

Dispersion of Nanoscale BaTiO₃ Suspensions by a Combination of Chemical and Mechanical Grinding/Mixing Processes

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ABSTRACT: The colloidal stability of aqueous nanometer- and micrometer-scale barium titanate (BaTiO₃) utilizing poly(methacrylic acid) (PMAA-Na) and polyacrylamide/(α -N,N-dimethyl-N-acryloyloxyethyl)ammonium ethanate (PDAAE) was investigated. In addition to chemical dispersants, the effects of mechanical milling using either conventional ball milling or nanogrinding/-mixing on the dispersion of BaTiO₃ suspensions were also studied. Characterization of the particle size distribution (d_{50}), viscosity, and morphology of BaTiO₃ particles in the suspensions revealed that a sole chemical dis-

persant or mechanical milling was insufficient to achieve nanometer-scale dispersion. The best dispersion results were obtained with a combination of PMAA-Na dispersant and nanogrinding/-mixing, which could provide sufficient electronic repulsive force and shear force to disperse the 80-nm BaTiO₃ powders uniformly in the aqueous suspension. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1550–1556, 2007

Key words: BaTiO₃; nanometer-scale dispersion; chemical dispersant; nanogrinding

INTRODUCTION

The recent development of thinner multilayer ceramic capacitors (MLCCs) demands the use of smaller-sized raw ceramic powders. When the thickness of an individual layer in an MLCC is scaled down to a 2- μ m nanometer scale, ceramic powders are required to produce defect-free layers.

Tape casting is commonly adopted to prepare green tapes for use in multilayer ceramic substrates, ceramic capacitors and inductors, and so forth. To achieve green tape with a high packing density and a uniform microstructure, a slurry with fine dispersion is essential.¹ However, dispersion of ceramic powders on a nanometer scale is difficult compared with on a micrometer scale because nanoscale powders have a larger specific surface area (SSA) and attractive van der Waals forces.² Aqueous suspensions can be stabilized by electrostatic, steric, or electrosteric mechanisms.^{3–6} Ceramic powders generally are dispersed in aqueous suspensions that use polyelectrolyte additives. For instance, Cesarano III et al. demonstrated

that alumina suspensions can be stabilized with a sufficient amount of sodium salt of poly(methacrylic acid) (PMAA-Na), ammonium salt of poly(methacrylic acid) (PMAAN), or poly(acrylic acid) (PAA).⁵ Chen, Jean, and Wang² reported that either PAA or PMAAN might stabilize BaTiO₃ slurries under specific pH conditions. In particular, for BaTiO₃ powder, it was suggested that slurries be processed in basic conditions because a substantial amount of Ba⁺² might leach out from powders to solutions when the pH was less than 7.^{6,7} However, the adsorption of acrylic acid-based dispersants on BaTiO₃ particles was found to decrease with an increased pH because the polymers were more negatively dissociated.⁸

BaTiO₃ has many applications because of its high dielectric constant, ferroelectric properties, and positive temperature coefficient of electrical resistivity (PTCR).⁹ The present work investigated the dispersion of nanoscale BaTiO₃ powder in aqueous suspensions containing PMAA-Na or PDAAE at a pH of 9.5. The effects of chemical dispersants and grinding/mixing methods on the dispersion of BaTiO₃ particles as well as the stability of suspensions were analyzed by characterizing viscosity and measuring zeta potential and particle size distribution and using scanning electron microscopy (SEM). It was found that a hybrid process of chemical dispersant and mechanical milling was required to achieve a nanoscale dispersion of BaTiO₃ in aqueous suspensions with satisfactory colloidal stability.

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EXPERIMENTAL

Raw materials and sample preparation

Two types of high-purity BaTiO₃ powders with different particle sizes were used in the study: 200-nm BaTiO₃ with Ba/Ti = 1.001 and SSA = 9.18 m²/g (Seedchem, Australia) and 1- μ m BaTiO₃ with Ba/Ti = 1.001 and SSA = 2.45 m²/g (Prosperity Dielectric, Taiwan). The chemical dispersants include an Na⁺ salt of PMAA-Na (Echo Chemical Co.) with an average molecular weight of 10⁴ g/mol and a self-prepared amphibious copolymer of PDAAE with a similar molecular weight. The PDAAE was prepared from acrylamide and (α -N,N-dimethyl-N-acryloyloxyethyl)ammonium ethanate (DAAE) through free-radical polymerization; the procedures for preparing PDAAE were published previously.^{17,18} The chemical structures of these two chemical dispersants are depicted in Figure 1. PDAAE possesses two kinds of functional groups: an anionic functional group (—COO[−]) that is the same as that in PMAA-Na and a cationic functional group (—N⁺R₃). The cationic functional group in PDAAE was expected to provide a different dispersive behavior in nanoscale BaTiO₃ suspensions. Analytical-grade chemicals (HNO₃ and NH₄OH) purchased from Hsinchy, Taiwan, were used to adjust the pH of the solutions.

