

Amphoteric Water-Soluble Copolymer for Barium Titanate Slurries. I. Synthesis and Dispersing Ability

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ABSTRACT: An amphoteric water-soluble copolymer, polyacrylamide/[α -*N,N*-dimethyl-*N*-(3-(β -carboxylate)acrylamino)propyl] ammonium ethanate (PAM/DAE) was synthesized and used as a dispersion agent for BaTiO₃ 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 structure of this copolymer was verified by IR and ¹H-NMR spectra. The dispersing effects of PAM/DAE were examined by measuring the viscosity and sedimentation of BaTiO₃ suspensions, and by analyzing the

particle size. The results indicate that this copolymer could uniformly disperse the particles, and the resulting suspensions were less viscous, more stabilized, and contained powder with smaller particle size. The dispersing/stabilizing ability of PAM/DAE is close to, or slightly better than, that of a commercial dispersant, ammonium salt of poly(methacrylic acid). © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1443–1450, 2005

Key words: polyelectrolytes; synthesis; barium titanate; dispersions; structure

INTRODUCTION

Water-soluble polymers have been applied in many areas such as mineral processing, water treatment, and coatings.^{1,2} Another important area of application is in the wet processing of ceramic powders.^{3,4} These polymers, called polymeric surfactants or polyelectrolytes, have often been used as dispersants or stabilizers. They primarily serve to uniformly disperse solid particles and to stabilize ceramic slurries with less agglomeration or segregation during processing. Therefore, ceramic green parts with a uniform microstructure and high packing density can be prepared, and sintered compacts without defects or pores are obtained.

It is reported that these polyelectrolytes, after being adsorbed on ceramic particles, will create electrostatic repulsions, a steric effect, or both.^{4–7} This results in the dissociation of the agglomerates into primary particles with a significant decrease in the viscosity and thus achieving a stable cloudy state of suspensions. Among commercial dispersants, acrylic acid-based polyelectrolytes are commonly used for ceramic powders. For example, Cesarano III et al.^{5,6} showed that alumina suspensions can be stabilized with a sufficient amount

of sodium salt of poly(methacrylic acid), ammonium salt of poly(methacrylic acid) (PMAAN), or polyacrylic acid (PAA). Chen et al.⁷ and Jean and Wang⁸ found that either PAA or PMAAN can stabilize the barium titanate slurries under certain pH conditions. De Laat and Van den Heuvel⁹ reported that the molecular weight fraction of adsorbed PAA salts onto BaTiO₃ depends on the molecular weight distribution of dispersants. Ramay and Zhang¹⁰ reported that PMAAN is a suitable dispersant for aqueous hydroxyapatite slurries. Oliveira et al.¹¹ reported sodium polymethacrylate can disperse cement particles and substantially reduce the viscosity of suspensions. Although some good results have been achieved, there are still some aspects that remain for further improvement. Specifically, for barium titanate powder, the resulting slurries are better processed in a basic condition because a substantial amount of dissolved Ba⁺² would occur in solutions at pH < 7.^{12,13} However, the adsorption of acrylic acid-based dispersants on BaTiO₃ particles was found to decrease with increasing pH because the polymers are more negatively dissociated.^{8,14} Usually, more adsorption or greater surface coverage of dispersants is preferred because larger electrostatic, steric, or electrosteric forces are generated. In addition, the added dispersant molecules are expected to enhance Ba⁺² leaching as a result of their interactions with barium ions. This would generate exaggerated grain growth in the later sintering process and result in a low sintered density.^{12,13,15} Therefore, new and more effective dispersants are worth being developed.

