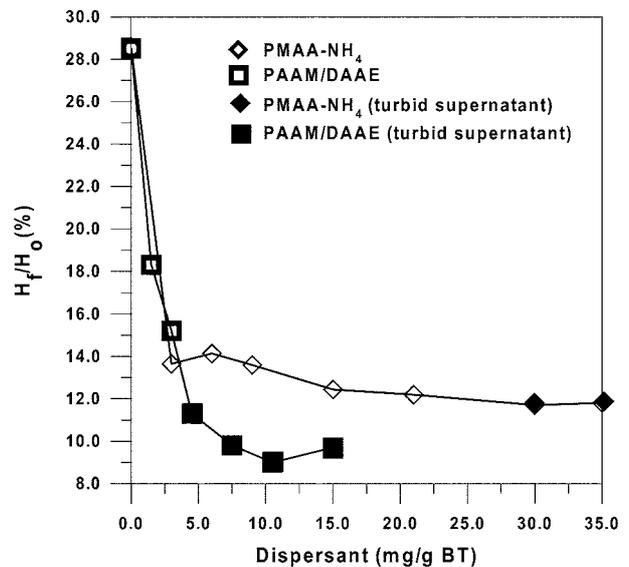


**Fig. 3.** Adsorption of dispersants on BT surface as a function of the initial amount of dispersants.

from 105 ppm to 4 ppm in the supernatant of 3 vol% BT suspension with PAAM/DAAE addition. With an increase of PMAA-NH<sub>4</sub> addition, Ba<sup>2+</sup> dissolution initially increases from 105 ppm to about 1300 ppm and then reached a plateau; at higher concentrations, the ion concentration decreases to 930 ppm.

**Adsorption of Dispersants on BaTiO<sub>3</sub>**

Figure 3 shows the specific adsorption of the two dispersants on the BT powder as a function of initial concentration of the dispersants in suspensions. There are the characteristic plateaus in the adsorption curves. The plateaus correspond to the amount of PAAM/DAAE and PMAA-NH<sub>4</sub> required for monolayer cover-



**Fig. 4.** Sedimentation result of BT suspension with PAAM/DAAE or PMAA-NH<sub>4</sub>. The filled symbols represent that the supernatant is still turbid after sedimentation for 40 days.

age on BT surfaces. The concentration of PAAM/DAAE was 13 mg/g BT in aqueous suspension and there was about 6.5 mg/g BT PAAM/DAAE adsorbed on BT surfaces. The concentration of PMAA-NH<sub>4</sub> was 30 mg/g BT in aqueous suspension and only 0.3 mg/g BT adsorption on BT surfaces.

The adsorption curves reflect that, the critical adsorption amount of dispersants on BT surfaces reaches the adsorption plateau at 7 mg PAAM/DAAE per gram BT, but needs only 0.3 mg PMAA-NH<sub>4</sub> per gram BT at pH 12. In addition, the concentration of PMAA-NH<sub>4</sub> in the slurry must be higher than 25 mg/g BT in order to reach the critical adsorption level.

### Sedimentation and green density

The colloidal stability of the aqueous BT slurries with PAAM/DAAE and PMAA-NH<sub>4</sub> can be confirmed by sedimentation experiments. A smaller sedimentation ratio ( $H_f/H_0$ , the ratio of sediment height to suspension height) and a turbid supernatant are essential and indicative phenomenon of a good dispersion. Aqueous suspensions with 3 vol% BT powder were prepared for the sedimentation experiments, and the sedimentation ratios ( $H_f/H_0$ ) are shown in Fig. 4. The supernatant of the BT suspension remains clear until more than 30 mg/g BT of PMAA-NH<sub>4</sub> is added. By contrast, only 4.5 mg/g BT of PAAM/DAAE is needed to reach a turbid condition. PMAA-NH<sub>4</sub> has been used in some cases to disperse BT powder [18, 19], and reported to be an effective dispersant in basic conditions. Based on similar dispersive conditions, the suspension needs PMAA-NH<sub>4</sub> five times more in mass than PAAM/DAAE.

