

Dispersion properties of $\text{BaTi}_4\text{O}_9/\text{Ba}_2\text{Ti}_9\text{O}_{20}$ colloids with amphoteric polyelectrolytes

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Abstract

An amphoteric water-soluble copolymer, i.e., polyacrylamide/(α -*N,N*-dimethyl-*N*-(3-(β -carboxylate)acrylamino)propyl) ammonium ethanate (PAM/DAE) was synthesized and used as a dispersion agent for $\text{BaTi}_4\text{O}_9/\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ($\text{BT}_4/\text{B}_2\text{T}_9$) particles. PAM/DAE was prepared from acrylamide and (α -*N,N*-dimethyl-*N*-(3-(β -carboxylate)acrylamino)propyl) ammonium ethanate in a basic condition through a free radical polymerization. The dispersing property of this copolymer was examined by means of rheology, particle size, and leached Ba^{2+} concentration measurements. The results indicate that PAM/DAE could reduce the viscosity of slurries greatly, and cause $\text{BT}_4/\text{B}_2\text{T}_9$ particle sizes a shift to smaller values. Compared with a commercial dispersant, ammonium salt of poly(methacrylic acid) (PMAA- NH_4), PAM/DAE is as effective in preparing dispersed suspensions. More importantly, PAM/DAE could lessen the leached Ba^{2+} concentration.

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1. Introduction

Barium titanates are widely used materials in making electronic devices. For example, BaTiO_3 (BT) is used as multilayer capacitors and piezoelectric sensors; BT_4 and B_2T_9 are used as resonators and filters for microwave communications.^{1–4} 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 barium titanate 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.^{5,6}

In preparing well-dispersed aqueous slurries, dispersing agents are usually incorporated into the system. Among commercial dispersants, acrylic acid-based polyelectrolytes are often used for barium titanate and other ceramic powders.^{5–17} For

example, Cesarano III et al.^{7,8} 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- NH_4), or polyacrylic acid (PAA). Chen et al.⁹ and Jean and Wang⁶ found that either PAA or PMAA- NH_4 could stabilize BT slurries under certain pH conditions. Shih and Hon¹⁵ studied the stability of colloidal silicon nitride suspensions with PMAA- NH_4 , 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.¹⁶ 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 barium titanate powder, the resulting slurries were suggested to be processed in basic conditions because of substantial amount of Ba^{2+} leached out from the particles to the solutions at $\text{pH} < 7$.² 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.^{1,6} 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 Ba^{2+} leaching due to their interactions with barium ions.¹⁸ This would cause a

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change in the Ba/Ti ratio on the particle surface, thus resulting in a variation of sintered density and dielectric properties.^{19,20} Therefore, new and more effective dispersants continue to be developed.^{21–24}

In this study, we evaluated an amphoteric water-soluble copolymer as a dispersant for BT₄/B₂T₉ powder. This copolymer is PAM/DAE.²⁵ The dispersing effects of PAM/DAE on viscosity, and particle size of BT₄/B₂T₉ 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.

2. Experimental

2.1. Materials

A BT₄/B₂T₉ powder (Prosperity Dielectrics, Taoyuan, Taiwan) was used. The powder has a median size (d_{50}) of 0.72 μm and a BET specific surface area of 5.13 m²/g. Two dispersants were used. One is PAM/DAE, which was prepared from acrylamide (AAM) and (α -N,N-dimethyl-N-acryloyloxyethyl) ammonium ethanate (DAE) through free radical polymerization. Detailed preparation procedure of PAM/DAE can be found elsewhere.²⁵ The prepared PAM/DAE polymer has a fixed AAM/DAE molar ratio of 5/1, and a weight-average molecular weight (M_w) of 1.3×10^5 . The other is a commercial dispersant, ammonium salt of poly(methacrylic acid) (PMAA–NH₄) with $M_w = 1.5 \times 10^4$, which was used for comparison. The molecular weight of PAM/DAE and PMAA–NH₄ polymers were measured by the GPC mentioned elsewhere.²⁴ Fig. 1 shows the chemical structures of these two polymers.

2.2. Preparations of BT₄/B₂T₉ suspensions

Aqueous suspensions containing either 20 or 60 wt.% BT₄/B₂T₉ powder were prepared. They contained dispersant of 0–2 wt.%. The suspensions were milled and mixed in a ceramic jar with a fixed amount of zirconia balls for 24 h. In this study, deionized and distilled water was used and the pH value of the prepared suspensions was adjusted by the addition of either HCl_(aq) or NaOH_(aq). Unless specified otherwise, the pH value of suspensions was controlled at 9.

2.3. Determination of dissociation of dispersants

The percent dissociation of dispersant in aqueous solutions at various pH values was determined by a titration method reported elsewhere.⁷

2.4. Zeta potential measurements

BT₄/B₂T₉ 20 wt.% suspensions with or without dispersants present were prepared at various pH values. After being 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, NY, USA).

2.5. Adsorption measurements of dispersants

BT₄/B₂T₉ 20 wt.% suspensions with either PAM/DAE or PMAA–NH₄ were prepared at pH 9. These suspensions were mixed and centrifuged to obtain supernatants. The residual dispersant concentration in the supernatants was determined by a titration procedure mentioned above. The amount of dispersant adsorbed on BT₄/B₂T₉ was calculated from the difference in dispersant concentration before and after adsorption.

2.6. Viscosity measurements

The viscosity of 60 wt.% BT₄/B₂T₉ suspensions with or without dispersants present was determined by a viscometer (Brookfield DV-II, Middleboro, USA) using either #1 or #4 spindle at a rotation speed of 6.3 rad/s.

2.7. Particle size measurements

BT₄/B₂T₉ 20 wt.% suspensions with or without dispersants present were prepared. After being 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, UK).

2.8. Ba²⁺ concentration measurements

BT₄/B₂T₉ 20 wt.% suspensions with or without dispersants present were prepared. After being mixed and centrifuged, a small amount of supernatant was taken and the Ba²⁺ concentration in the supernatant was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (JOBIN YVON JY24, France).

3. Results and discussion

3.1. Dissociation of dispersants in solutions

As shown in Fig. 1, the PAM/DAE molecule contains the carboxyl group (–COONa), cationic group (–N⁺), and amide group

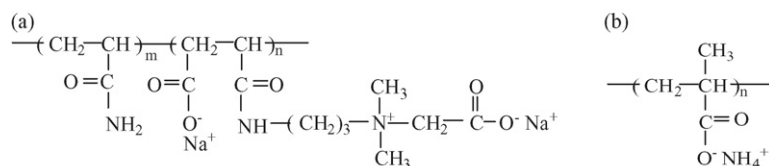


Fig. 1. Chemical structures of (a) PAM/DAE and (b) PMAA–NH₄ polymers.

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