

# Effects of Amphoteric Copolymer Structure on the Properties of Barium Titanate Suspensions

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**ABSTRACT:** The effect of the molecular structure of an amphoteric copolymer, i.e., poly[acrylamide/(( $\alpha$ -*N,N*-dimethyl-*N*-(3-( $\beta$ -carboxylate)acrylamino)propyl)ammonium ethanate)] (PAD) on the interactions with BaTiO<sub>3</sub> (BT) particles in water and on the stability of BT suspensions was examined by means of adsorption,  $\zeta$  potential, sedimentation, and viscosity measurements. The results indicate that the adsorption of PAD onto BT particles follows the Langmuir adsorption isotherm. As the added PAD containing greater ionic group fraction, both the saturated amount of adsorbed polymer

and the amount of the polymer required to reach the minimal  $\zeta$  potential decrease. Whatever the ionic group fraction in PAD, BT suspensions become stable and less viscous when saturated amount of the polymer was adsorbed on particle surface. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1025–1030, 2007

**Key words:** water-soluble polymer; barium titanate; dispersion; adsorption; viscosity

## INTRODUCTION

Water-soluble polymers have been applied in many areas, such as mineral-processing, water treatment, or coatings.<sup>1,2</sup> Another important area of application is the wet processing of ceramic powder.<sup>3,4</sup> 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.<sup>4–7</sup> 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 (BT), alumina, zirconia, and silicon nitride.<sup>5–12</sup>

As dispersant is an essential chemical in the processing of ceramic slurries, new and more effective dispersants continue to be developed. For example, Kirby et al.<sup>13</sup> reported that poly(acrylic acid)–poly(ethylene oxide) comb polymers could impart stability to BT nanoparticle suspensions over a wide range of pH, ionic strength, and ion valency conditions where pure poly(acrylic acid) fails. Wang et al.<sup>14</sup> indicated that sodium salt of poly(aspartic acid) could reduce leached Ba<sup>2+</sup> from BT surface, which should improve the quality of BT tapes. Hsu et al.<sup>15</sup> also reported an amphoteric copolymer, that is, poly[acrylamide/(( $\alpha$ -*N,N*-dimethyl-*N*-acryloyloxyethyl) ammonium ethanate)], which has the ability to lessen leached Ba<sup>2+</sup>. Previously, we have synthesized another amphoteric copolymer, that is, poly[(acrylamide)/(( $\alpha$ -*N,N*-dimethyl-*N*-(3-( $\beta$ -carboxylate)acrylamino)propyl) ammonium ethanate)] (PAD), which could act as a dispersant to improve the dispersion of BT particles in aqueous solutions.<sup>16</sup> In this article, interactions between BT particles and PAD was further studied. The effect of reactant ratio of this polymer on the dispersion of BT colloids was also examined, as the reactant ratio of a copolymer affects its dispersing properties of the ceramic slurries.<sup>17–19</sup>

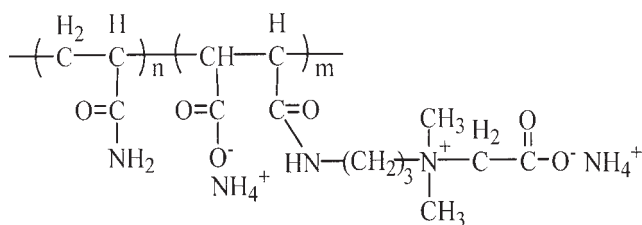
## EXPERIMENTAL

### Materials

PAD was used as the dispersant in this study. This polymer was prepared from acrylamide (AAM) and ( $\alpha$ -*N,N*-dimethyl-*N*-(3-( $\beta$ -carboxylate)acrylamino)propyl) ammonium ethanate (DAE) through a free-radical

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**Figure 1** Chemical structure of PAD polymer.

polymerization. Detailed procedure about the preparation of this dispersant was described elsewhere.<sup>16</sup> Figure 1 shows the chemical structure of PAD. The prepared PAD samples have close molecular weight and different DAE fractions, as listed in Table I. The molecular weight of these samples was measured with gel permeation chromatography, and the DAE fraction of the polymer determined by analyzing the amount of carboxylate groups through a titration method described elsewhere.<sup>5,15</sup>

The ceramic powder used was high purity BT from Prosperity Dielectrics (Taoyuan, Taiwan). The powder had a Ba/Ti ratio of 0.995, a median size of 0.82  $\mu\text{m}$ , and a Brunauer-Emmett-Teller (BET) specific surface area of 4.01  $\text{m}^2 \text{g}^{-1}$ . The basic properties of the BT powder are listed in Table II.