The green density is a direct consequence, which is able to reveal the quality of BT sediments or of the tape after casting. The higher the green density, the

better the dielectric properties of the sediment. In addition, denser sediments obtained from sedimentation usually reveal better colloidal stability. Figure 5 is the results of green density measurement of the sediments with different amounts of PAAM/DAAE and PMAA-NH<sub>4</sub>. This figure shows that the green density increases with the amount of dispersant. The green density of the samples with PAAM/DAAE is superior to that of PMAA-NH<sub>4</sub>. The best green density of the BT sediment from this measurement is 54% theoretical density (T.D.) by adding 15 mg/g BT PAAM/DAAE or 30 mg/g BT PMAA-NH<sub>4</sub>. The results show that the suspensions with PAAM/DAAE not only require less dispersant to achieve a turbid state, but also achieves a smaller sedimentation ratio and higher green density.

## Discussion

### Surface Chemistry of BaTiO<sub>3</sub>

Barium titanate is not stable in aqueous suspension when the pH value is less than 10, and the reaction of BaTiO<sub>3</sub> with water could be written as equation (2). Over the past two decades, several research groups have studied this reaction [4, 20]. In acidic aqueous solution, the reaction in eq. (1) is enhanced. Where the activities of solid and neutral species in eq. (2) are set to equal to 1, then the concentration of Ba<sup>2+</sup> would be expressed as a function of pH:

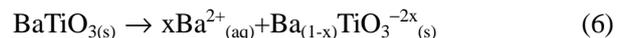
$$[\text{Ba}^{2+}][\text{OH}^-]^2 = K \quad (3)$$

$$\text{and } \log K = \log [\text{Ba}^{2+}] + 2 \log [\text{OH}^-] \quad (4)$$

Base on the published standard Gibbs function data [21, 22], the above equation can be:

$$\log [\text{Ba}^{2+}] = 20.08 + 2\text{pH} \quad (5)$$

It is clear that the equilibrium concentration of Ba<sup>2+</sup> ion should be very high for all normal pH values from above relation. Osseo-Asare *et al.* [23] proposed a theoretical stability diagram for the system of Ba-Ti-H<sub>2</sub>O. BaTiO<sub>3</sub> can only exist in equilibrium with Ba<sup>2+</sup><sub>(aq)</sub> and TiO<sub>2(s)</sub> in strongly basic solutions. BaTiO<sub>3</sub> particles would release Ba<sup>2+</sup> ions from the surfaces until the formation of a TiO<sub>2</sub>-rich skin and the appearance of negative charges (Ba<sub>(1-x)</sub>TiO<sub>3</sub><sup>-2x</sup>) on the surface:



Further Ba<sup>2+</sup> dissolution should then be controlled by the diffusion of Ba<sup>2+</sup> through the surface film, until the equilibrium concentration of Ba<sup>2+</sup> is attained in the solution [2].

The dissociation data of two dispersants have been shown in a previous paper [18]. The curve of dissociation fraction ( $\alpha$ ) of PMAA-NH<sub>4</sub> is similar to the results of PAA given by Cesarano and Aksay [15]. At pH  $\geq$  10, the dissociation fraction equals 1. This means all NH<sub>4</sub><sup>+</sup> ions are released from the PMAA-NH<sub>4</sub>, and

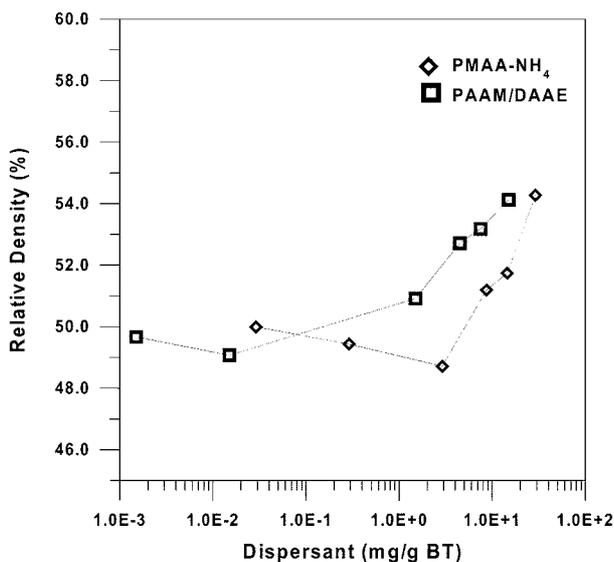


Fig. 5. Green density of the BT sediments with PMAA-NH<sub>4</sub> or PAAM/DAAE dispersant. The density measurements were within an accuracy of  $\pm 0.5\%$ .

