An Amphoteric Water-Soluble Copolymer. II. Effect of Its Molecular Weight on the Dispersion of Barium Titanate in Water

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ABSTRACT: An amphoteric water-soluble copolymer, that is, polyacrylamide/(α-N,N-dimethyl-N-acryloyloxyethyl)-ammonium ethanate (PAAM/DAAE) was synthesized and it showed the ability to disperse BaTiO$_3$ (BT) particles in aqueous solutions. In this work, the effect of molecular weight of this polymer on the dispersing properties was further examined. The results indicate that the effectiveness of three polymer samples with different molecular weights in the dispersion of BT particles is P2 ($M_w = 1.1 \times 10^5$) > P1 ($M_w = 1.2 \times 10^4$) > P3 ($M_w = 3.0 \times 10^5$). Apparently, P2 is most effective in dispersing the particles, reducing the viscosity of the suspensions, and obtaining highest green and sintered densities. This is attributed to the highest adsorption of this polymer onto BT powder, and causes strongest electrostatic and steric repulsions. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 886–891, 2006

Key words: PAAM/DAAE; molecular weight; dispersion; adsorption; BaTiO$_3$

INTRODUCTION

Water-soluble polymers have been applied in many areas, such as mineral-processing, water treatment, or coatings.[1,2] Another important area of application is the wet processing of ceramic powder.[3,4] These polymers, called polymeric surfactants or polyelectrolytes, have often been used as dispersants or stabilizers. Their roles are mainly 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 a high packing density can be prepared, and sintered compacts without defects or pores can be obtained.

The dispersing mechanism of these polymeric surfactants is that, after being adsorbed onto ceramic particles, they create electrostatic, steric, or electrosteric forces.[4–7] This results in the dissociation of the agglomerates into primary particles with a significant decrease in the viscosity and a stable cloudy state of suspensions. Among commercial dispersants, acrylic acid-based polyelectrolytes are commonly used and reported to be effective for ceramic powders such as barium titanate, alumina, zirconia, and silicon nitride.[5–12]

It is clear that dispersant is an essential chemical in the processing of ceramic slurries. Therefore, new and more effective dispersants are worth developing. Previously, we have synthesized an amphoteric water-soluble copolymer as a dispersant for barium titanate powder. The synthesized copolymer is poly acrylamide/(α-N,N-dimethyl-N-acryloyloxyethyl)ammojnium ethanate (PAAM/DAAE), which was prepared from acrylamide (AAM) and (α-N,N-dimethyl-N-acryloyloxyethyl)ammonium ethanate (DAAE) through a free-radical polymerization. PAAM/DAAE was found to be capable of dispersing the BaTiO$_3$ (BT) particles, and apparently even more effective than the commercial dispersant, ammonium salt of poly-(methacrylic acid).[13] It is well recognized that the molecular weight of the polymeric dispersant is an influential factor in governing the dispersing properties of the resulting ceramic slurries.[10,14] In this work, the effect of molecular weight of PAAM/DAAE on the dispersion of BT colloids is examined and discussed.

EXPERIMENTAL

Materials

AAM, 2-dimethylamino ethylacrylate, and sodium chloroacetate were used without further purification. PAAM/DAAE was prepared from chemicals mentioned earlier. The prepared PAAM/DAAE samples

TABLE I
Basic Properties of the BaTiO$_3$ Powder

Ba/Ti	1/1
Purity (%)	99.76
SrO (%)	0.0667
Nb$_2$O$_5$ (%)	0.008
Al$_2$O$_3$ (%)	0.0428
SiO$_2$ (%)	0.0152
Median particle size (μm)	0.9
Moisture (%)	0.16
Ignition loss (%)	0.23
Compressed density (g/cm^3)	3.269
BET specific surface area (m^2/g)	2.45

TABLE II
Molecular Weights of PAAM/DAAE Samples

Polymer	M_w	M_n
P1	1.2×10^4	3.5×10^3
P2	1.1×10^5	2.1×10^4
P3	3.0×10^5	6.0×10^4

have a fixed AAM/DAAE ratio of 10/1 and different molecular weights.

The ceramic powder used was high purity BT from Prosperity Dielectrics (Taoyuan, Taiwan). The powder had a Ba/Ti ratio of 1/1, a median size of 0.9 μm, and a Brunauer-Emmett-Teller (BET) specific surface area of 2.45 m^2/g. Table I lists the basic properties of the BT powder. Deionized and distilled water was used, and the pH was adjusted to 12 by the addition of aqueous NaOH.