Aqueous suspensions (100 g) containing either 20 or 60 wt % BT were prepared. They contained 0–1.0 wt % PAD 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. Unless specified otherwise, the pH value of the BT suspensions was adjusted to 9 by the addition of aqueous NaOH.

## Measurements

### Adsorption measurements of dispersants

BT aqueous suspensions (20 wt %), with different concentrations of PAD were prepared at pH 9. These suspensions were turbo-mixed 24 h and centrifuged at a speed of  $4 \times 10^3$  rpm for 20 min. The samples were taken from the top of the supernatant layer in the centrifugation tube. The supernatant sample should be clear without any particles been seen. The residual dispersant concentration in the supernatants was analyzed and determined by a titration procedure mentioned elsewhere.<sup>5</sup> The amount of dispersant adsorbed

**TABLE I**  
Characteristics of PAD Samples

Polymer	DAE fraction (%)	$M_w^a$
PAD(10)	10	$9.5 \times 10^4$
PAD(29)	29	$1.0 \times 10^5$
PAD(41)	41	$1.0 \times 10^5$

<sup>a</sup> Weight-average molecular weight.

**TABLE II**  
Basic Properties of the BT Powder

Ba/Ti	0.995
Purity (%)	99.73
SrO (%)	0.0779
Nb <sub>2</sub> O <sub>5</sub> (%)	0.0071
Al <sub>2</sub> O <sub>3</sub> (%)	0.0316
SiO <sub>2</sub> (%)	0.0124
Median particle size ( $\mu\text{m}$ )	0.82
Moisture (%)	0.12
Compressed density ( $\text{g cm}^{-3}$ )	3.49
BET specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	4.01

on BT was calculated from the difference in dispersant concentration before and after adsorption.

### $\zeta$ potential measurements

BT aqueous suspensions (20 wt %), with or without dispersants present, were prepared at various pH values. The tested samples were made by mixing 1.5- $\mu\text{L}$  BT suspension with 100-mL deionized water. The  $\zeta$  potential of the remaining powders in the samples was measured by a Zeta-Meter 3.0+ (Zeta-Meter, Staunton, VA).

### Determination of dissociation of dispersants

The percent dissociation of either PAD in aqueous solutions at various pH values was determined by a titration method reported elsewhere.<sup>5</sup>

### Sedimentation tests

BT aqueous suspensions (20 wt %), with or without dispersants present at pH 9, were prepared and poured into 50-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.

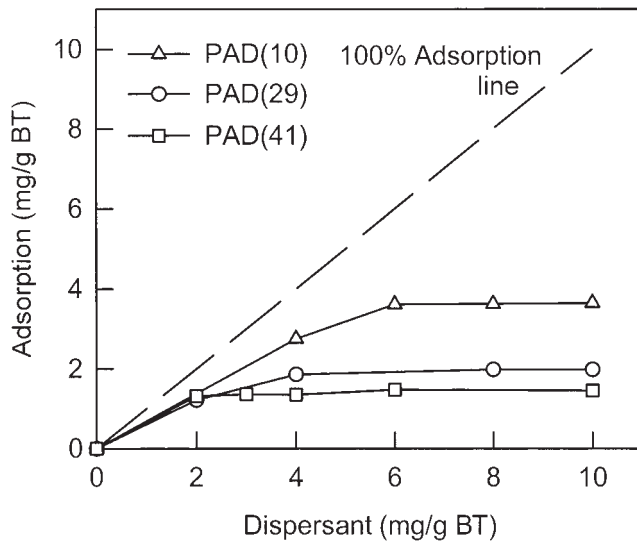
### Viscosity measurements

The viscosity of 60 wt % BT aqueous suspensions at pH 9, with or without dispersants present, was determined by a viscometer (Brookfield DV-II, Brookfield Engineering Laboratories, Middleboro, MA) at various shear rates.