Characterization of properties and morphology

Viscosity

The viscosity of 60 wt % BaTiO₃ suspensions with or without chemical dispersants subjected to nano-grinding/-mixing process via a laboratory mill (MiniZeta 03, NETZSCH-Feinmahltechnik GmbH) was evaluated by a viscometer (Brookfield DV-II, USA) using either a #1 or #4 spindle at a rotation speed of 60 rpm.

Particle size distribution

Aqueous suspensions of 30 wt % BaTiO₃ (origin particle size = 200 nm) with or without dispersants were prepared at a pH of 9.5. At this pH the BaTiO₃ slurries with PMAA-Na or PDAAE were stable and dissociable.^{2,17,18} After mechanical grinding/mixing with the MiniZeta mill, a small amount of slurry was taken out and sent to a particle size analyzer (Malvern Mastersizer 2000, UK) for examination of the size distribution of powders in the slurry.

Adsorption of dispersant

Aqueous suspensions of 30 wt % BaTiO₃ (origin particle size = 200 nm) with different concentrations of chemical dispersants were prepared at a pH of 9.5.

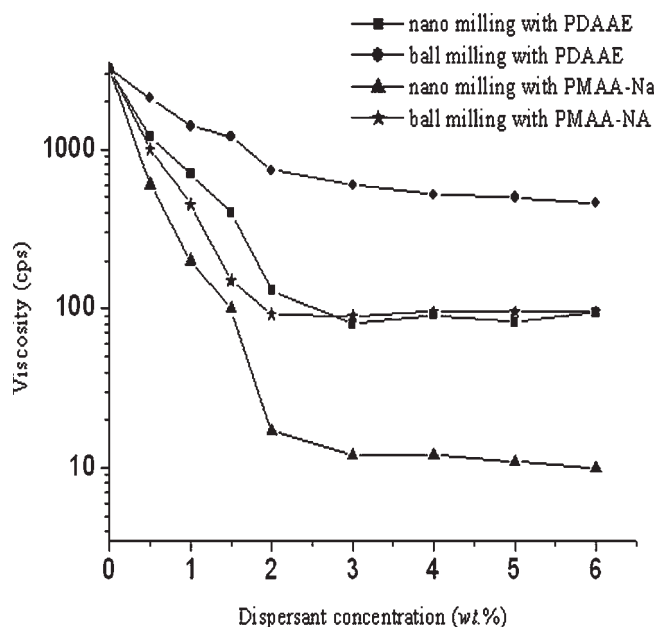


Figure 1 Chemical structures of dispersants: (a) PDAAE and (b) PMAA-Na.

Dispersion utilizing the MiniZeta mill or a conventional ball mill was then executed. After the mechanical milling, the suspensions were centrifuged at a speed of 6000 rpm for 30 min. The residual dispersant concentration in the supernatants was analyzed by the potentiometric titration procedure. The total amount of dispersant adsorbed on BaTiO₃ was calculated based on a mass balance of dispersant.^{2,17,18}

Zeta potential

After mechanical milling, a small amount of supernatant was removed from the BaTiO₃ slurries by centrifugation, and the zeta potential of the remaining powders in the supernatant was then measured with a zeta meter (PEN KEN Inc. 501, France).

Morphology

The grain sizes and morphology of the sintered specimens were examined with a scanning electron microscope (JEOL JSM-6300).

RESULTS AND DISCUSSION

Rheological behavior

Viscosity measurement is commonly adopted to evaluate the extension of dispersion of concentrated suspensions. Figure 2 shows the effect of dispersant concentration on the viscosity of 60 wt % BaTiO₃ suspensions subjected to conventional ball milling or nanogrinding/-mixing via a MiniZeta mill. The viscosity of the suspensions without dispersion treat-