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TABLE I
Basic Properties of BaTiO₃ Powder

Ba/Ti	1/1
Purity, %	99.88
SrO, %	0.022
Nb ₂ O ₅ , %	0.001
Al ₂ O ₃ , %	0.033
SiO ₂ , %	0.016
D ₅₀ , μm	0.46
Moisture, %	0.25
Ignition loss, %	0.6
Compressed density, g/cm ³	3.269
BET specific surface area, m ² /g	4.53

Previously, we reported an amphoteric water-soluble copolymer [polyacrylamide/(α -*N,N*-dimethyl-*N*-acryloyloxyethyl) ammonium ethanate] as an effective dispersing agent for aqueous BaTiO₃ slurries.¹⁶ In this study, we have synthesized another amphoteric water-soluble copolymer, polyacrylamide/(α -*N,N*-dimethyl-*N*-acryloyloxyethyl) ammonium ethanate (PAM/DAE), as a dispersant for barium titanate powder. PAM/DAE was prepared from acrylamide (AM) and (α -*N,N*-dimethyl-*N*-acryloyloxyethyl) ammonium ethanate (DAE) through a free-radical polymerization. The dispersing ability of this copolymer was examined from viscosity, sedimentation, and particle size measurements. Furthermore, a commercial dispersant, Darven C, was also tested for comparison.

EXPERIMENTAL

Materials

Acrylamide (AM), maleic anhydride, *N,N*-dimethyl-1,3-propanediamine, sodium chloroacetate, ammonium persulfate, and sodium thiosulfate were used without further purification. As will be described below, polyacrylamide/[α -*N,N*-dimethyl-*N*-(3-(β -carboxylate)acrylamino)propyl] ammonium ethanate (PAM/DAE) was prepared from the chemicals mentioned earlier. The prepared PAM/DAE polymer has a fixed AM/DAE (= 10/1) ratio and a weight-average molecular weight of 1.5×10^5 . In addition, a commercial dispersant (Darven C) was also used for comparison. The chemical formula of Darven C is an ammonium salt of poly(methacrylic acid) (PMAAN), which has a weight-average molecular weight of 1.3×10^4 . The molecular weights of PAM/DAE and PMAAN polymers were measured by the GPC mentioned below.

The ceramic powder used was a high purity BaTiO₃ which is from Prosperity Dielectrics (Taoyuan, Taiwan). The powder has a Ba/Ti ratio of 1, an average (d_{50}) particle size of 0.46 μm, and a BET specific surface area of 4.53 m²/g. Table I lists the characteristics of BaTiO₃ powder. Deionized and distilled water was

used, and the pH was adjusted by the addition of NaOH_(aq).

Preparations of PAM/DAE resins

PAM/DAE was prepared from AM and [α -*N,N*-dimethyl-*N*-(3-(β -carboxylate)acrylamino)propyl] ammonium ethanate (DAE) through a free-radical polymerization.¹⁷ Ammonium persulfate, together with sodium thiosulfate, was used as the initiator. DAE was prepared from β -carboxylate-*N*-(3-dimethyl aminopropyl) acrylamide (CDPA) and sodium chloroacetate. In turn, CDPA was prepared from maleic anhydride and dimethyl-1,3-propylene diamine. The reaction equations for preparing DAE and PAM/DAE are as follows:

An example of preparing DAE and PAM/DAE with AM/DAE = 10/1 is as follows:

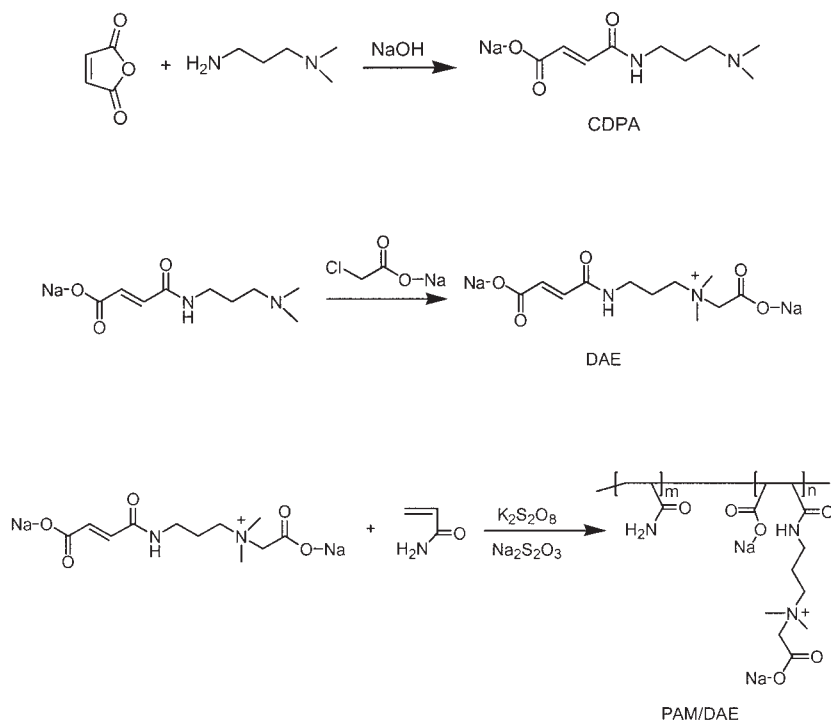
Maleic anhydride (19.6 g) was dissolved in 80 g of acetone, and then 20.4 g of dimethyl-1,3-propylene diamine was added dropwise into a 250-mL stirred reactor. The reaction proceeded for 2 h at room temperature. After the reaction, the mixture was vacuum filtered, washed with acetone, and the filtered solid powder was dried in a vacuum oven at room temperature for 2 days to collect CDPA.

