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Dispersion properties of $BaTi_4O_9/Ba_2Ti_9O_{20}$ colloids with amphoteric polyelectrolytes

Chin-Hao Chen, Kung-Chung Hsu *

Department of Chemistry, National Taiwan Normal University, Taipei 116, Taiwan, ROC

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 $BaTi_4O_9/Ba_2Ti_9O_{20}$ (BT_4/B_2T_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 BT_4/B_2T_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.

Keyword: Amphoteric copolymer; $BaTiO_3$ and titanates; Suspensions

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 Wang[6] found that either PAA or $PMAA–NH_4$ could stabilize BT slurries under certain pH conditions. Shih and Hon[15] 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 $pH < 7$.[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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* Corresponding author. Tel.: +886 2 29309088; fax: +886 2 29324249.
E-mail address: kchsu@ntnu.edu.tw (K.-C. Hsu).

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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 BT_4/B_2T_9 powder. This copolymer is PAM/DAE.[25] The dispersing effects of PAM/DAE on viscosity, and particle size of BT_4/B_2T_9 suspensions were examined. In addition, the concentration of Ba^{2+} leached from the particles was also measured. The results were compared with those of a commercial dispersant, $PMAA–NH_4$.

2. Experimental

2.1. Materials

A BT_4/B_2T_9 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 m^2/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) ($PMAA–NH_4$) with $M_w = 1.5 \times 10^4$, which was used for comparison. The molecular weight of PAM/DAE and $PMAA–NH_4$ polymers were measured by the GPC mentioned elsewhere.[24] Fig. 1 shows the chemical structures of these two polymers.

2.2. Preparations of BT_4/B_2T_9 suspensions

Aqueous suspensions containing either 20 or 60 wt.% BT_4/B_2T_9 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

BT_4/B_2T_9 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

BT_4/B_2T_9 20 wt.% suspensions with either PAM/DAE or $PMAA–NH_4$ 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 BT_4/B_2T_9 was calculated from the difference in dispersant concentration before and after adsorption.

2.6. Viscosity measurements

The viscosity of 60 wt.% BT_4/B_2T_9 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

BT_4/B_2T_9 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. Ba^{2+} concentration measurements

BT_4/B_2T_9 20 wt.% suspensions with or without dispersants present were prepared. After being mixed and centrifuged, a small amount of supernatant was taken and the Ba^{2+} 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

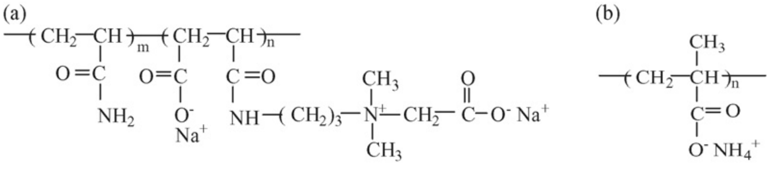

Fig. 1. Chemical structures of (a) PAM/DAE and (b) $PMAA–NH_4$ polymers.

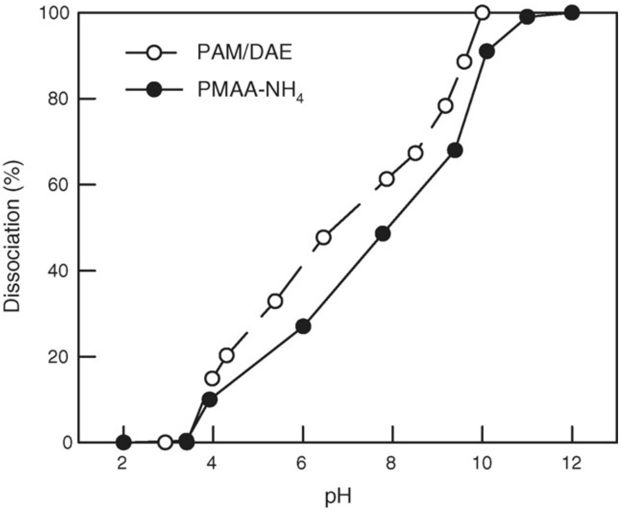

Fig. 2. Percent dissociation of dispersant molecules as a function of pH.

