Synthesis and Application of an Anionic Water-Soluble Copolymer as a Dispersant for Barium Titanate Slurries

Lung-Pin Chen, Hsin-Hsuan Wu, Kung-Chung Hsu

Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan 116, Republic of China

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ABSTRACT: An anionic water-soluble copolymer, poly(acrylamide/4-carboxylamino-4-oxo-2-butenate) (PAAM/COB), was synthesized and used as a dispersion agent for $BaTiO_3$ particles. PAAM/COB was prepared from acrylamide and 4-carboxylamino-4-oxo-2-butenate in basic conditions through free-radical polymerization. The structure of this copolymer was verified by IR and ^{1}H-NMR spectra. We examined the dispersion effects of PAAM/COB by measuring the viscosity and sedimentation of $BaTiO_3$ suspensions and by analyzing the particle sizes. The results indicate that this copolymer was indeed effective in dispersing the particles, for the resulting suspensions were less viscous, more stabilized, and contained powder with smaller particle sizes.
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Key words: dispersions; polyelectrolytes; synthesis

INTRODUCTION

Water-soluble polymers have been applied in many areas, including adhesion, coatings, cosmetics, and water treatment.[1,2] In addition, they are used as dispersion agents or stabilizers in the preparation of stable ceramic slurries with solid particles dispersed uniformly. Consequently, ceramic green parts with a uniform microstructure and high packing density can be prepared, and sintered compacts with good qualities are achieved.[3,4]

These polymers, called *polyelectrolytes*, create electrostatic, steric, or electrosteric forces when they were adsorbed on ceramic particles.[4–7] As a result, the agglomerates are dissociated into primary particles, and the resulting suspensions become less viscous and more stable. Apparently, acrylic acid-based polymers are the most commonly used dispersants for ceramic powders. For example, Cesarano III and coworkers[5,6] showed that alumina suspensions could be stabilized with a sufficient amount of sodium salt of poly(methacrylic acid), ammonium salt of poly(methacrylic acid) (PMAAN), or poly(acrylic acid) (PAA). Chen et al.[7] and Jean and Wang[8] found that either PAA or PMAAN could stabilize the barium titanate slurries under certain pH conditions. De Laat and Van den Heuvel[9] reported that the molecular weight fraction of adsorbed PAA salts onto $BaTiO_3$ depended on the molecular weight distribution of dispersants. Shih and Hon[10] studied the stability of colloidal silicon nitride suspensions with PMAAN and concluded that conformation of the polymer chain along with the electrostatic interactions was the major factor in the determination of the stability of the slurries. Ramay and Zhang[11] revealed PMAAN was a suitable dispersant for aqueous hydroxyapatite slurries. Oliveira et al.[12] reported sodium polymethacrylate could disperse cement particles and reduce the viscosity of suspensions significantly. Mahdjoub et al.[13] constructed a stability map of highly concentrated zirconia suspensions with PAA.

Although acrylic acid-based polymers can provide good dispersion effects for most ceramic powders, new and more effective dispersants continue to be developed. For example, Baklouti et al.[14] examined sulfonic copolymer dispersants and determined the optimum conditions to ensure stable aluminum suspensions. Wang et al.[15] reported the dispersion effects on a sodium salt of poly(aspartic acid) at different pH's on barium titanate suspensions. Kirby et al.[16] studied the effects of a PAA–poly(ethylene oxide) comb polymer on the stability of aqueous $BaTiO_3$ nanoparticle suspensions. Their results indicate that the presence of poly(ethylene oxide) teeth enhanced the stability of the suspensions. In our laboratory, we prepared an amphoteric copolymer, polyacrylamide/(α-*N*,*N*-dimethyl-*N*-acryloyloxyethyl) ammonium ethanate, and showed that this polymer was more effective dispersant for aqueous $BaTiO_3$ suspensions than PMAAN.[17] In this study, we synthesized an anionic water-soluble copolymer, poly(acrylamide/4-carboxylamino-4-oxo-2-butenate) (PAAM/COB), as a