After obtaining the CDPA, the formation of the monomer DAE was performed. That is, 19.8 g of CDPA was dissolved in 60 g of distilled water. The solution was adjusted to a pH of about 9–10, followed by addition of 11.7 g of sodium chloroacetate. Thereafter, the solution was mixed at room temperature for about 6 h. A majority of the solvent was removed in a vacuum condenser, followed by washing with acetone. After the acetone was removed, the sample was dried in a vacuum oven at room temperature for 2 days to collect the DAE monomer.

After obtaining the DAE monomer, PAM/DAE was synthesized; that is, 30 g of acrylamide and 11.8 g of DAE monomer were dissolved in 136 g of distilled water, followed by addition of an aqueous solution containing 2.14 g of potassium persulfate and 0.428 g of sodium thiosulfate. After mixing in a nitrogen atmosphere for several minutes, the mixture was sealed and allowed to settle, and PAM/DAE was produced, purified, dried, and collected after 3 days.

Identification of prepared resin

The dried CDPA, DAE, and PAM/DAE resins were further ground into powder before structure determination or other uses. In identifying the chemical structure, proper amounts of powder samples were mixed with predried KBr and pressed into disks. Transmission infrared spectra of the disks were recorded using a Paragon 500 FT-IR spectrometer (Perkin Elmer, Boston, MA). Moreover, some powder samples were also



Scheme 1

dissolved in D₂O and analyzed by an EX-400 NMR spectrometer (JEOL, Tokyo, Japan).

Gel permeation chromatography (GPC) measurements

The molecular weight of dispersants was determined by GPC, which contains a liquid chromatograph (Jasco, Tokyo, Japan), equipped with three coupled columns Shodex OHpak KB802.5, KB804, and KB806; a pump (Jasco PU-980); 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 MWs (1.8×10^3 , $8. \times 10^3$, 3.5×10^4 , 1.0×10^5 , 1.3×10^6) were used as calibration standards.

Preparations of BaTiO₃ suspensions

Aqueous suspensions (100 g) containing either 20 or 60 wt % BaTiO₃ were prepared. They contained 0–2.0 wt % dispersant relative to the weight of dry BaTiO₃ powder. The suspensions were milled and mixed in a ceramic jar with a fixed amount of zirconia balls for 24 h. The 24-h time period of milling is believed to be long enough to reach a homogeneously dispersed state.

Viscosity measurements

The viscosity of 60 wt % BaTiO₃ aqueous suspensions at pH = 12, with or without dispersants present, was determined by a viscometer (Model DV-II, Brookfield Engineering Laboratories, Middleboro, MA) using either #1 or #4 spindle at a rotation speed of 60 rpm.

Sedimentation tests

BaTiO₃ aqueous suspensions (20 wt %), with or without dispersants present at pH = 12, were prepared and poured into 200-mL graduated cylinders. These suspensions were left in the cylinders for 30 days, and the change of sedimentation height along with elapsed time was measured and recorded.