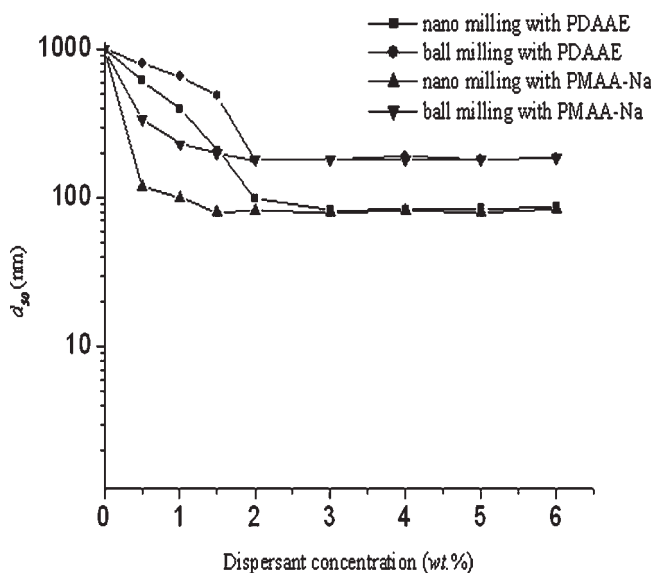


Figure 2 Effect of dispersant concentration on the viscosity of 60 wt % BaTiO₃ suspensions subjected to various grinding/mixing processes.

ment was about 3200 cps. For the suspensions subjected to different mechanical milling processes, viscosity decreased when PMAA-Na or PDAAE was incorporated. The viscosity of suspensions first decreased with an increase in dispersant concentration and then reached a plateau. At some dispersant concentrations, the viscosity of suspensions subjected to nanogrinding/-milling was lower than that of suspensions subjected to conventional ball milling. For the suspensions subjected to nanogrinding/-mixing, the optimum chemical dispersant concentrations in BaTiO₃ suspensions were about 2 wt % for PMAA-Na and 3 wt % for PDAAE, which resulted in lowest viscosities of 15 and 76 cps, respectively.

Figure 2 also shows that the suspension containing PMAA-Na exhibited the sharpest decrease in viscosity and required a smaller amount of PMAA-Na to achieve the lowest viscosity than did that containing PDAAE. As PMAA-Na and PDAAE have similar molecular weights, the difference in the rheological behavior was attributed to the difference in chemical structure. PMAA-Na is an anionic polyelectrolyte that causes mainly electrostatic repulsion when adsorbed on BaTiO₃ particles. Though PDAAE also causes electrostatic repulsion when adsorbed on BaTiO₃ surfaces, its effect is not as strong because it is an amphibious polyelectrolyte.

Particle size distribution

In conventional ball milling, slurry and grinding media are sealed in a bottle, and the grinding/mixing is achieved by the rotation motion of grinding balls. Such a milling process provides a relatively

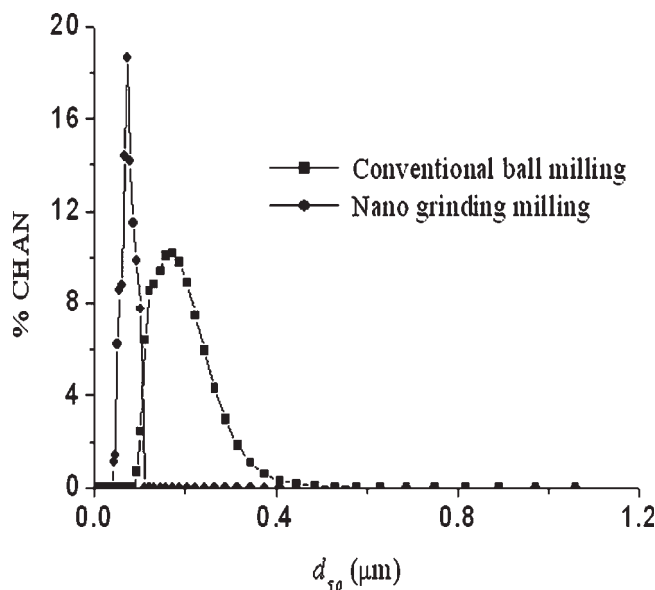


Figure 3 Effect of dispersant concentration on the mean particle size (d_{50}) of powder in 30 wt % BaTiO₃ suspensions subjected to different grinding/mixing processes.

low shear force that is insufficient for achieving nanoscale dispersion. In the present work, a Mini-Zeta mill using 5-mm-diameter ZrO₂ balls as grinding media was able to grind the BaTiO₃ powder to sizes smaller than 100 nm. By using the principle of agitator bead mills, a special agitator shaft rotating at speeds as high as 3600 rpm accelerated the grinding media in the MiniZeta mill chamber. It not only provided superfine grinding but also generated a rather large shear force to disperse the slurry. In