Preparations of the PAAM/DAAE samples

PAAM/DAAE was prepared from AAM and DAAE through a free-radical polymerization. Ammonium persulfate and sodium thiosulfate were used as the initiator. Details of the preparation procedure were described elsewhere.[13] Figure 1 shows the chemical structure of PAAM/DAAE. In this study, polymer samples with an AAM/DAAE ratio of 10/1 and different molecular weights were prepared and tested. The molecular weights of polymer samples were obtained by varying the initiator concentration and are listed in Table II. The molecular weight of polymer was determined by gel permeation chromatography, as described elsewhere.[13]

Preparations of BT suspensions

Aqueous suspensions (100 g) containing either 22.7 wt % (5 vol %) or 60 wt % BT were prepared. They contained 0–4.8 wt % dispersant with respect to the weight of the dry BT powder. The suspensions were milled and mixed in a ceramic jar with a fixed number
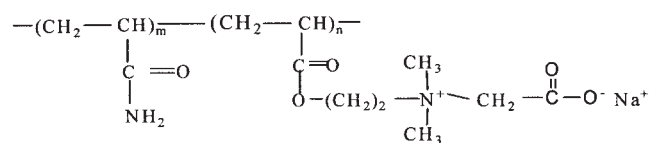
of zirconia balls for 24 h. The 24-h time period of milling is believed to be long enough for a homogeneously dispersed state to be reached.

Viscosity measurements

The viscosity of 60 wt % BT aqueous suspensions at pH 12, with or without dispersants present, was determined with a Brookfield DV-II viscometer (Middleboro, MA). For a typical viscosity measurement, the cup-spindle assembly was mounted securely and leveled on a laboratory stand. The viscometer was zeroed first and then the spindle was attached (no. 1 or 4) to the lower shaft. About 150 g BT suspensions was put in the sample cup. The spindle was inserted into the test sample concentric to the cup. The spindle was placed in such a way that the level of the sample was at the immersion groove in the spindle's shaft. The viscosity measurement was started and data collected at room temperature with different shear rates by changing the rotation speed of the spindle.

Particle size measurements

BT aqueous suspensions (5 vol %) at pH 12 with or without dispersants present were prepared. After 24-h ball-milling and mixing, the particle size of BT particles in aqueous slurries was determined with a Mastersizer 2000 particle size analyzer (Malvern, Worcestershire, UK).

Compact density measurements

Green compacts were made from the gravitational settlement and consolidation of 60 wt % BT suspensions with or without the presence of dispersants. Some sintered compacts were made from green parts. Sintering was carried out in air, with heating and cooling rate of 10°C/min and 6 h soaking time at 1280°C. Both the green density and sintered density of compacts were determined by the Archimede's method.

Figure 1 Chemical structure of PAAM/DAAE.

Adsorption measurements

BT aqueous suspensions (5 vol %) with different concentration of PAAM/DAAE were prepared at pH 12. After 24-h ball-milling and mixing, the suspensions
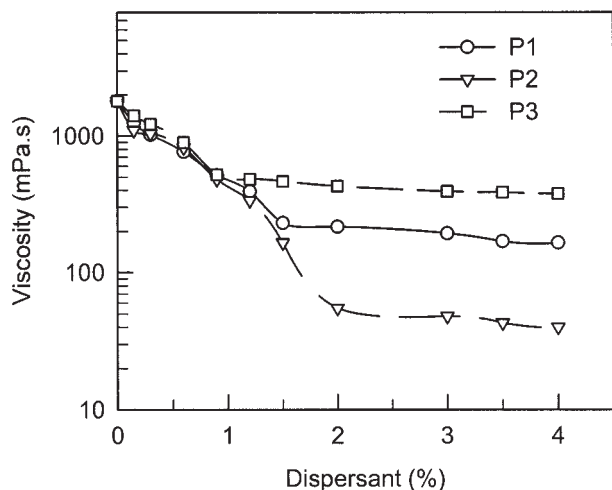
Figure 2 Viscosity of 60 wt % BT suspensions containing PAAM/DAAE with different molecular weights at various polymer concentrations at pH 12.

were centrifuged at a speed of 1×10^4 rpm for 15 min to obtain supernatants. The residual dispersant concentration in the supernatants was analyzed and determined by a titration procedure from the literature.[8] The amount of dispersant adsorbed on BT was calculated from the difference in the dispersant concentration before and after adsorption.