Particle size measurements

BaTiO₃ aqueous suspensions (20 wt %), with or without dispersants present, were prepared. After ball-milling, small amounts of slurries were taken. The particle size of powder in samples was determined by using a particle size analyzer (Mastersizer 2000, Malvern Instruments, Worcestershire, UK).

SEM observations

The microstructures of BaTiO₃ green compacts made from gravitational settlement and consolidation of 60

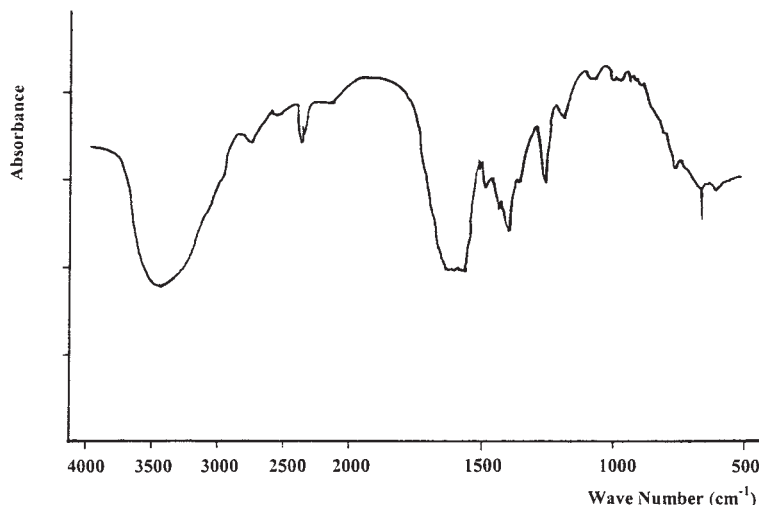


Figure 1 IR spectrum of DAE.

wt % BaTiO₃ suspensions, with or without dispersants present, were observed by a scanning electron microscope (JEOL JSM-6300).

RESULTS AND DISCUSSION

Structure of prepared resins

The structures of typically prepared DAE and PAM/DAE were verified from their IR and ¹H-NMR spectra, as shown in Figures 1–4, respectively. Figure 1 shows the IR spectrum of DAE, which displays an N—H stretching band at 3447 cm⁻¹, a C=O stretching band overlapped with a C=C stretching band at 1635 cm⁻¹, and an N—H bending band at about 1569 cm⁻¹. The

¹H-NMR spectrum in Figure 2 gives signals at δ = 2.0 (4H), 3.2 (6H), 3.3 (3H), 3.5 (5H), 3.8 (7H), 5.9 (1H), and 6.3 ppm (2H), respectively. Figure 3 shows the IR spectrum of PAM/DAE, which displays N—H stretching bands at 3183 and 3383 cm⁻¹, a C=O stretching band at 1671 cm⁻¹, and an N—H bending band at about 1605 cm⁻¹. As shown in Figure 4, the ¹H-NMR spectrum gives signals at δ = 1.4–1.6 (1H), 2.0–2.2 (overlap of 2H and 3H), 2.8 (5H), 3.1 (4H), and 3.8 ppm (6H), respectively.

Compared to Figure 1, the IR spectrum in Figure 3 lacks the C=C absorption band and shows a sharper C=O stretching band at 1671 cm⁻¹, attributed to the polymerization of AM and DAE. Besides, this spec-