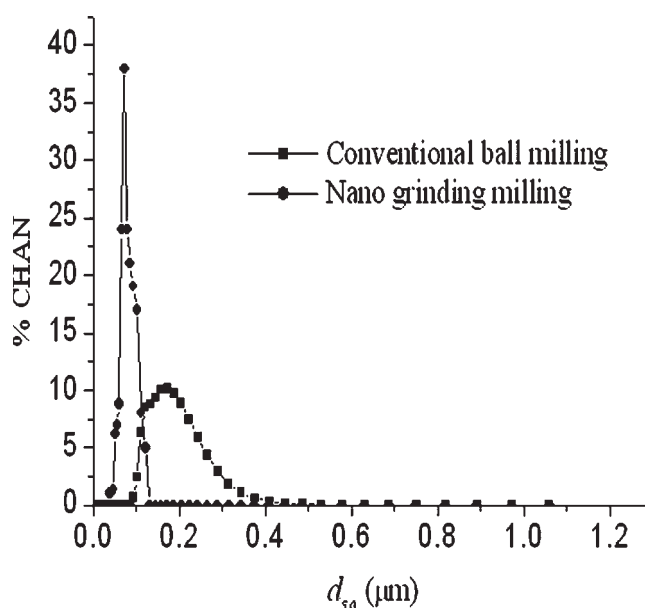


Figure 4 Particle size distribution of BaTiO₃ powder containing 2 wt % PMAA-Na subjected to conventional ball milling and nanogrinding/-mixing processes.

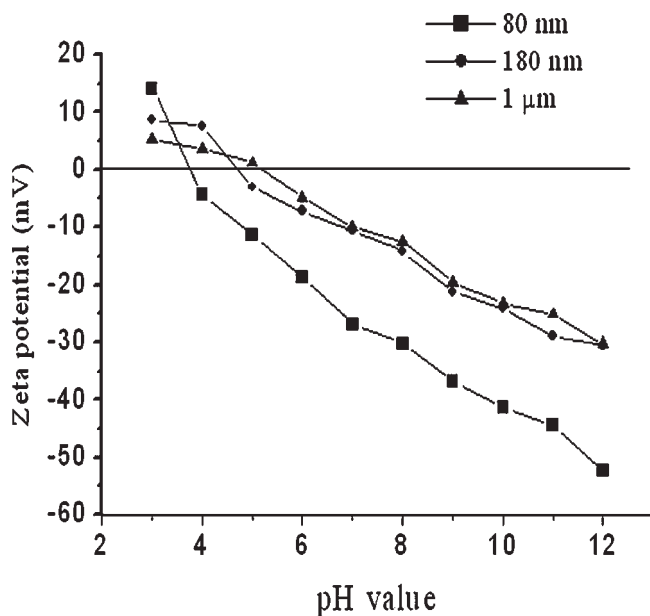


Figure 5 Particle size distribution of BaTiO₃ powder containing 3 wt % PDAAE subjected to conventional ball milling and nanogrinding/-mixing processes.

addition, the multipassage grinding/mixing path adopted by the MiniZeta mill was able to reduce the size of BaTiO₃ powder in a relatively short time.

Figure 3 presents the mean particle size (d_{50}) of powder as a function of dispersant concentration in 30 wt % BaTiO₃ suspensions subjected to nano- or conventional milling processes. The initial value of d_{50} of powder in the suspensions was 1 μm. With the increasing amount of chemical dispersant, the d_{50} of powders in all types of suspensions decreased. As shown in Figure 3, the variation in d_{50} with the dispersant concentration was much the same as that of viscosity presented in Figure 2. The smallest d_{50} of BaTiO₃ suspensions occurred at about 2 wt % for PMAA-Na and 3 wt % for PDAAE, equal to 80 and 83 nm, respectively. Apparently, more PDAAE was required to achieve the smallest d_{50} in suspensions, and the minimum particle size in suspensions containing PDAAE was slightly larger than that in suspensions containing PMAA-Na.

Figures 4 and 5 show the particle size distributions of 30 wt % BaTiO₃ slurries containing 2 wt % PMAA-Na and 3 wt % PDAAE subjected to conventional and nanomilling processes, respectively. The d_{50} values of suspensions subjected to the nanogrinding/-mixing were 80 nm for PMAA-Na and 83 nm for PDAAE, whereas those of suspensions subjected to conventional ball milling were 180 nm for PMAA-Na and 181 nm for PDAAE. Furthermore, a narrower distribution curve implied a more uniform size of the BaTiO₃ particles in the suspensions subjected to nanogrinding/-mixing process. It was also