## RESULTS AND DISCUSSION

### Adsorption of PAD on BT

Figure 2 shows the adsorption amount of PAD with different DAE content onto the BT surface in aqueous suspensions as a function of the initial dispersant concentration at pH 9. For all tested polymer samples, the adsorbed amount was shown to increase with dispersant concentration initially, and then reaches a charac-



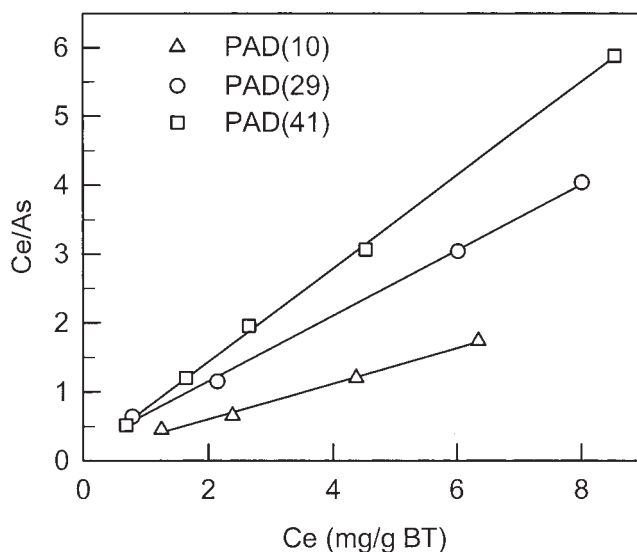
**Figure 2** Effect of dispersant concentration on the adsorbed amount of PAD at pH 9.

teristic plateau. The value at the plateau accounts for the amount of polymers ( $C_m$ ) required for the formation of monolayer on the particle surface. The deviation of the adsorption curve from the 100% adsorption line at low polymer concentration indicates a low-affinity adsorption.

The  $C_m$  value for each PAD can be determined quantitatively using the following Langmuir adsorption equation:<sup>20</sup>

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

where  $C_e$  is the equilibrium concentration of polymer in solution expressed in milligrams per gram BT.  $A_s$  is the amount of adsorbed polymer expressed in milli-



**Figure 3** Relationship between  $C_e/A_s$  and  $C_e$ .

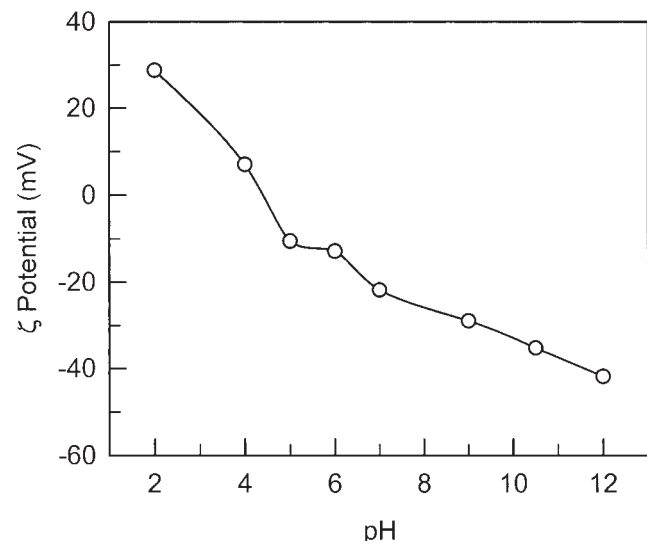
**TABLE III**  
Saturated Adsorption Amount of PAD on Particle Surface

Polymer	$C_m$ (experimental, $\text{mg g}^{-1}$ BT)	$C_m$ (calculated from eq. (1), $\text{mg g}^{-1}$ BT)
PAD(10)	3.65	3.90
PAD(29)	1.99	2.11
PAD(41)	1.45	1.48

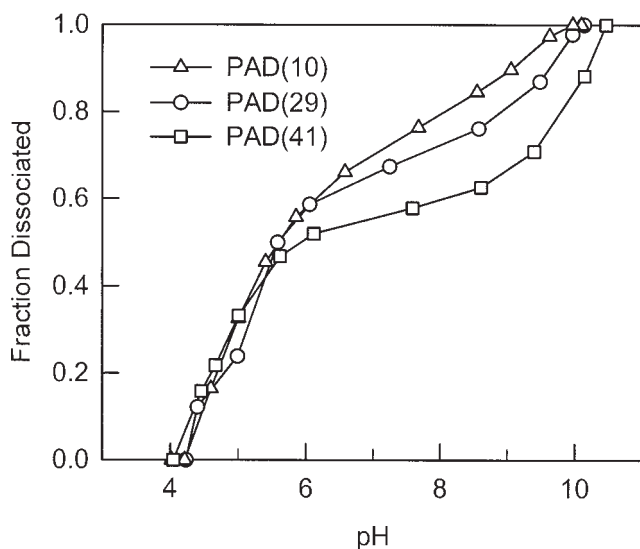
grams per gram BT and  $K$  is an adsorption constant. Figure 3 shows the relationship of  $C_e/A_s$  and  $C_e$  for three PAD polymers at pH 9. A linear relationship was observed for each curve in Figure 3, indicating the adsorption behavior of PAD indeed follows the Langmuir adsorption model and only a monolayer of polymer molecules was adsorbed on particle surface. From the slope of each line in Figure 3,  $C_m$  could be determined. Table III summarizes the results. The  $C_m$  values determined from the Langmuir adsorption equation are 3.90, 2.11, and 1.48  $\text{mg g}^{-1}$  BT for PAD(10), PAD(29), and PAD(41), respectively. These values are close to those determined from Figure 2. It is clear the monolayer adsorbed amount of PAD decreases as the DAE fraction increases.