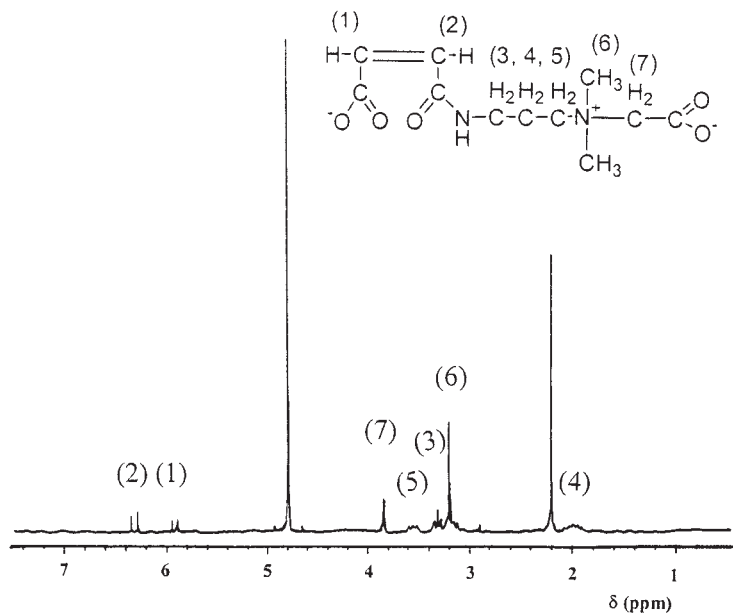


Figure 2 ¹H-NMR spectrum of DAE.



Figure 3 IR spectrum of PAM/DAE.

trum in Figure 3 shows two distinct N—H stretching bands at $3100\text{--}3500\text{ cm}^{-1}$, indicating PAM/DAE contains the primary amide group. Furthermore, the signals related to the protons in $-\text{CH}=\text{CH}-$ at $\delta = 5.9\text{--}6.3\text{ ppm}$ in Figure 2 were not found in Figure 4, and new signals related to the protons in $-\text{CH}-\text{CH}-$ at $\delta = 1.4\text{--}1.6$ and $2.0\text{--}2.2\text{ ppm}$ appear in Figure 4. This indicates the formation of copolymer from its two monomers.^{18–20}

Rheological behavior

The viscosity measurement is an appropriate way to evaluate not only the degree of powder dispersion in concentrated suspensions but also the effectiveness of a dispersing agent.¹³ Usually, powder agglomeration causes a concentrated suspension to become very viscous. The viscosity of a suspension could be decreased if a suitable dispersant was incorporated. The extent of

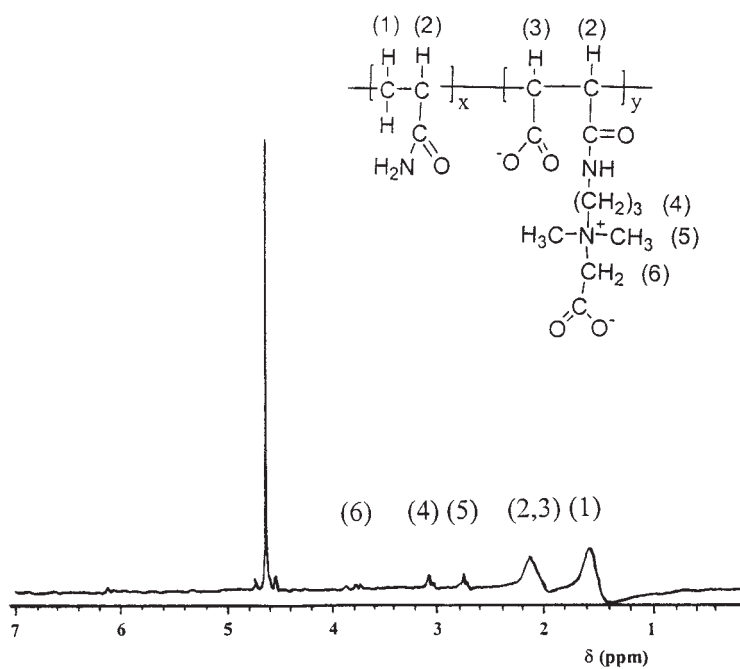


Figure 4 $^1\text{H-NMR}$ spectrum of PAM/DAE.

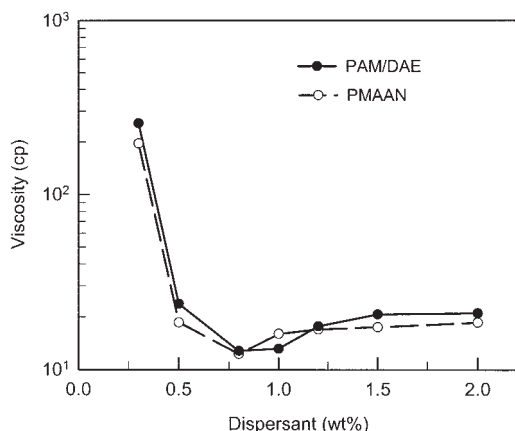


Figure 5 Effect of dispersant concentration on the viscosity of 60 wt % BaTiO_3 suspensions at $\text{pH} = 12$.