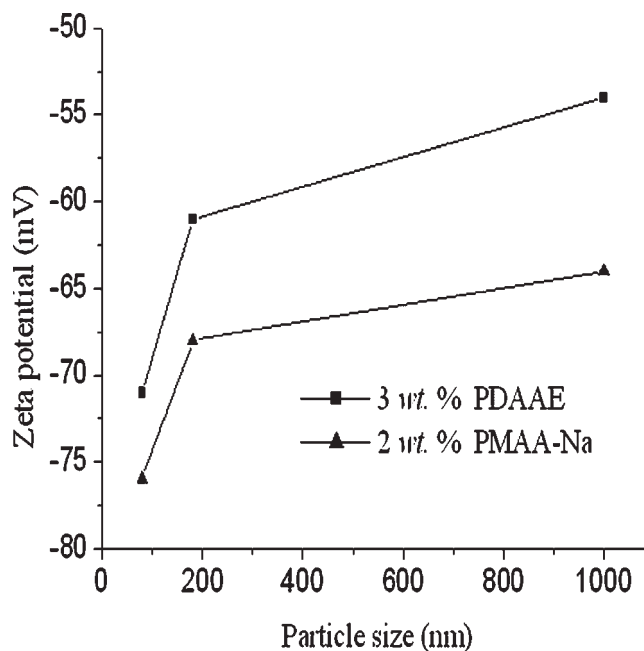


Figure 6 Zeta potentials of BaTiO₃ suspensions of different particle sizes.

found that the average size of BaTiO₃ in suspensions without any mechanical milling was in the range of 200 nm. This indicated that the high shear force provided by an appropriate mechanical milling process was also beneficial to the stability of the suspensions. Because of the larger SSA and van der Waals forces, the nanoscale particles in slurry tended to agglomerate. In addition to a chemical dispersant, a mechani-

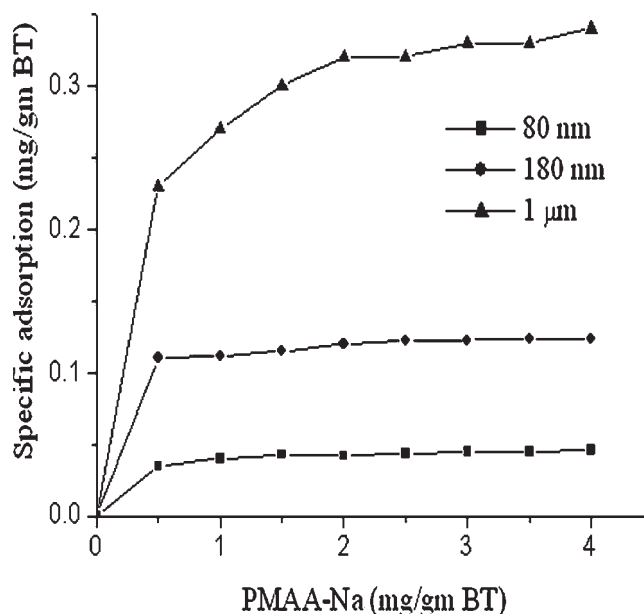


Figure 7 Zeta potentials of BaTiO₃ suspensions containing different chemical dispersants.

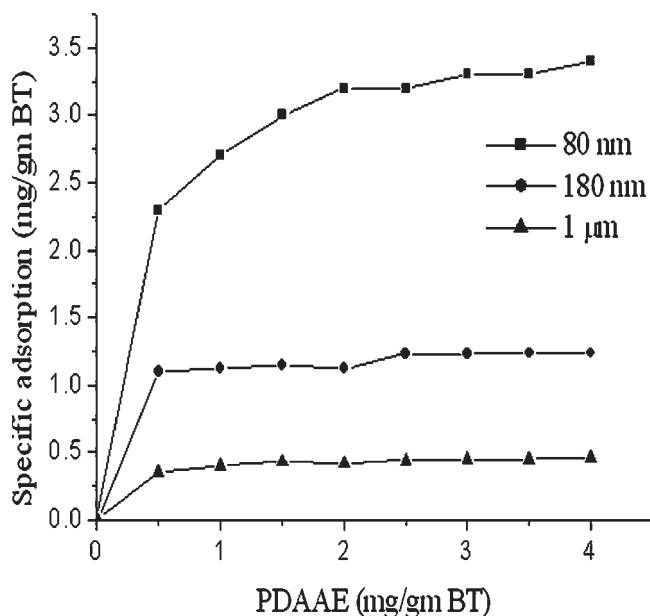


Figure 8 Specific adsorption of PMAA-Na on BaTiO₃ of different particle sizes.

cal milling process able to provide sufficient shear force is required in order to achieve satisfactory dispersion of nanoscale BaTiO₃ particles in an aqueous suspension.