the polymer dispersant becomes anionic in solutions. As  $\text{pH} \leq 3$ , the dissociation fraction is zero. This implies that there is almost no dissociated PMAA-NH<sub>4</sub> and the macromolecules exist in the solution without electric charging. A similar dissociation behavior occurs for PAAM/DAAE, the fraction of dissociation increases from 0 at  $\text{pH} \approx 3$  to 1.0 at  $\text{pH} \approx 10$ . Within the range of measurements, the dissociation of PMAA-NH<sub>4</sub> is greater than PAAM/DAAE.

PAAM/DAAE is an amphoteric polymeric dispersant, which contains an anionic functional carboxyl group, (COO<sup>-</sup>), and a cationic functional, quaternary amine (N<sup>+</sup>) group. The quaternary amine is a kind of strong electrolyte. The fraction of dissociation of the carboxyl functional group could be 100% above pH 9 from the experiments of potentiometric titration.

The iep of the BT powder in aqueous solutions without dispersant addition was at e.g. pH 5.3, which changed as a function of solid concentration, Ba/Ti ratio, particle size, measurement method, and etc [24]. Comparing with the results of Jean and Wang [25], the iep of their BT powder was at pH 4.3. Their Ba/Ti ratio and particle size are dissimilar to the powder used in this experiment. More Ba ions may have dissolved from their powder surfaces, as a consequence, resulting in the iep close to pH 5, which is the iep value of TiO<sub>2</sub> [2].

The iep values of BT powder dispersed with two dispersants indicate that the surface potential of BT powder in the suspension was more negative than that of BT powder without a dispersant. The reasons are two fold. One is from the surface adsorbed anionic dispersants. The second is that the fraction of the dissociation of the polyelectrolytic dispersants increases with the pH of the suspension.

### Adsorption of Dispersant on BT Powder

In this study, the suspensions were prepared in a sequence of firstly well mixing of dispersants and deionized water, then adding of the powder. The dispersants dissociate instantly in deionized water. There are present -COO<sup>-</sup> and NH<sub>4</sub><sup>+</sup> when PMAA-NH<sub>4</sub> dissociates in water, and -COO<sup>-</sup>, NH<sub>4</sub><sup>+</sup> and N<sup>+</sup> when PDAAE dissociates. However, after the powder is added, other reactions may occur in the water. One possibility is dissolution of Ba ions from the surface. The surface of BaTiO<sub>3</sub> particles is negatively charged due to either the dissolution of Ba ions into water as mentioned in Eq. (6), or by the adsorption of anionic molecules.

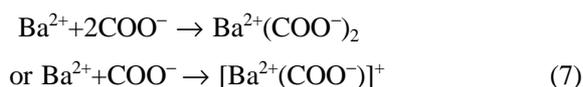
The functional group of the polymer and the surface of BT particles are both negatively charged in the PMAA-NH<sub>4</sub> system. PMAA-NH<sub>4</sub> is difficult to adsorb on negative BT particles because of Coulombic repulsive forces at pH 12. This is confirmed in the adsorption results in Fig. 3. The adsorption is minimal even when the initial concentration of PMAA-NH<sub>4</sub> is over 25 mg/g BT. The critical adsorption amount on BT surfaces

was only 0.3 mg/g BT, due to strong electric repulsion between the negatively charged PMAA and polymer.