Correspondence to: K.-C. Hsu (kchsu@cc.ntnu.edu.tw).
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dispersant for barium titanate powder. Barium titanate was selected because it is an important electronic material widely used in making devices such as multilayer capacitors, communications filters, and piezoelectric sensors. PAAM/COB was prepared from acrylamide (AAM) and 4-carboxylamino-4-oxo-2-butenate (COB) through free-radical polymerization. The dispersing ability of this copolymer was examined from viscosity, sedimentation, and particle size measurements. In addition, a commercial dispersant, Darven C, was also tested for comparison.

EXPERIMENTAL

Materials

AAM, maleic anhydride, ammonium carbamate, potassium persulfate, and sodium thiosulfate, were used without further purification. PAAM/COB was prepared from the chemicals mentioned previously. The prepared PAAM/COB polymer had a fixed AAM/COB ratio of 10/1 and a weight-average molecular weight of 1.2×10^5. In addition, a commercial dispersant, Darven C, was also used for comparison. The chemical formula of Darven C is ammonium salt of poly(methacrylic acid) (PMAAN), which has a weight-average molecular weight of 1.3×10^4. The molecular weight of the PAAM/COB and PMAAN polymers were measured by gel permeation chromatography (GPC), as discussed later.

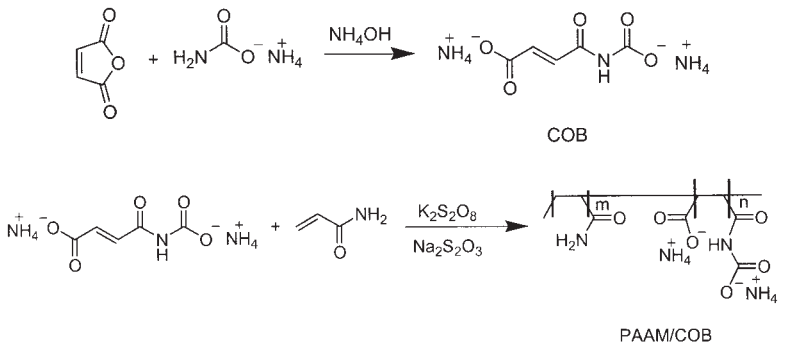
The ceramic powder used was a high-purity $BaTiO_3$ and was from Prosperity Dielectrics (Taoyuan, Taiwan). The powder had a Ba/Ti ratio of 1, an average particle size (d_{50}) of 0.46 μm, and a Brunauer–Emmett–Teller (BET) specific surface area of 4.53 m^2/g. Table I lists the characteristics of the $BaTiO_3$ powder. Deionized and distilled water was used, and the pH was adjusted by the addition of aqueous NaOH.

TABLE I
Basic Properties of $BaTiO_3$ Powder

Ba/Ti	1/1
Purity (%)	99.88
SrO (%)	0.022
Nb_2O_5 (%)	0.001
Al_2O_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

Preparation of the PAAM/COB resins

PAAM/COB was prepared from AAM and COB through free-radical polymerization. Potassium persulfate, together with sodium thiosulfate, was used as the initiator. COB was prepared from maleic anhydride and ammonium carbamate. The reaction equations for the preparation of COB and PAAM/COB are shown below:



COB and PAAM/COB were prepared as follows. Maleic anhydride (19.6 g) and ammonium carbamate (15.6 g) were dissolved in 80 g of acetone, and the mixture was added to a 250-mL stirred reactor. The reaction proceeded at 60°C for 2 h. The solvent was then removed by filtration. The filtered precipitate was washed with acetone twice and dried in a vacuum oven at room temperature for 1 day.

The dried precipitate was dissolved in 80 mL of deionized water and the pH of the solution was adjusted to 10 with 1*N* aqueous NH_4OH. The mixture was added to a 250-mL stirred reactor. The reaction proceeded at room temperature for 1 h. The solvent was then removed by filtration. The filtered precipitate was washed twice with acetone and dried in a vacuum oven at room temperature for 1 day. The dried precipitate was COB (18.6 g).