The experimental results of viscosity and particle size distribution also indicated that a single mechanical milling process was insufficient to disperse nanosized BaTiO₃ particles in suspensions. Though nanogrinding/-mixing via the MiniZeta mill provided a large shear force to disperse the particles, it could not stabilize the suspensions. Because of the large SSA and van der Waals forces, the particles subjected to nanogrinding/-mixing still tended to agglomerate if the suspensions were free of chemical dispersant. Hence, in addition to mechanical milling, an appropriate amount of chemical dispersant had to be added to provide sufficient electrostatic repulsion and steric effect in suspensions so that a stable, uniform dispersion on a nanometer scale could be obtained.

Zeta potentials

Electrokinetic measurements are widely used to assess the magnitude and sign of particle surface charge as a function of pH in suspensions.¹⁰ Figure 6 presents the zeta potentials of 30 wt % BaTiO₃ powder as a function of the pH of the suspension. The isoelectric points were at a pH of 3.8 for 80-nm BaTiO₃, at a pH of 4.5 for 180-nm BaTiO₃, and at a pH of 5.2 for 1-μm BaTiO₃. This indicates the BaTiO₃ particles tended to stabilize in high-pH aqueous solutions.

The hydrolysis of BaTiO₃ in an acidic environment is as follows:^{11,12}

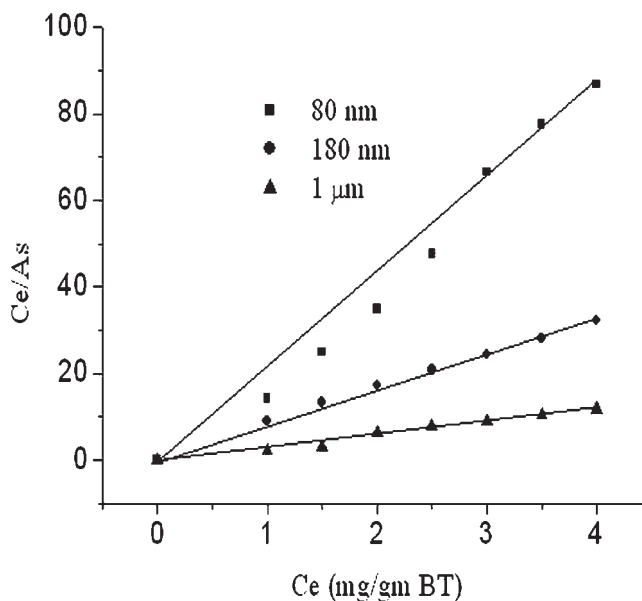
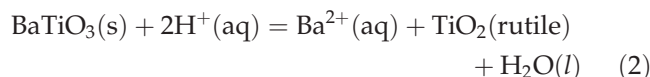
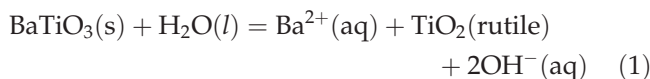


Figure 9 Specific adsorption of PDAAE on BaTiO₃ particles of different particle sizes.



Nanoscale BaTiO₃ particles possess a large SSA. When HNO₃(aq) was added to the suspension, the pH decreased, and more Ba²⁺ ions tended to leach out from the surface of the BaTiO₃. The Ba²⁺ ions could have nullified some negative charges on the surface of the BaTiO₃, so the zeta potential was more positive, as revealed by eq. (2). On the other hand, when NH₄OH was added to the suspension, the pH increased and the resulting OH⁻ ions were able to neutralize the positive charges on the surface of the BaTiO₃, so the negative trend of the zeta potential increased.

Figure 7 shows that the zeta potentials for BaTiO₃ suspensions containing PMAA-Na or PDAAE at a pH of 9.5. It can be seen that at the same particle size, the zeta potential for the suspension containing PMAA-Na was more negative than that containing PDAAE. At pH = 9.5, the surfaces of nanoscale BaTiO₃ particles were highly negative charged, so

TABLE I
Critical Dispersant Concentrations to Reach Adsorption Plateau (per Gram of BaTiO₃)

Dispersant	Particle size		
	80 nm	180 nm	1 μm
PMAA-Na	0.03–0.04 mg	0.11–0.12 mg	0.25–0.3 mg
PDAAE	2.8–3.3 mg	1.1–1.2 mg	0.3–0.4 mg