(–CONH$_2$) in the structural unit. Among these three groups, only the carboxyl group will dissociate in an aqueous solution. Fig. 2 shows the percent dissociation of carboxyl groups in dispersant molecules as a function of pH. The PAM/DAE molecule was found to be unassociated at pH < 3. It starts to dissociate at pH > 3, and becomes more dissociated at higher pH value. At pH > 9, the polymeric molecule is dissociated completely and become amphoteric.

Similarly, the PMAA–NH$_4$ molecule will not dissociate at pH < 2. The carboxyl group begins to dissociate at higher pH value, and the percent dissociation increases with pH. At pH > 11, the polymeric molecule is totally dissociated, and becomes anionic. This result agrees well with that reported previously.[6] Although the dissociation behaviors of these two dispersants appear to be similar, their dissociation degree at a given pH value differs slightly, for these two chemicals have different molecular weights and contain different functional groups in the structure.

3.2. Zeta potential of BT$_4$/B$_2$T$_9$ particles in suspensions

Fig. 3 shows the zeta potential of particles in 20 wt.% BT$_4$/B$_2$T$_9$ suspensions as a function of pH. The surface charge or zeta potential of particles is positive at low pH values, and becomes negative at high pH values. The isoelectric point occurs at about pH 5.3. In Fig. 4 the zeta potential of particles in 20 wt.% BT$_4$/B$_2$T$_9$ suspensions with dispersants at pH 9 is shown. Incorporation of dispersant causes a decrease of zeta potential as a consequence of the adsorption of the anionic polymer on the particle surface. In general, the zeta potential decreases first with increasing polymer concentration, and then reaches a plateau. The critical polymer concentration for PAM/DAE is about 1 wt.%, which is greater than that for PMAA–NH$_4$. Nevertheless, the zeta potential at plateau for suspensions with either dispersant is close to each other.

At lower dispersant additions, the zeta potential of the PAM/DAE suspension is less negative than that of the PMAA–NH$_4$ suspension. At pH 9, the PAM/DAE molecule is totally dissociated, contains both anionic (COO$^-$) and cationic (–N$^+$) groups, and becomes amphoteric. Furthermore, the prepared PAM/DAE is a copolymer with an AAM (polar unit)/DAE (ionic unit) ratio of 5/1. The ionic unit only accounts for about 17% of the polymeric molecule. In contrast, the PMAA–NH$_4$ molecule becomes anionic and contains 50% ionic group. This explains why this dispersant, after adsorbed on solid particles, induces more negative charges than another one.

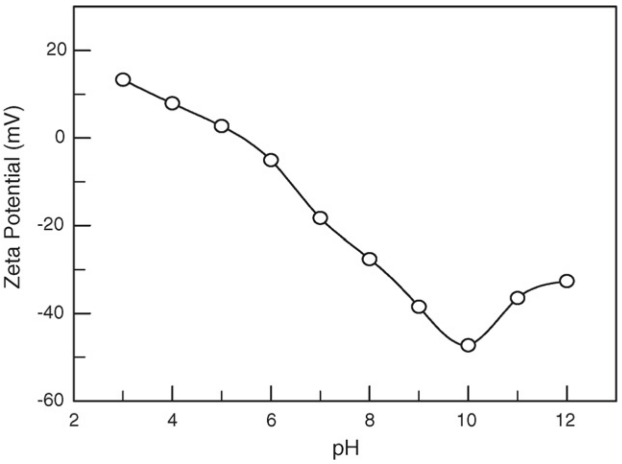

Fig. 3. Zeta potential of 20 wt.% BT$_4$/B$_2$T$_9$ suspensions at various pH values.

3.3. Adsorption of dispersants onto BT$_4$/B$_2$T$_9$ particles in suspensions

Fig. 5 shows the amount of these two dispersants adsorbed onto BT$_4$/B$_2$T$_9$ particles as a function of the initial dispersant concentration at pH 9. In general, the amount adsorbed increases quickly with dispersant concentration, and then reaches a plateau. The value at the plateau accounts for the amount of polymers required for the formation of monolayer on the particle surface. This value is about 3.0 mg/g with respect to the BT$_4$/B$_2$T$_9$ powder, which is about three times greater than that for PMAA–NH$_4$ (=1.1 mg/g BT$_4$/B$_2$T$_9$).