decrease in viscosity depends on the effectiveness of the dispersant in reducing the agglomerate size. Figure 5 shows the viscosity of 60 wt % BaTiO_3 suspensions at $\text{pH} = 12$, as a function of dispersant concentration. The viscosity of BaTiO_3 suspensions without dispersant is >1000 mPa·s. The suspension becomes less viscous when PAM/DAE is incorporated, indicating that this copolymer can enhance the dispersion of BaTiO_3 particles. As PAM/DAE concentration is increased, the viscosity of suspensions was found to decrease sharply at first, reaching a minimum value, and then increasing slightly. The amount that gives the lowest viscosity value is about 0.8 wt %. Similar rheological behavior was also observed from Figure 5 for the BaTiO_3 suspension containing PMAAN. The required amount of PMAAN to achieve the lowest value is also about 0.8 wt %, which is close to that of PAM/DAE. Furthermore, the achieved minimum viscosity values of suspensions with either PMAAN or PAM/DAE are also close to each other.

Although similar rheological behavior was observed for 60 wt % BaTiO_3 suspensions containing either PAM/DAE or PMAAN, the dispersing mechanism is clearly different for these two polymers. PMAAN would cause mainly electrostatic repulsions when adsorbed on BaTiO_3 particles, given that its molecules are anionic polyelectrolytes. In contrast, PAM/DAE molecules also cause electrostatic repulsions when adsorbed on BaTiO_3 particles. However, this effect is thought to be less than that by PMAAN molecules because they belong to the class of amphoteric polyelectrolytes. Besides, PAM/DAE is expected to produce a greater steric effect than that produced by PMAAN because the former has a higher molecular weight and the molecules contain longer side chains.

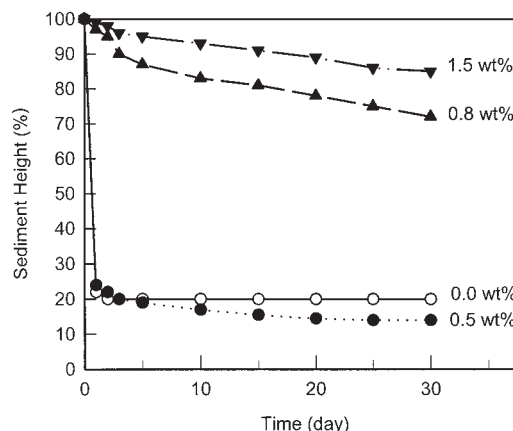


Figure 6 Effect of PAM/DAE concentration on the sediment height of 20 wt % BaTiO_3 suspensions at $\text{pH} = 12$.

Sedimentation

Observation and measurement of sedimentation is another way of indicating the colloidal stability. A good dispersant will cause suspensions to remain cloudy, resulting in a small final sediment height because of denser packing of particles.^{7,8} Figure 6 shows the sediment height of 20 wt % BaTiO_3 suspensions with various amounts of PAM/DAE at $\text{pH} = 12$. The sediment height refers to the percentage of the height of the dispersed particles relative to the initial height of the suspension. For suspensions without any dispersants present, they are not stable and separate into two layers after 1-day sedimentation; a clear boundary exists between a sediment layer and an upper clear aqueous layer. When 0.5 wt % PAM/DAE was added, the resulting suspensions also separated into two layers after 1-day sedimentation. However, the final sediment height is less than that of the BaTiO_3 suspension without any dispersant. When the amount of incorporated PAM/DAE is >0.8 wt %, the resulting suspen-

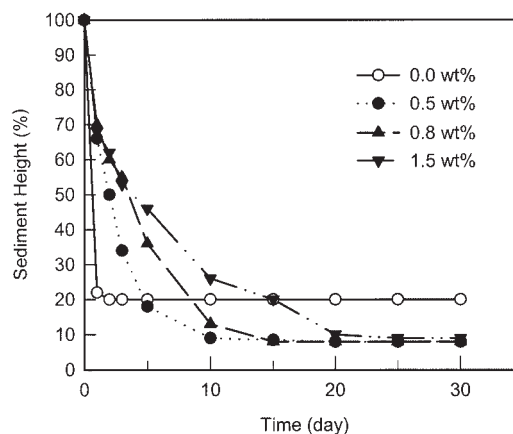


Figure 7 Effect of PMAAN concentration on the sediment height of 20 wt % BaTiO_3 suspensions at $\text{pH} = 12$.