ζ-potential measurements

BT aqueous suspensions (5 vol %) at pH 12, with or without dispersants present, were prepared. After ball-milling and centrifugation, a small amount of supernatant was taken. The ζ potential of remaining powders in the supernatant was measured with a PenKem Laser ZeeMeter Model 501. (Bedford Hills, NY)

RESULTS

Rheological behavior

For concentrated suspensions, viscosity measurement is an appropriate way to evaluate their dispersed extent and the effectiveness of the added dispersant.[13] Figure 2 shows the viscosity of 60 wt % BT suspensions containing PAAM/DAAE with different molecular weights at pH 12, as a function of polymer concentration. Generally, the viscosity of suspensions depends on the viscosity of polymer solutions and the volume fraction of solid particles. When polymer concentration increases, the resulting suspensions are expected to be more viscous. However, the viscosity of suspensions could be decreased if the added polymer is able to disperse particles. As shown in Figure 2, the viscosity of BT suspensions without any dispersant is

about 2000 mPa s. The ceramic suspension becomes less viscous when PAAM/DAAE is incorporated, indicating that PAAM/DAAE indeed can enhance the dispersion of BT particles. Along with increasing polymer concentration, the viscosity was found to decrease first, and then reach a plateau. The critical optimum dispersant concentration, that is, the amount that gives the lowest viscosity, is about 0.5–1.5 wt %, depending on the molecular weight of the dispersant. Apparently, P2 ($M_w = 1.1 \times 10^5$) is more effective than either P1 ($M_w = 1.2 \times 10^4$) or P3 ($M_w = 3.0 \times 10^5$), for the resulting BT suspensions containing the former become less viscous.

Particle size

The measurement of particle size in ceramic slurry is another way to determine colloidal stability and examine the effectiveness of the incorporated dispersant. A good dispersant will stabilize suspensions with less agglomeration or segregation and result in a small particle size. Figure 3 shows the median (d_{50}) particle size of 5 vol % BT suspensions, with various amounts of PAAM/DAAE of different molecular weights. For suspensions without any dispersant present, the d_{50} value of the BT slurry after 24-h ball-milling and mixing was 2.5 μm, which is much greater than the true median particle size (0.9 μm) provided by the supplier. This indicates that particles in the slurry are not stable and agglomerate with each other. When PAAM/DAAE was added, the resulting suspensions became more stable and particle size shifted to smaller value. Different molecular weight of PAAM/DAAE causes different degree of shift in particle size. Again, polymer with P2 appears to be more effective than P1
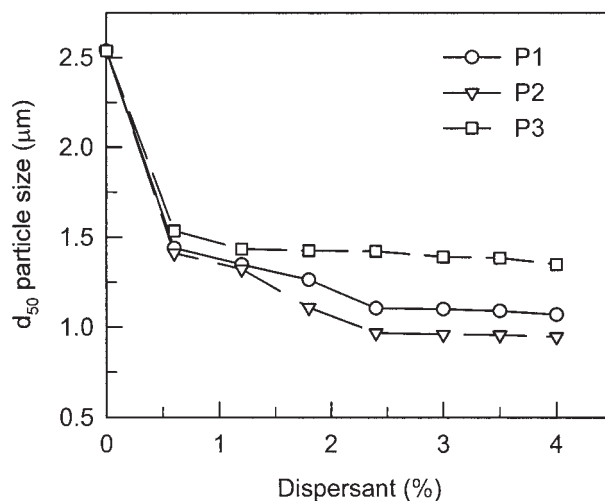