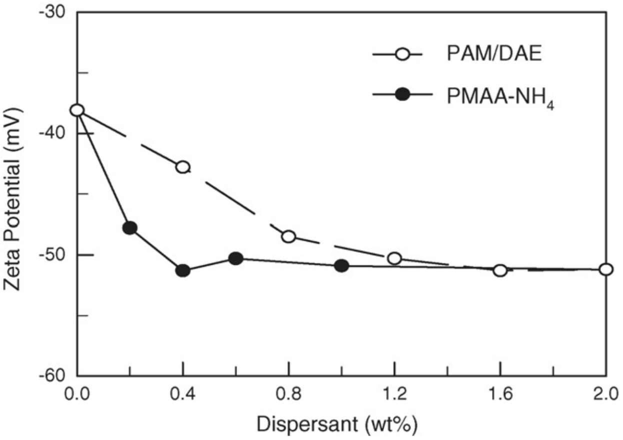

Fig. 4. Effect of dispersant concentration on the zeta potential of 20 wt.% BT$_4$/B$_2$T$_9$ suspensions at pH 9.

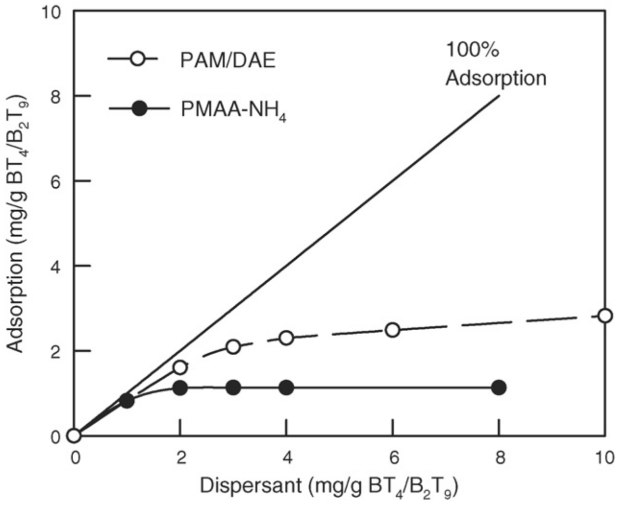

Fig. 5. Adsorption amount of dispersants as a function of the initial dispersant concentration at pH 9.

The reason for the difference in adsorbed amount of polymers is attributed to the different chemical natures of these two dispersants. At pH 9, the surface charge of particles is negative, which is difficult for the adsorption of negatively charged PMAA–NH$_4$ molecules onto the particle surface when they are completely dissociated. On the contrary, PAM/DAE molecules become amphoteric in a basic solution. Their cationic groups ($-N^+$) would favor themselves to be adsorbed onto BT$_4$/B$_2$T$_9$ surface. In addition, the amide functional group ($-CONH_2$) in the structural unit could also interact with the particle surface by hydrogen bonding and enhance the adsorption.

Furthermore, the adsorption of PMAA–NH$_4$ molecules onto BT$_4$/B$_2$T$_9$ particles would be in a relatively flat conformation, as it was reported that polyacrylate molecules become stretched and expanded when they are totally dissociated.[7] In contrast, the adsorbed PAM/DAE molecules would be more coiled in the structure, and the adsorbed layer is thicker. Accordingly, the adsorbed amount of the copolymer is greater than that of another polymer.

3.4. Rheological behavior of BT$_4$/B$_2$T$_9$ suspensions

Fig. 6 shows the effect of dispersant concentration on the viscosity of 60 wt.% BT$_4$/B$_2$T$_9$ suspensions. The viscosity of suspensions without dispersant is about 3.7 Pa·s. The value becomes less when PAM/DAE is incorporated. As PAM/DAE concentration is increased, the viscosity of suspensions first decreases, and then reaches a plateau at dispersant concentration of about 0.8 wt.%. This result indicates that the amount required for monolayer coverage of PAM/DAE from the zeta potential and adsorption measurements correlate well with the amount required to attain the minimum viscosity. In contrast, the viscosity of suspensions is decreased rather sharply with PMAA–NH$_4$ concentration, and then reaches a minimum value at dispersant concentration of about 0.4 wt.%.