AAM (28.4 g) and COB (7.72 g) were dissolved in 144 mL of deionized water, and then, the mixture was added to a 250-mL stirred reactor. The reactor was purged with N_2 gas. Potassium persulfate (4.28 g) and sodium thiosulfate (0.856 g) were added to the reactor, and the polymerization was carried out at room temperature for 3 days, with the reactor sealed. After the

Figure 1 IR spectrum of COB.

reaction, the mixture was precipitated and purified with acetone. The acetone was removed in a vacuum oven at room temperature. The dried precipitate was a PAAM/COB resin (32 g).

Identification of the prepared resins

The dried COB and PAAM/COB resins were further ground into a powder before the determination of their structures or other procedures. In identifying the chemical structures, we mixed proper amounts of the powder samples with predried KBr and pressed them into disks. Transmission IR spectra of the disks were recorded with a PerkinElmer (Boston) Paragon 500 Fourier transform infrared spectrometer. Moreover, some powder samples were also dissolved in D_2O and analyzed with a Jeol (Tokyo) JNM-ECX 400 NMR spectrometer.

GPC measurements

The molecular weight of the dispersants was determined by a gel permeation chromatograph, which consisted of a Jasco (Tokyo) liquid chromatograph equipped with three coupled columns (Shodex OHpak KB802.5, KB804, and KB806), a pump (Jasco PU-980), and a refractive index detector (Jasco RI-930). The samples were analyzed with a 0.1*M* KCl/methanol (80/20) aqueous solution as the eluent at a flow rate of 1 mL/min. Monodispersed poly(styrene sulfonates) of different molecular weights (1600, 4000, 6500, and 16,000) were used as calibration standards.

Preparations of the $BaTiO_3$ suspensions

Aqueous suspensions (100 g) containing either 20 or 60 wt % $BaTiO_3$ were prepared. They contained 0–2.0 wt % dispersant with respect to the weight of dry $BaTiO_3$ powder. The suspensions were milled and mixed in a ceramic jar with a fixed number of zirconia balls for 24 h. The 24-h period of milling was believed long enough for a homogeneously dispersed state to be reached.

Viscosity measurements

The viscosity of 60 wt % $BaTiO_3$ aqueous suspensions at pH 12 with or without dispersants present was determined with a Brookfield (Middleboro, MA) LVDV-II viscometer with a #1 or #4 spindle at a rotation speed of 60 rpm.

Sedimentation tests

$BaTiO_3$ aqueous suspensions (20 wt %) at pH 12 with or without dispersants present were prepared and poured into 200-mL graduated cylinders. These suspensions were left in the cylinders for 30 days, and the change in sedimentation heights with time was measured and recorded.

Particle size measurements

$BaTiO_3$ aqueous suspensions (20 wt %) at pH 12 with or without dispersants present were prepared. After they were ball-milled, small slurries were taken. The particle size of the powder in the samples was determined with a Malvern (Worcestershire, UK) Mastersizer 2000 particle size analyzer.

Scanning electron microscopy (SEM) observations

The microstructures of $BaTiO_3$ green compacts with or without dispersants present were observed by a Jeol JSM-6300 scanning electron microscope.

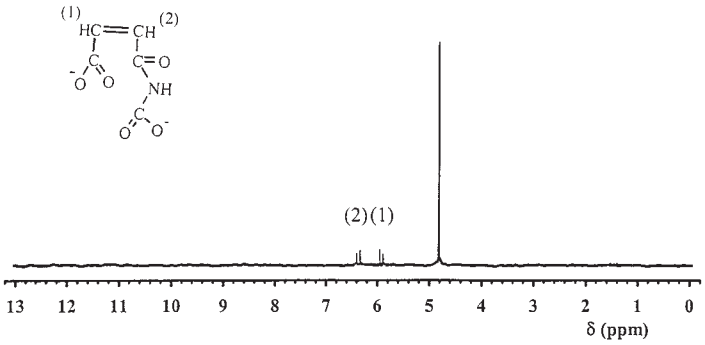


Figure 2 ^{1}H-NMR spectrum of COB.