Figure 3 d_{50} value of 5 vol % BT suspensions with various amounts of PAAM/DAAE of different molecular weights at pH 12.
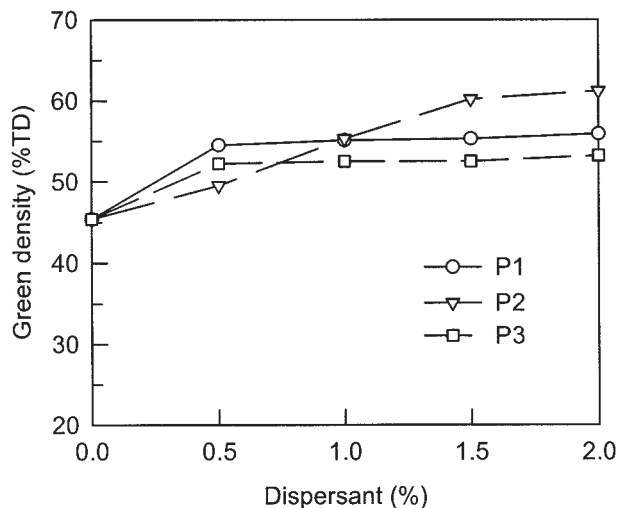
Figure 4 Relative green density of the BT compact with various amounts of PAAM/DAAE of different molecular weights.

Figure 5 Relative sintered density of the BT compact with various amounts of PAAM/DAAE of different molecular weights.

and P3, as the d_{50} value of BT suspensions including the former is lower.

Compact density

The relative green density of the powder compact obtained from gravitation, sedimentation, and consolidation of the suspension is shown in Figure 4. For BT compacts without any dispersant, the green density is 45.4% theoretical density (TD). The density value increased when PAAM/DAAE was incorporated in the compact. Furthermore, the value increased with increasing polymer concentration up to a maximum value. As expected, the molecular weight of added dispersant affects the green density of the resulting compact. Compacts containing P2 show the higher green density than those containing polymer with the other two molecular weights, confirming that the former generates better packing efficiency than the latter. Figure 5 shows the relative sintered density of the BT compact with various amounts of PAAM/DAAE of different molecular weights. The effects of polymer concentration and molecular weight on the sintered density of BT compacts are similar to those in Figure 4. This proves that P2 is the most effective in dispersing BT particles.

DISCUSSION

The previous results indicate that PAAM/DAAE could disperse BT particles so that the resulting suspensions become less viscous and the particles are less agglomerated. As a result, BT compacts with the prepared polymer show higher packing efficiency, and gre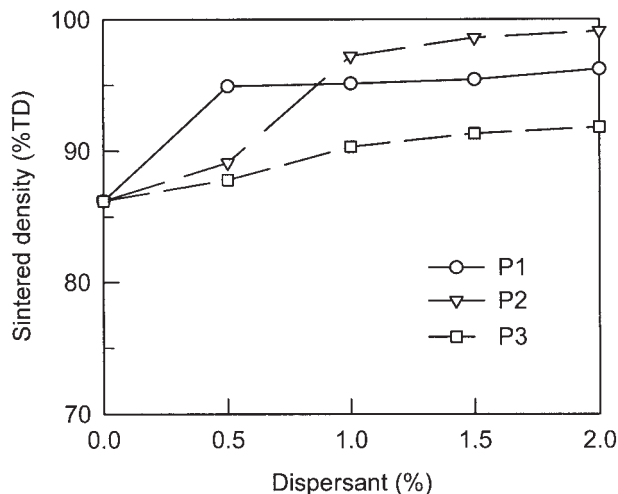ater green and sintered densities. Polymer with different molecular weight exhibits different effects on the dispersion of solid particles. This could be explained by the adsorption behavior of PAAM/DAAE onto BT particles.

The adsorption behavior of PAAM/DAAE with different molecular weights onto the surface of BT powder was studied. Figure 6 shows the adsorption amount of polymer on the BT surface in aqueous suspensions (pH 12), at different initial polymer concentrations. For all tested polymer samples, Figure 6 shows that the amount of adsorbed polymer increases with dispersant concentration initially, and then reaches a characteristic plateau. The plateau corresponds to the saturated amount of polymer (C_m) required for a monolayer coverage.
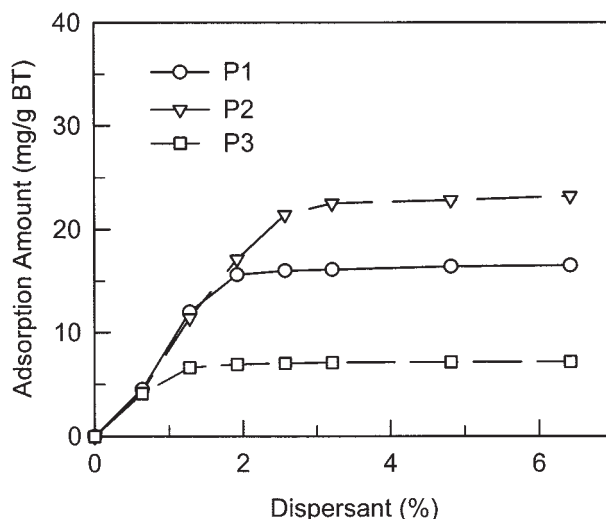