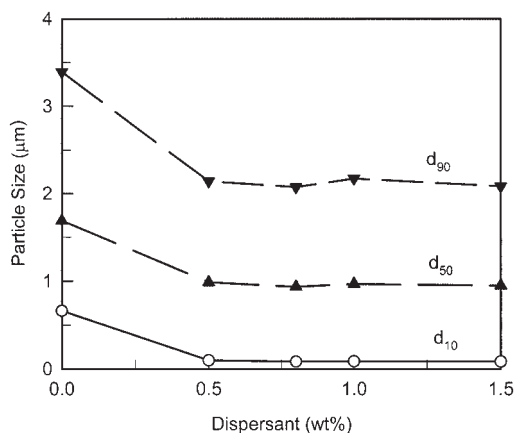


Figure 8 Effect of PAM/DAE concentration on the particle sizes in 20 wt % BaTiO₃ slurries.

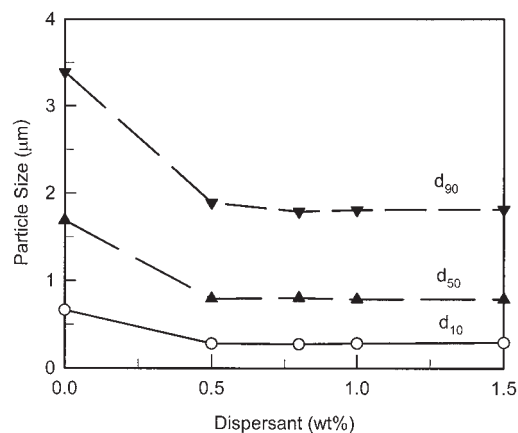


Figure 9 Effect of PMAAN concentration on the particle sizes in 20 wt % BaTiO₃ slurries.

sion becomes stable and remains cloudy for 30 days. Besides, a clear layer above the cloudy layer appeared in suspensions when the sedimentation time was more than 5 days. Different amounts of PAM/DAE cause only some changes on the thickness of the cloudy layer. Figure 7 shows the effect of PMAAN concentration on the sediment height of 20 wt % BaTiO₃ suspensions at pH = 12. When PMAAN was added, the stability of suspensions improved. The resulting suspensions become more stable and remained in a cloudy state longer if more PMAAN was incorporated. Nevertheless, the suspensions become unstable and separate into two layers when the sedimentation time is >20 days, even if the amount of added PMAAN reaches 1.5 wt %. This suggests that the prepared polymer is more effective than the commercial one in stabilizing BaTiO₃ particles in suspensions.

Particle size

Figure 8 shows the particle sizes of the barium titanate suspensions at different weight percentages of the dispersants. The d_{10} , d_{50} , and d_{90} particle sizes in the suspension, without the presence of dispersant, are 0.66, 1.7, and 3.4 μm , respectively. The average (d_{50}) particle size of powders in suspensions is greater than that from the supplier, as listed in Table I. The difference in particle size originates from powder agglomeration. The higher the extent of powder agglomerated, the greater the difference in particle size. When PAM/DAE was added to the suspension, the measured particle size decreased. The d_{10} , d_{50} , and d_{90} particle sizes show a quick decrease initially, reach minimum values, and then increase slightly afterward. The minimum (d_{10} , d_{50} , and d_{90}) values, which occur at a polymer concentration of about 0.8 wt %, are 0.085, 0.94, and 2.1 μm , respectively.