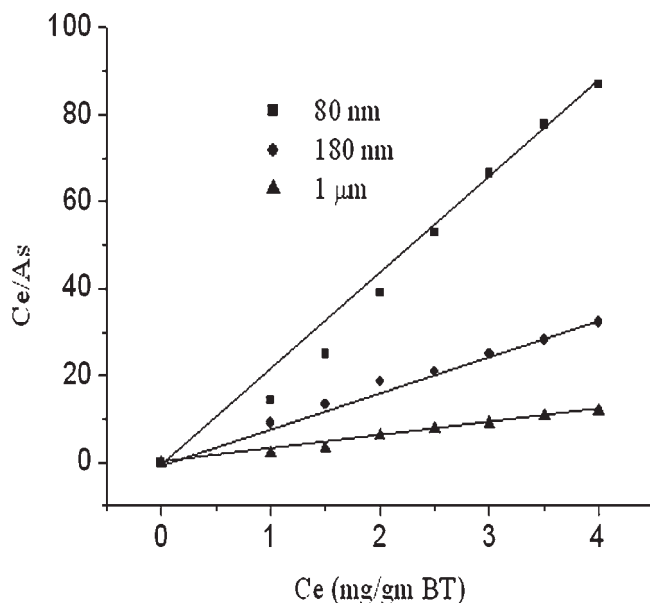


Figure 10 Langmuir analysis of the suspension containing PMAA-Na.

that the adsorption of dispersant on particle surface was more difficult than were the microscale particles. This suggests that the rejection was caused by the net negative electric charge of the particles, and for PMAA molecules, rejection became more severe when the particle size was down to a nanometer scale. However, the PDAAE molecules became amphibious in a basic solution (i.e., at pH = 9.5). Molecules containing cationic functional groups ($-N^+R_3$) would be favored for adsorption on the surface of BaTiO₃ particles.

Adsorption of dispersants on BaTiO₃

Figures 8 and 9 show the specific amounts of PMAA-Na and PDAAE, respectively, adsorbed on the BaTiO₃ particles in suspensions at pH = 9.5. The specific adsorption behavior of both types of suspensions suggests a monolayer adsorption concentration on the particle surface; however, the critical dispersant concentrations to reach the adsorption plateau were different. For PMAA-Na, the critical value decreased with a decrease in particle size and vice versa for PDAAE. The concentrations of dispersant critical for reach an adsorption plateau for these two types of suspensions are listed in Table I.

Table I clearly shows that the critical value and amount of adsorbent were greater for PDAAE than for PMAA-Na. The differences between the adsorbents in these values were attributed to the different chemical structures of the two dispersants. At a pH of 9.5, the surface charge of the BaTiO₃ particles was negative. For PMAA-Na, its molecules were completely dissociated and became negatively charged.

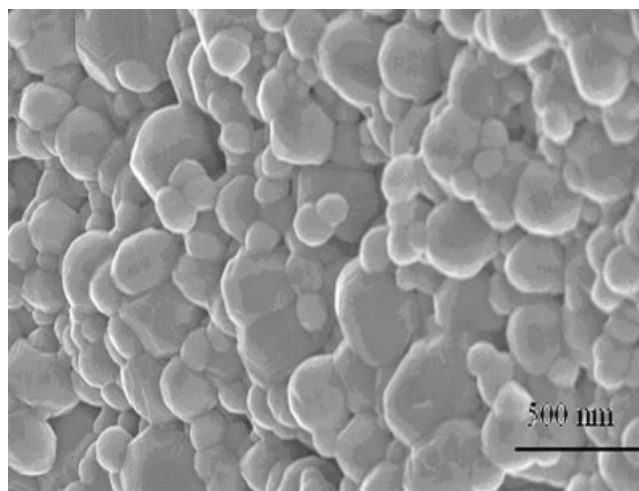


Figure 11 Langmuir analysis of the suspension containing PDAAE.

Therefore, it was difficult for the PMAA-Na molecules to be adsorbed on the BaTiO₃ surface. In contrast, the PDAAE molecules became amphibious in a basic solution, and the existence of cationic functional groups ($-N^+R_3$) favored the absorption of PDAAE on the BaTiO₃ surface. In addition, the amide functional group ($-CONH_2$) in the structural unit of PDAAE could also interact with Ba²⁺ ions and enhance the adsorption. Accordingly, the amount of PDAAE molecules adsorbed was more than that of PMAA-Na molecules.