Figure 6 Adsorption amount of PAAM/DAAE with different molecular weights on the BT surface in aqueous suspensions at pH 12.
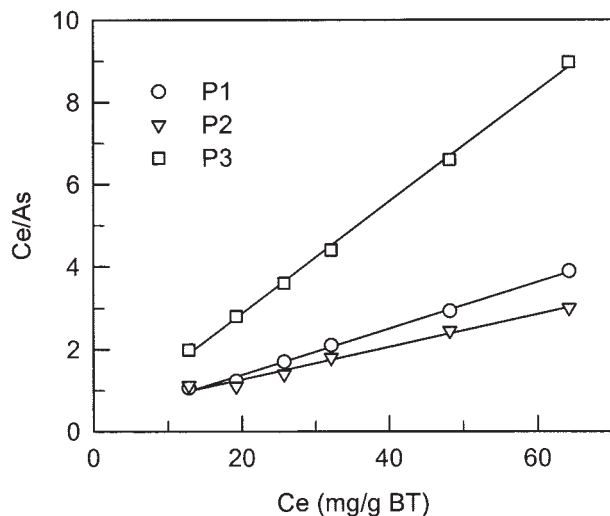
Figure 7 Relationship of C_e/A_s and C_e for PAAM/DAAE with three different molecular weights.

Alternatively, the saturated amount of dispersant can be determined using the following Langmuir adsorption equation:[8]

$$C_e/A_s = C_e/C_m + 1/(K\ C_m) \qquad (1)$$

where C_e is the equilibrium concentration of polymer in solution expressed in mg/g BT. C_m is the saturated amount of adsorbed polymer expressed in mg/g BT. A_s is the amount of adsorbed polymer expressed in mg/g BT, and K is an adsorption constant. Figure 7 shows the relationship of C_e/A_s and C_e for PAAM/DAAE with three different M_ws. A linear relationship was observed for each curve in Figure 7, indicating the adsorption behavior of PAAM/DAAE follows the Langmuir adsorption model, and only a monolayer of polymer molecules was adsorbed on BT particles. From the slope of each line in Figure 7, C_m could be determined. Table III summarizes the results. It is clear that the C_m values determined from Figure 6 and those from the Langmuir adsorption equation are close to each other. The C_m values are 17.2, 24.2, and 7.3 mg/g of BT for P1, P2, and P3, respectively. Clearly P2 ($M_w = 1.1 \times 10^5$) was more adsorbed than P1 and P3.

The adsorption of polymer is related to the interaction between BT surface and polymer functional groups. At pH 12, the particle surface should be negative because the isoelectric point is about 5.6; the PAAM/DAAE molecules are completely dissociated, and contain two ionic groups ($-N^+(CH_3)_2-$, $-COO^-$) and one polar group ($-NH_2$).[15] PAAM/DAAE adsorption onto BT surface is mainly due to the attraction between the positive groups $-N^+(CH_3)_2-$ and the negative sites of ceramic surface. A similar result was indicated by Walter et al. in investigating the adsorption of the ampholytic diblock copolymer poly(methacrylic acid)-block-poly(dimethylamino)-ethyl methacrylate) on silicon substrates from dilute aqueous solution. They reported that a polyampholyte containing both positive and negative charges would lead to a strong attractive interaction between different chains. Still, ionic bonds between positively charged groups of the polyampholyte and the negatively surface can be formed, which results in the adsorption in a dense conformation with a highly adsorbed amount.[16]

The influence of molecular weight of PAAM/DAAE on the saturated amount of adsorbed polymer is indicated in Table III. Increase of M_w of the dispersant will increase the C_m value, reach a maximum value, and then decrease afterwards. For PAAM/DAAE with low molecular weight, the adsorbed chains tend to develop a train structure. In contrast, the conformation of adsorbed polymer with high molecular weight would be more likely to form loops, as more unadsorbed functional groups remain and extend away from the particle surface. These phenomena have been reported in other systems as well.[17,18]