Compared with PMAA–NH$_4$, PAM/DAE requires a greater amount to reach a minimum viscosity and the approached value is higher. Two factors account for this difference. First, the viscosity of PAM/DAE aqueous solution itself is higher, because this polymer has greater molecular weight than PMAA–NH$_4$. Secondly, these two chemicals induce different dispersion actions.

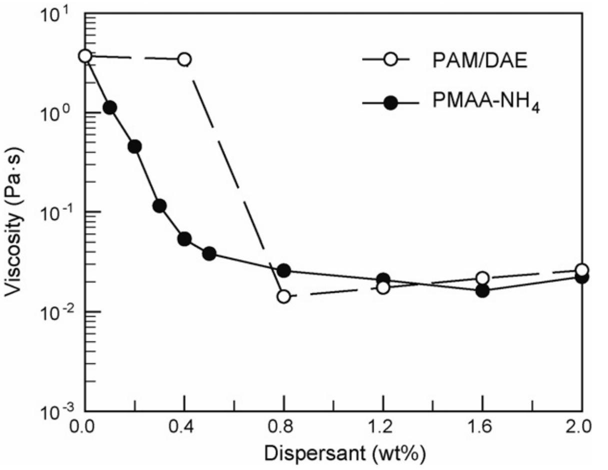

Fig. 6. Effect of dispersant concentration on the viscosity of 60 wt.% BT$_4$/B$_2$T$_9$ suspensions at pH 9.

3.5. Particle size of BT$_4$/B$_2$T$_9$ powder in suspensions

Fig. 7 shows the effect of dispersant concentration on the particle size of powder in 20 wt.% BT$_4$/B$_2$T$_9$ suspensions. For suspensions without dispersants, the d_{50} value is 2.8 μm. Generally, particles become less agglomerated and particle sizes shift to smaller values when dispersants were incorporated in the suspensions. For the PAM/DAE suspension, the d_{50} value was found to increase slightly with the dispersant concentration initially up to a maximum, then decrease afterwards and reach a minimum at about 0.8 wt.%. The trend is similar to that

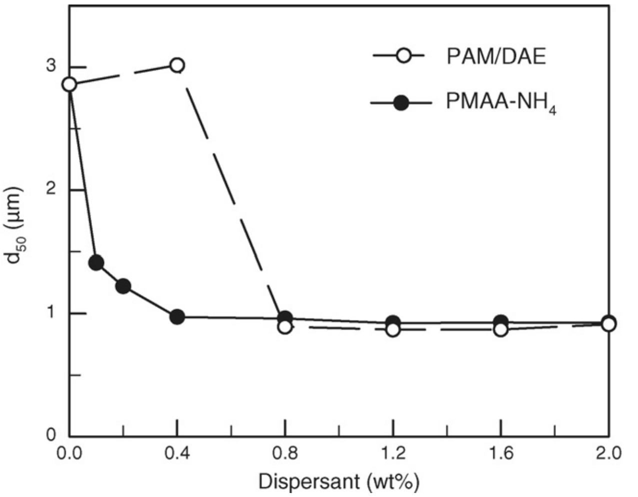

Fig. 7. Effect of dispersant concentration on the particle size of powder in 20 wt.% BT$_4$/B$_2$T$_9$ suspensions.