The surface potential of the BT suspension with PMAA-NH<sub>4</sub> is more negative than that with PAAM/DAAE. One reason is the fraction of dissociation of PMAA-NH<sub>4</sub> is higher than that of PAAM/DAAE at pH <10. At pH 6.5, the fraction of PMAA-NH<sub>4</sub> is 0.7 and that of PAAM/DAAE is 0.2. Another reason is that the PAAM/DAAE is an amphoteric polymer. The charging of PAAM/DAAE would be weak in either acidic or basic conditions, because there would be present an alio-functional group of opposite charge on the polyelectrolyte. The other reason is that the Ba<sup>2+</sup> is fixed on the BT surface by PAAM/DAAE whose anionic functional group acts with Ba<sup>2+</sup> ions and cationic functional groups adsorbed on the negative BT surface by an attractive force. The re-deposited Ba ions covering the BT surface result in a lower surface charge. By contrast, PMAA-NH<sub>4</sub> becomes anionic when it is dissociated and adsorbed on BT powder, where the surface potential of BT powder would be more negative.

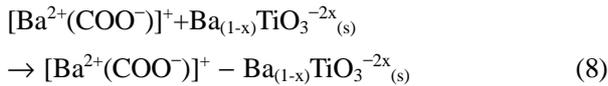
Fukuda *et al.* [26], and Biggs [27] used atomic force microscope (AFM) to determine the repulsive and cohesive forces on particle surfaces with different amounts of PAA-NH<sub>4</sub> (ammonium salt of polyacrylic acid). The results showed that PAA-NH<sub>4</sub> actually adsorbed on alumina particles. However, there is still no report presenting evidence to show how the PMAA-NH<sub>4</sub> is adsorbed on BT powder. At soon as a BT particle is negatively charged at pH <12, PMAA-NH<sub>4</sub> could not attach the BT surface due to repulsion of each other by electrostatic forces. However, the adsorption of PMAA-NH<sub>4</sub> maybe utilizes -COO-Ba<sup>+</sup>, which is the result of the reaction of -COO<sup>-</sup> with Ba<sup>2+</sup> ion dissolved in suspension [27]. This model might explain why the dissolution of Ba<sup>++</sup> decreased and a turbid state of the supernatant could be obtained with a greater addition of PMAA-NH<sub>4</sub> (shown in Fig. 4).

From the results of this study, several reactions may occur on the surface of BaTiO<sub>3</sub> colloids. In the first stage, leaching of Ba ions from the surface is reaction-controlled, In this situation, the charge balance is obtained by two -COO<sup>-</sup> functional groups caught by one Ba<sup>2+</sup> ion as Eq. (7):



Ba ions continue to dissolve from the BT surface to reach the equilibrium of the reaction with polymeric electrolytes. This means that Ba ions leach out from the BT surface and react with a high concentration of the -COO<sup>-</sup> group by Le Chatelier's principle. This is the reason why the equilibrium concentration of Ba ions (ca. 1000 ppm) by the dissolution of BaTiO<sub>3</sub> in aqueous suspension is 10 times greater than that without PMAA-NH<sub>4</sub> (Fig. 2).

In the second stage, it is most difficult for the Ba ions to dissolve from the particle surface than in the first stage because the control mechanism changes to diffusion control. The rate of dissolution is slowed down as the Ti-rich skin grows thicker. Due to the residual positive charges, the  $[\text{Ba}^{2+}(\text{COO}^-)]^+$  complex can be adsorbed on the negative surface of BT particles. As shown in eq. (8), the concentration of Ba ions in the slurry decreases because of the reposition of  $[\text{Ba}^{2+}(\text{COO}^-)]^+$  on the Ti-rich surface:



The result is consistent with that reported by Foissy *et al.* [28] that PAA adsorption onto ceramic surfaces is often promoted by the addition of multivalent cations to the solution. Multivalent cations could bond to the carboxyl functional groups of the polymer to form complexes in solutions.

The formation of complexes may affect the PMAA-adsorption onto ceramic surfaces at  $\text{pH} > \text{pH}_{\text{iep}}$  in several ways. First, it can enhance adsorption by lowering the net charge on the polymer, and consequently reducing the solubility of the PMAA-cation complex. Second, the formation of complexes of ionic species is expected to change the PMAA-formation in solution at high pH. If the multivalent Ba ions exhibit specific interactions with its surface sites, the sites may even serve as an "anchor" group in the adsorption process.