Furthermore, an interesting behavior of the adsorption isotherms was observed in this work. For BaTiO₃ particles of different sizes, the initial adsorption behavior was distinctly different when different dispersant was added. This clearly suggested that nanoscale particles possess a highly negative charge on the surface that inhibits the adsorption of negatively charged dispersant or increases the adsorption of amphibious charged dispersant. Another possible explanation was that the dispersants might adsorb on the large-sized particles in an orientation that permits a greater extent of adsorption on the particle surface.¹³

To determine the PMAA-Na and PDAAE monolayer adsorption quantitatively, the data shown in Figures 8 and 9 were analyzed using the Langmuir monolayer adsorption equation:

TABLE II
Monolayer Adsorption of Dispersants on BaTiO₃ Surface (per Gram of BaTiO₃)

Dispersant	Particle size		
	80 nm	180 nm	1 μm
PMAA-Na	0.04 mg	0.12 mg	0.32 mg
PDAAE	3.2 mg	1.2 mg	0.4 mg

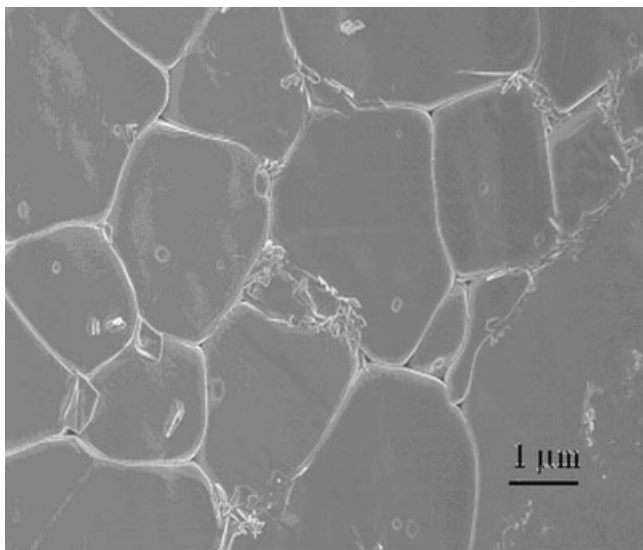


Figure 12 SEM micrographs of sintered specimens prepared with suspensions containing (a) nanoscale BaTiO₃ powders and (b) microscale BaTiO₃ powders.

$$\frac{C_e}{A_s} = \frac{C_e}{C_m} + \frac{k}{C_m} \quad (3)$$

where C_e is the equilibrium concentration of dispersants in solution, A_s is the adsorbent of the dispersant, C_m is the monolayer adsorbent of the dispersant, and k is a constant. The plots of C_e/A_s versus C_e for these two types of suspensions are shown in Figures 10 and 11, respectively. The slopes of the straight lines represent the reciprocal of the monolayer adsorption of dispersant ($1/C_m$), and the results are summarized in Table II. It can be seen that the amount of monolayer PMAA-Na adsorption decreased with a decrease in particle size and vice versa for the PDAAE. However, the results of adsorption and zeta potential indicated that both PDAAE and PMAA-Na could successfully stabilize the nanoscale BaTiO₃ slurry. The dispersive capability of PDAAE is a steric effect and electrostatic repulsion, but that of PMAA-Na is solely electrostatic repulsion.

Figure 12(a,b) presents the SEM micrographs of sintered specimens prepared using the nanoscale and microscale BaTiO₃ suspensions, respectively. The specimen based on nanoscale BaTiO₃ powder clearly possesses a fine-nanograin structure in comparison with that based on microscale BaTiO₃ powder. Hence, dramatic improvement in the dielectric properties was expected.

CONCLUSIONS

This work has demonstrated that adding an appropriate amount of PMAA-Na or PDAAE to BaTiO₃

suspensions followed by a nanogrinding/-mixing process was able to reduce the viscosity of the suspensions and the average particle size (d_{50}) of BaTiO₃. The experimental results revealed that structural differences in the chemical dispersants caused distinct absorption behaviors on the particle surface. In basic condition (pH = 9.5), the adsorption of PMAA-Na on the BaTiO₃ particle surface decreased with a decrease in particle size and vice versa for PDAAE. Because the surface of the nanoscale BaTiO₃ became highly negatively charged, the cationic quaternary amine ($-N^+R_3$) functional group favored absorption of PDAAE on the BaTiO₃ particle surface, whereas for PMAA-Na, the anionic group ($-COO^-$) caused repulsion on the BaTiO₃ particle surface. Although the adsorption of PDAAE on nanosized BaTiO₃ was larger than that of PMAA-Na, the PMAA-Na with anionic features offered greater electrical repulsive force on BaTiO₃ particles than did PDAAE. Hence, the PMAA-Na exhibited better dispersion capability for suspensions containing nanosized BaTiO₃, as revealed by the viscosity and particle size (d_{50}) measurements.

In addition, this work also demonstrated that mechanical milling process able to provide sufficient shear force is required for the fine dispersion of nanosized BaTiO₃. In fact, a hybrid of chemical dispersant and nanogrinding/-mixing process utilizing, for instance, a Minizeta mill was not only an efficient way to disperse the nanosized BaTiO₃ particles in suspensions but also provided good colloidal stability for the aqueous solutions.

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