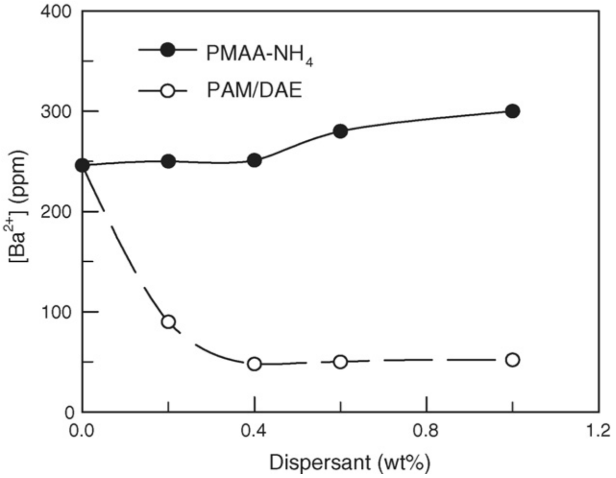

Fig. 8. Effect of dispersant concentration on the leached Ba^{2+} concentration.

observed in viscosity measurements. In contrast, the d_{50} value of the PMAA–NH_4 suspension increases sharply with the dispersant concentration initially, then reach a minimum at dispersant concentration of 0.4 wt.%. Clearly, the suspensions incorporated with PAM/DAE require greater amount of dispersant but contain BT_4/B_2T_9 powder with particle size close to those incorporated with PMAA–NH_4.

3.6. *Ba^{2+} dissolution*

When BT_4/B_2T_9 powder was milled in deionized water, Ba^{2+} ions were expected to leach out from the powder. The amount of leached Ba^{2+} ions is a function of pH value, solid loading, and the addition of dispersant of BT_4/B_2T_9 slurries. Controlling the dissolution of BT_4/B_2T_9 in aqueous suspensions is essential to avoid composition deviation, exaggerated grain growth, and degradation of sintered properties. Fig. 8 shows the effect of dispersant concentration on Ba^{2+} dissolution concentration of 20 wt.% BT_4/B_2T_9 suspensions. The dissolved $[Ba^{2+}]$ was found to increase or decrease with dispersant content, depending on which dispersant was incorporated. In other words, the suspension with PAM/DAE contains lower Ba^{2+} concentration than that without. The more the polymer incorporated, the less Ba^{2+} is leached. The leached $[Ba^{2+}]$ reaches a minimum value when the dispersant concentration is of about 0.4 mg/g BT_4/B_2T_9. In contrast, PMAA–NH_4 causes opposite effect on the leaching of Ba^{2+} from BT_4/B_2T_9 powder.

It was reported that dispersants contain anionic (–COO^-) group could interact with Ba^{2+} ions.[18] When PMAA–NH_4 is added into the suspensions, the interaction between the –COO^- groups of polymer and Ba^{2+} ions will promote the leaching of barium ions from the particles. As a result, $[Ba^{2+}]$ in the slurries with PMAA–NH_4 was observed from Fig. 8 to be slightly higher than that without any dispersant present. Although PAM/DAE can also enhance the dissolution of Ba^{2+} from the powder, an appreciated fraction of released Ba^{2+} ions would redeposit and chemically link with the adsorbed polymer on the particle surface. As mentioned earlier, PAM/DAE has stronger interactions with barium ions and the adsorbed amount of this polymer at the plateau (3.0 mg/g BT_4/B_2T_9) is higher than that of PMAA–NH_4 (1.1 mg/g BT_4/B_2T_9). Therefore, addition of PAM/DAE causes a decrease in the leached Ba^{2+} concentration in the resulting suspensions. It is further noted that the leached $[Ba^{2+}]$ in Fig. 8 approaches a constant value, which corresponds to the adsorbed amount of PAM/DAE at the plateau in Fig. 5. This suggests that the adsorption of PAM/DAE is a key factor in reducing the leached $[Ba^{2+}]$ in BT_4/B_2T_9 slurries.

4. Conclusions

An amphoteric copolymer, PAM/DAE, was evaluated as a dispersing agent for BT_4/B_2T_9 suspensions. Incorporation of PAM/DAE could reduce the viscosity and cause particle sizes to shift to smaller values. Compared with PMAA–NH_4, the copolymer is as effective. More importantly, PAM/DAE could lessen the leached Ba^{2+} concentration. This is because PAM/DAE contains cationic groups (–N^+), which would favor themselves to be adsorbed onto BT_4/B_2T_9 surface. As the leached Ba^{2+} ions redeposit and interact with the adsorbed polymer on the particle surface, their dissolution from BT_4/B_2T_9 powder becomes less.

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