Separately, for a lower molecular-weight polymer molecule, fewer segments are available for the polymer to be adsorbed onto particles. Furthermore, the adsorbed polymer molecules would have a chance to be desorbed or displaced in the colloids than those of higher molecular weight. The adsorption tends to be reversible. On the contrary, for a higher molecular-weight polymer molecule, there are more points of attachment of the adsorbed polymer onto particles. Although each polymer segment may be adsorbed reversibly, the probability of all adsorbed segments in a given polymer molecule being desorbed simultaneously will be very small. As a result, the adsorption tends to be irreversible, and the adsorption amount increases with molecular weight.[10,19,20] However, there exists a critical molecular weight. For the polymer having molecular weight greater than the critical value, the adsorption amount on solid particles would be decreased, as a large size of polymeric molecules leads to a big geometric constraint to prevent this chemical from anchoring on the power surface.[17,21] For PAAM/DAAE adsorbed on BT particles, the critical Mw is about 1.1×10^5.

As shown in Figure 1, PAAM/DAAE molecules contain COO^- groups, and would cause electrostatic

TABLE III
Adsorption Amount of PAAM/DAAE

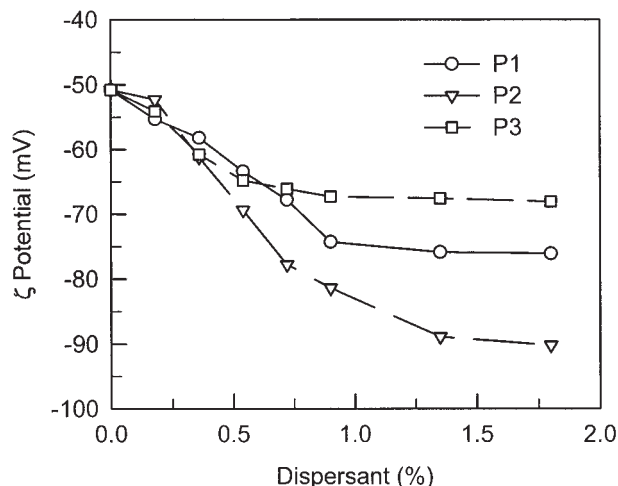| Polymer	C_m (experimental, mg/g BT)	C_m (calculated from eq. (1), mg/g BT)
P1	16.5	17.8
P2	23.2	25.2
P3	7.15	7.38

Figure 8 Effect of PAAM/DAAE concentration on the ζ potential of 5 vol % BT suspensions at pH 12.

repulsions when adsorbed on BT particles. Except for electrostatic repulsion, this adsorbed dispersant would also generate some steric repulsion, as the polymer molecules have side chains linked to the backbones. Figure 8 shows the effect of dispersant concentration on the ζ potential of 5 vol % BT suspensions at pH 12. The ζ potential of suspensions without dispersant is –50.8 mV. The potential value becomes more negative when PAAM/DAAE was present in the suspensions. It has been reported[7,22] that a minimum ζ potential of 50 mV is required to have sufficient electrostatic repulsions between ceramic particles and to achieve stable suspensions. Results in Figure 8 indicate that the BT suspension without any dispersant present would be relatively stable at pH 12, since its ζ potential is about 50 mV in absolute value. Along with increasing PAAM/DAAE concentration, the BT suspensions become more stable, because the ζ potential is more negative. As the adsorption amount of P2 on BT particles is more than P1 and P3, the ζ potential becomes more negative and induces more electrostatic repulsions. Consequently, PAAM/DAAE with $M_w =$ 1.1×10^5 is more effective in dispersing BT particles, the resulting suspensions become less viscous, and BT compacts show greater green and sintered densities than the other ones with different molecular weight.

CONCLUSIONS

In this study, an amphoteric water-soluble copolymer, that is, PAAM/DAAE, was synthesized. As this co-

polymer could uniformly disperse the BT particles, the resulting suspensions become less viscous and contain less agglomerated particles, and the resulting compacts are more consolidated and show higher green and sintered densities. Among three PAAM/DAAE samples, P2 ($M_w = 1.1 \times 10^5$) appears to be more effective than P1 ($M_w = 1.2 \times 10^4$) and P3 ($M_w = 3.0 \times 10^5$) in dispersing BT particles, for its adsorption amount on the particles is higher, causing stronger electrostatic and steric repulsions.

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