RESULTS AND DISCUSSION

Structures of the prepared resins

The structures of typically prepared COB and PAAM/COB were verified from their IR and ^{1}H-NMR spectra, as shown in Figures 1–4, respectively. Figure 1 shows that the IR spectrum of COB displayed an N—H stretching band at 3200 cm^{-1}, a C═O stretching band overlapped with a C═C stretching band at 1676 cm^{-1}, and a N—H bending band at about 1560 cm^{-1}. The ^{1}H-NMR spectrum in Figure 2 gave signals at δ = 5.7–5.8 (1H) and 6.1–6.3 ppm (2H). Figure 3 shows that the IR spectrum of PAAM/COB displayed a N—H stretching band at about 3230 cm^{-1}, a C═O stretching band at 1705 cm^{-1}, and N—H bending bands at 1575 and at 1666 cm^{-1}. As shown in Figure 4, the ^{1}H-NMR spectrum gave signals at δ = 1.4–1.8 (1H) and 2.0–2.4 (2H). Clearly, the signals related to the protons in —CH═CH— at δ = 5.7–6.3 ppm in the spectrum in Figure 2 were not found in the spectrum in Figure 4, and new signals related to the protons in —CH—CH— at δ = 1.4–1.8 and 2.0–2.4 ppm appeared. This indicated the formation of a copolymer from its two monomers.[18–20]

Rheological behavior

Viscosity measurement is an appropriate way to evaluate the degree of powder dispersion in concentrated suspensions and the effectiveness of a dispersion agent.[13–17] Usually, powder agglomeration causes a concentrated suspension to become very viscous. The viscosity of a suspension can be decreased if a suitable dispersant is incorporated. The extent of the decrease in viscosity depends on the effectiveness of the dispersant in reducing the agglomerate size. Figure 5 shows the viscosity of the 60 wt % $BaTiO_3$ suspensions at pH 12 as a function of dispersant concentration. The viscosity of $BaTiO_3$ suspensions without dispersant was greater than 1000 mPa·s. The suspension became less viscous when PAAM/COB was incorporated, which indicates that this copolymer enhanced the dispersion of $BaTiO_3$ particles. As PAAM/COB concentration was increased, the viscosity of suspensions

Figure 3 IR spectrum of PAAM/COB.

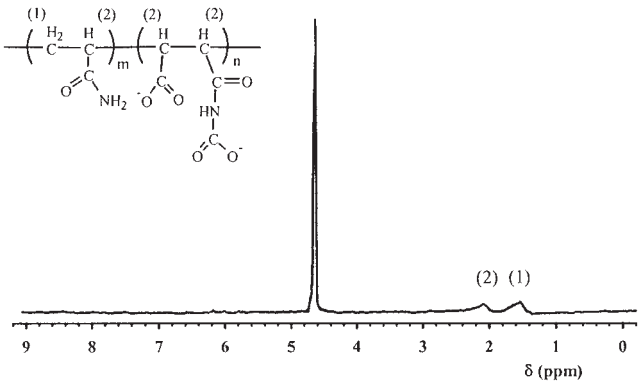


Figure 4 ^{1}H-NMR spectrum of PAAM/COB.