A similar trend in the variation of particle size of BaTiO₃ powder was observed in Figure 9 for suspen-

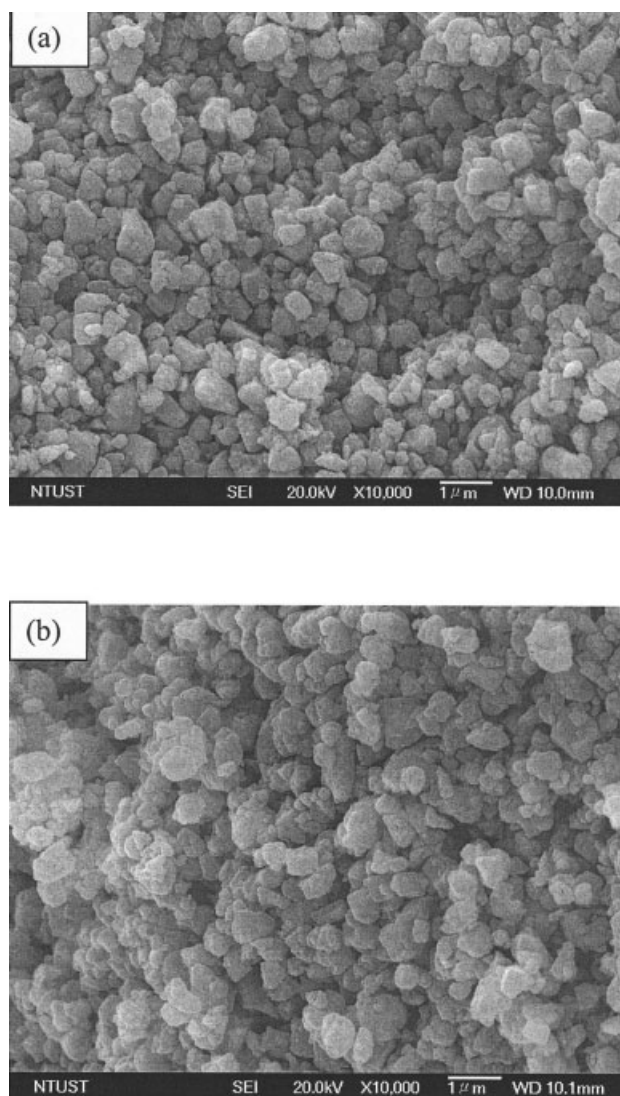


Figure 10 SEM micrographs of BaTiO₃ green compacts with 1.0 wt % (a) PAM/DAE, and (b) PMAAN.

sions with PMAAN present. The minimum (d_{10} , d_{50} , and d_{90}) values, which occur at a polymer concentration of about 0.5 wt %, are 0.27, 0.80, and 1.8 μm , respectively. Although the suspension with PAM/DAE contains slightly greater average (d_{50}) particle size of powder than that with PMAAN, the former consists of smaller d_{10} value (0.085 μm) than the latter (0.27 μm). Apparently, PAM/DAE provides a better dispersion than does PMAAN to the smaller size of barium titanate particles.

Because the particles in the barium titanate slurry incorporated with PAM/DAE contains smaller d_{10} particle size, the particles would be more densely packed. To confirm this, the microstructures of green compacts made from gravitational settlement and consolidation of 60 wt % BaTiO_3 suspensions were observed by a scanning electron microscope. Figure 10 shows SEM micrographs of BaTiO_3 green compact with the presence of 1.0 wt % dispersant. The compact with PAM/DAE dispersant appears to be less porous and particles are more uniformly dispersed than those with PMAAN. This proves that PAM/DAE is better than PMAAN in dispersing and packing BaTiO_3 particles.

CONCLUSIONS

In this study, an amphoteric water-soluble copolymer, PAM/DAE, was synthesized and the chemical structure verified by IR and $^1\text{H-NMR}$ spectra. Because PAM/DAE can uniformly disperse the BaTiO_3 particles, the resulting suspensions with this copolymer become less viscous and more stable, and the green compact is more consolidated. PAM/DAE was proved to be effective in dispersing and stabilizing BaTiO_3 particles in aqueous suspensions. The dispersing ability of this prepared polymer was found to be

close to, or slightly better than, that of the commercial dispersant Darvent C.

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