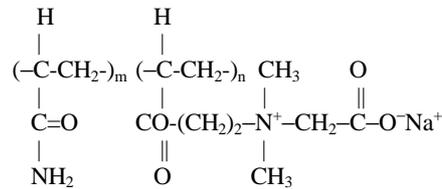
In the PAAM/DAAE system, the adsorption process should be different. The functional group  $\text{N}^+$  adsorbs on BT powder as the other functional group,  $-\text{COO}^-$ , reacted with Ba ions and forms complex  $[\text{Ba}^{2+}-(\text{COO}^-)_2-\text{N}^+-\text{Ba}_{(1-x)}\text{TiO}_3^{-2x}_{(s)}]$ . The adsorption of the PAAM/DAAE molecules would reduce the dissolution of Ba ions more significantly, because the  $\text{N}^+$  adsorbs on the BT powder surface and prevents Ba ions leaching from the BT surface. Evidence for this is shown in the results of the dissolution experiment of  $\text{BaTiO}_3$  in Fig. 2. After centrifuging, the concentration of Ba ions in the supernatant from the aqueous suspension dispersed with PAAM/DAAE is very low. With more PAAM/DAAE addition, the concentration of Ba ions in the suspension decreased about two orders more than that without the PAAM/DAAE addition. It implies that the fixation of Ba ions on BT powder surfaces is enhanced by the adsorption of PAAM/DAAE.

There are two possibilities to cause the deficiency of  $\text{Ba}^{2+}$  in solution with the addition of PAAM/DAAE. Although both dispersants contain the function group ( $-\text{COO}^-$ ) in the suspension, there are several significant differences in the chemical structure between these two dispersants. As mentioned previously, PAAM/DAAE has not only an anionic, but also a cationic functional group ( $\text{N}^+$ ). Additionally, there are two side chains in each PAAM/DAAE structural unit as shown in Table 1.

**Table 1.** Properties of polymeric additives

	PAAM/DAAE	PMAA-NH <sub>4</sub>
Chemical	Poly( $\alpha$ -N,N-dimethyl-N-acryloxyethyl) ammonium ethnate-acrylamide	Ammonium salt of polymethylacrylic acid
Formula	Shown as below (m:n=1:1)	$\begin{array}{c} \text{CH}_3 \\   \\ -(\text{C}-\text{CH}_2)_n \\   \\ \text{COO}-\text{NH}_4 \end{array}$
Function group	$\begin{array}{c}   \\ -\text{COONa} \text{ and } \text{N}^+ \\   \end{array}$	-COONH <sub>4</sub>
Outlook	Citrine liquid	Yellow liquid
Molecular weight (g/m)	300000	10000~16000
Solid loading (mass %)	15%	29%
Solution acidity.	pH 3~4	pH 7~8
Supplier	NTNU	S. T. Vanderbilt Co.

Formula of PAAM/DAAE:



These differences would easily make the  $\text{Ba}^{2+}$  form complex ions attached to the PAAM/DAAE, and decrease the concentration of  $\text{Ba}^{2+}$  in the BT suspensions. Moreover, PAAM/DAAE would catch more  $\text{Ba}^{2+}$  ions than PMAA-NH<sub>4</sub> due to its branched structure and higher molecular weight (ca. 300000 g/mol). In the PMAA-NH<sub>4</sub> system,  $\text{Ba}^{2+}$  dissolution must increase in order to maintain the equilibrium between the  $\text{Ba}^{2+}$  concentration and acidity in the suspension until the dissociation of  $\text{NH}_4^+$  from PMAA-NH<sub>4</sub> is complete.

### Effect on Sedimentation

From the investigations of sedimentation and of green bodies, the BT suspension with PAAM/DAAE disperses better than that with PMAA-NH<sub>4</sub>. The critical amount of PAAM/DAAE added in the BT slurry was much less than that of PMAA-NH<sub>4</sub>. The turbid state of the supernatant is easily obtained with a small amount of PAAM/DAAE. This is mainly due to the adsorption of the quaternary amine ( $\text{N}^+$ ) functional group of PAAM/DAAE on the negative  $\text{Ba}_{(1-x)}\text{TiO}_3^{-2x}_{(s)}$  surface. This is also because of electrosteric effects inducing by charging polymeric chains and branch structures.