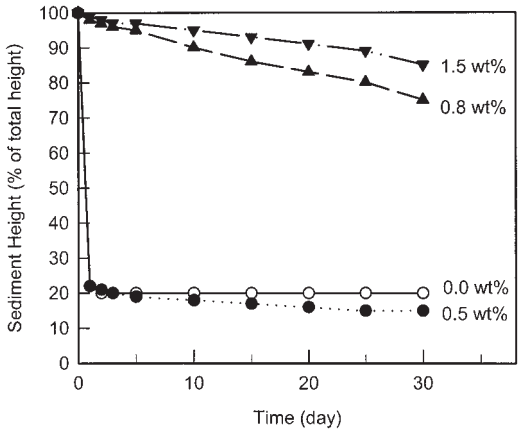


Figure 6 Effect of the PAAM/COB concentration on the sediment height of 20 wt % $BaTiO_3$ suspensions at pH 12.

decreased sharply at first, reached a minimum value, and then increased slightly. The amount that gave the lowest viscosity value was about 1.0 wt %. Similar rheological behavior was observed in Figure 5 for the $BaTiO_3$ suspension containing PMAAN. The amount of PMAAN required to achieve the lowest value was about 0.8 wt %, which was smaller than that of PAAM/COB. However, the achieved minimum viscosity values of the suspensions with either PMAAN or PAAM/COB were close to each other.

As mentioned previously, the 60 wt % $BaTiO_3$ suspensions containing either PAAM/COB or PMAAN showed similar rheological behaviors, and their viscosities were significantly lower than that without any dispersant present. This suggests that PAAM/COB, like PMAAN, was a good dispersant for $BaTiO_3$ powder. In fact, the dispersion mechanisms of these two polymers were expected to be similar to each other. Namely, both chemicals would cause mainly electrostatic repulsions when adsorbed on $BaTiO_3$ particles, for their molecules are anionic polyelectrolytes. However, PAAM/COB was expected to produce more steric effects than PMAAN because the former has a higher molecular weight and the molecules contain longer side chains.

Sedimentation

Sedimentation observation and measurement is another way to examine colloidal stability. A good dispersant will make suspensions remain cloudy and will result in a small final sediment height.[7,8] Figure 6 shows the sediment height of the 20 wt % $BaTiO_3$ suspensions with various amounts of PAAM/COB at pH 12. The sediment height refers to the percentage of the height of the dispersed particles relative to the initial height of the suspension. Suspensions without any dispersant present were not stable and separated into two layers after 1 day of sedimentation; a clear boundary existed between the sediment layer and the upper clear aqueous layer. When 0.5 wt % PAAM/COB was added, the resulting suspensions also separated into two layers after 1 day of sedimentation.

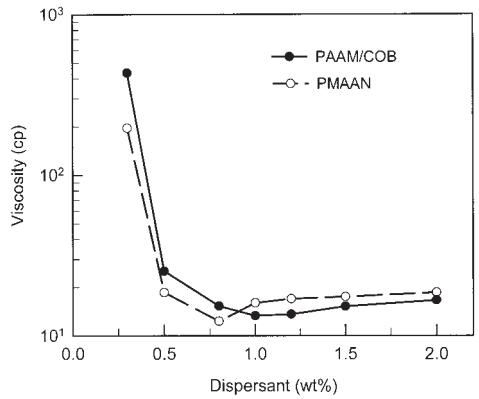


Figure 5 Effect of the dispersant concentration on the viscosity of 60 wt % $BaTiO_3$ suspensions at pH 12.

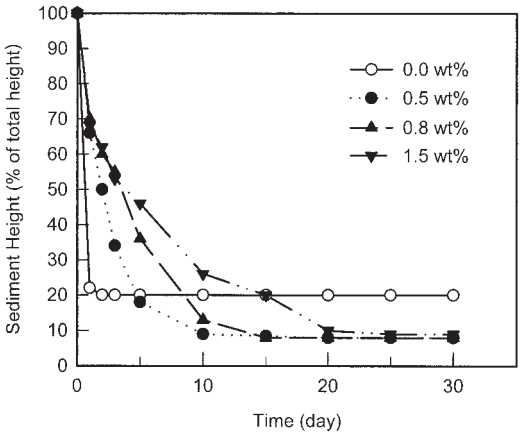


Figure 7 Effect of the PMAAN concentration on the sediment height of 20 wt % $BaTiO_3$ suspensions at pH 12.