The sedimentation results (Figs. 4 and 5) are consistent with the adsorption and dissolution of the aqueous  $\text{BaTiO}_3$  suspension with PMAA-NH<sub>4</sub>. The turbid state, adsorption of PMAA-NH<sub>4</sub> on the BT surface and lower Ba concentration of the BT supernatant are obtained when the initial concentration of PMAA-NH<sub>4</sub> is over 30 mg/g BT. The polymer at lower concentration disperses

the BT aqueous slurry by a mechanism of non-adsorptive steric-resistance [29, 30]. Only the adsorption of the dispersant occurs, the dispersion of the BT ceramic powder in the aqueous suspension follows an electro-steric mechanism.

From these experiments, only 0.45 mass% PAAM/DAAE is needed to reach the critical sedimentation height ratio ( $H_f/H_0$ ), 9%, in BT aqueous suspensions. However, for the PMAA-NH<sub>4</sub> system to get the critical ratio (12%) it needs 1.5 mass% dispersant. A well dispersive slurry would be cloudy due to fine powder. An effective dispersion stabilizes small particles in the supernatant, and prevents them from aggregating [31]. When the turbid state in a supernatant is achieved, the sedimentation ratio is small. This is because the particles are agglomerate-free and the fine fraction is still in the supernatant. As a result, the sedimentation ratio would be small due to good packing.

The green density of a ceramic sediment is an indication of the sedimentation behavior. When a dispersive state of the slurry is achieved, the resulting sediment is denser due to a slow settling motion and the well stacking of particles. The results of green density measurement were coincidental with that of the sedimentation tests. At typical amounts of dispersants (1 mass% to powder, or 10 mg/g powder), the green density of the sediment with PAAM/DAAE is 53.0% and that with PMAA-NH<sub>4</sub> is 51.0%.

## Conclusions

The effects of two dispersants, PAAM/DAAE and PMAA-NH<sub>4</sub>, on the dispersion of BaTiO<sub>3</sub> powders were investigated and compared. The cationic quaternary amine (N<sup>+</sup>), is the major functional group of PAAM/DAAE which attaches onto BaTiO<sub>3</sub> surface. The other COO<sup>-</sup> function group on the amphoteric polymer induces a stabilization effect of steric hindrance to disperse the colloids, and anchors the Ba ions on the colloidal particles. This prevents Ba<sup>+2</sup> ions from dissolution and results in a slow sedimentation in the slurry stage. The critical adsorption amount of the PAAM/DAAE dispersants on the BaTiO<sub>3</sub> surface to reach the adsorption plateau is 7 mg/g BaTiO<sub>3</sub>.

The anionic group (COO<sup>-</sup>) on PMAA-NH<sub>4</sub> can not adsorbed on negatively charged BaTiO<sub>3</sub> colloids, but may interact with Ba<sup>+2</sup> ions. The adsorption is minimal (0.3 mg/g BT) even when the initial concentration of PMAA-NH<sub>4</sub> is as concentrated as 25 mg/g BT. The adsorption of the PMAA<sup>-</sup> on a BT surface is less likely due to the strong electric repulsion between the negatively charged PMAA and the BT surface, unless a complex ion of COO<sup>-</sup> with Ba<sup>+2</sup> takes place. The complex (Ba<sup>+2</sup>-COO<sup>-</sup>) in the suspension will allow minimal adsorption of PMAA-NH<sub>4</sub>, but greatly enhance the dissolution of Ba<sup>+2</sup> from the BaTiO<sub>3</sub> surface.

Based on the sedimentation results, the critical con-

centration of dispersant for good dispersion, and the green density, the dispersion of a BaTiO<sub>3</sub> slurry with PAAM/DAAE is superior to that with PMAA-NH<sub>4</sub>.

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