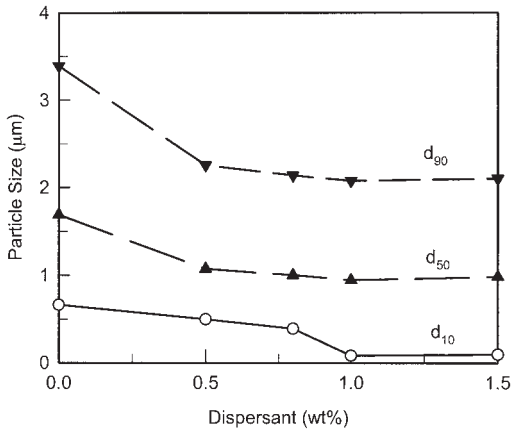


Figure 8 Effect of the PAAM/COB concentration on the particle sizes in 20 wt %$BaTiO_3$ slurries at pH 12.

However, the final sediment height was less than that of the $BaTiO_3$ suspension without any dispersant, which was an indication of the denser packing of particles. When the amount of incorporated PAAM/COB was greater than 0.8 wt %, the resulting suspension became stable and stayed cloudy for 30 days. In addition, a clear layer above the cloudy layer appeared in the suspensions when sedimentation time was greater than 5 days. Different amounts of PAAM/COB only caused some changes in the thickness of the cloudy layer. Figure 7 shows the effect of PMAAN concentration on the sediment height of the 20 wt % $BaTiO_3$ suspensions at pH 12. When PMAAN was added, the stability of the suspensions improved. The resulting suspensions became more stable and stayed in a cloudy state longer if more PMAAN was incorporated. Nevertheless, the suspensions became unstable and separated into two layers when the sedimentation time was more than 20 days, even when the amount of added PMAAN reached 1.5 wt %. This suggested the prepared polymer was more effective in

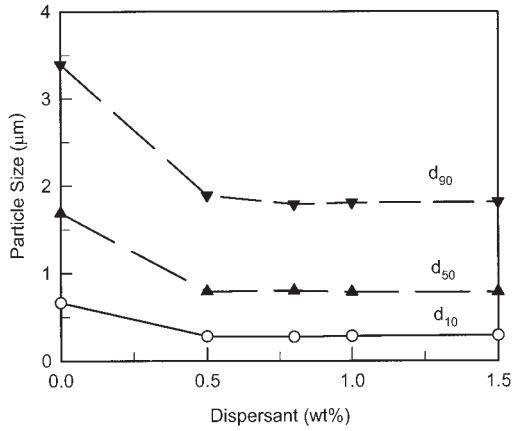
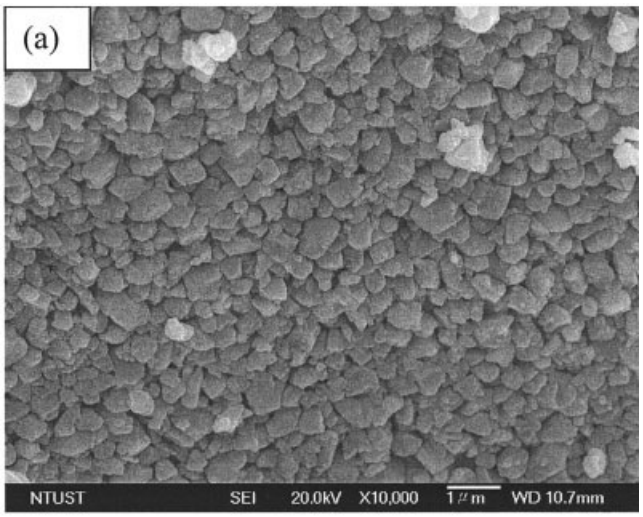


Figure 9 Effect of the PMAAN concentration on the particle sizes in 20 wt % $BaTiO_3$ slurries at pH 12.



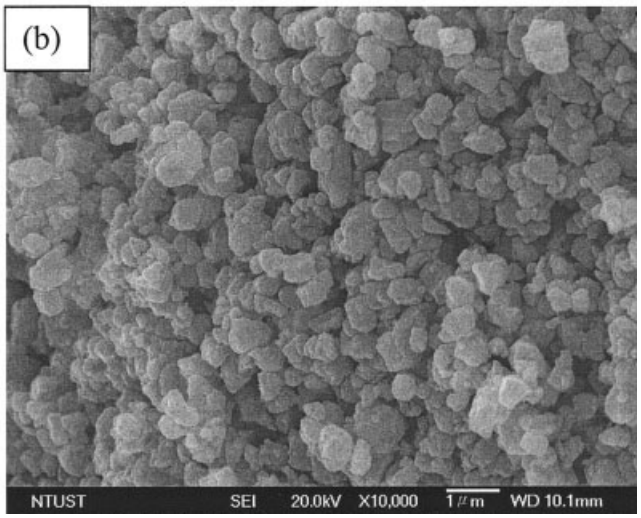


Figure 10 SEM micrographs of $BaTiO_3$ green compacts with 1.0 wt % (a) PAAM/COB and (b) PMAAN.

stabilizing $BaTiO_3$ particles in suspensions than the commercial one.

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 any presence of dispersant were 0.66, 1.7, and 3.4 μm, respectively. d_{10}, d_{50}, and d_{90}, are particle sizes corresponding to the cumulative weight fraction of $BaTiO_3$ powder of 10%, 50%, and 90%, finer than these sizes. d_{50} of the powders in suspension was greater than that from the supplier, as listed in Table I. The difference in particle size originates from powder agglomeration. The higher extent to which the powder is agglomerated, the greater the difference in particle size will be. When PAAM/COB was added to the

suspension, the measured particle size decreased. The d_{10}, d_{50}, and d_{90} particle sizes showed a quick decrease in the beginning, reached minimum values, and then increased slightly afterward. The minimum d_{10}, d_{50}, and d_{90} values occurred at a polymer concentration of about 1.0 wt %; the values were 0.085, 0.95, and 2.1 μm, respectively.

A similar trend in the variation of the particle sizes of $BaTiO_3$ powder was observed, as shown in Figure 9, for suspensions with PMAAN present. The minimum d_{10}, d_{50}, and d_{90} values occurred at a polymer concentration of about 0.5 wt %; the values were 0.27, 0.80, and 1.8 μm, respectively. Although the suspension with PAAM/COB contained a slightly greater d_{50} of powder than that with PMAAN, the former had a smaller d_{10} value (0.085 μm) than the latter (0.27 μm). Apparently, PAAM/COB provided a better dispersion to the smaller size barium titanate particles than PMAAN.

Because the particles in the barium titanate slurry incorporated with PAAM/COB had smaller d_{10} values, the particles were more densely packed. To confirm this, a scanning electron microscope was used to observe the microstructures of green compacts made from gravitational settlement and the consolidation of 60 wt % $BaTiO_3$ suspensions. Figure 10 shows the SEM micrographs of the $BaTiO_3$ green compacts with the presence of 1.0 wt % dispersant. The compact with PAAM/COB dispersant appeared to be less porous and the particles were more uniformly dispersed than those with PMAAN. This proved that PAAM/COB was better than PMAAN in dispersing and packing $BaTiO_3$ particles.

CONCLUSIONS

In this study, an anionic water-soluble copolymer, PAAM/COB, was synthesized and the chemical structure was verified by IR and ^{1}H-NMR spectra. As PAAM/COB could uniformly disperse the $BaTiO_3$ particles, the resulting suspensions with this copolymer became less viscous and more stable, and the green compacts were more consolidated. PAAM/COB was proven effective in dispersing and stabilizing $BaTiO_3$ particles in aqueous suspensions. The dispersing ability of this prepared polymer was close to or slightly better than the commercial dispersant, Darvent C.

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