The adsorption of PAD onto BT powder is related to the interaction between the particle surface and polymer functional groups. Figure 4 shows the  $\zeta$  potential of particles in 20 wt % BT suspensions as a function of pH. The surface charge or  $\zeta$  potential of particles was observed to be positive at low pH values, and become negative at high pH values. The isoelectric point occurs at about pH 4.5.

As is shown in Figure 1, the structural unit of PAD molecules contains three functional groups, that is, the cationic amine group ( $-\text{N}^+(\text{CH}_3)_2-$ ), carboxylate



**Figure 4**  $\zeta$  potential of 20 wt % BT suspensions as a function of pH.



**Figure 5** Fraction dissociated of PAD molecules as a function of pH.

group ( $-\text{COONH}_4$ ), and amide group ( $-\text{CONH}_2$ ). Among these three functional groups, only the carboxylate group will dissociate and become  $-\text{COO}^-$  ions in an aqueous solution. The fraction dissociated of the carboxylate group is clearly affected by the pH value of the solution. Figure 5 shows the fraction dissociated of PAD molecules as a function of pH. In general, the PAD molecule was found not to dissociate at  $\text{pH} < 4$ . It starts to dissociate at about  $\text{pH} = 4$ , and the fraction dissociated increases with increasing pH value. At the pH value of about 10, PAD molecules are dissociated completely and become effectively amphoteric. Besides, the dissociated fraction of PAD molecules with different DAE content is slightly different at same pH value; polymer molecules containing lower DAE fraction appears to have more dissociation.

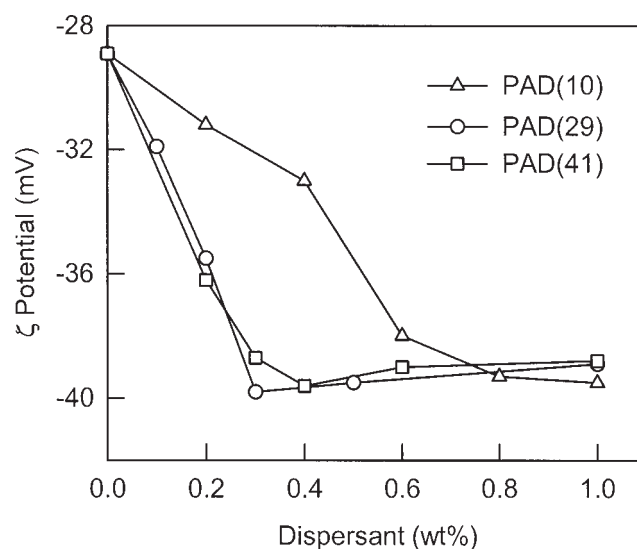
Therefore, the BT surface would be negative at pH 9, and about 66–89% of carboxylate groups in PAD molecules dissociate and become  $-\text{COO}^-$  ions, depending on the DAE fraction of polymer. The dissociated  $-\text{COO}^-$  ions in PAD molecules would generate repulsive forces with the negative sites of particle surface and hinder the adsorption of polymer onto BT particles. In contrast, the cationic amine group and amide group of the polymer would interact with the negatively charged BT particles by electrostatic interactions and hydrogen bonding. This promotes the adsorption of polymer onto ceramic particles. A similar situation was reported by Walter et al.<sup>21</sup> in investigating the adsorption of the amphoteric diblock copolymer poly(methacrylic acid)-*block*-poly(dimethylamino)-ethyl methacrylate) on silicon substrates from dilute aqueous solution. They mentioned 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 charged surface can be formed, which results in the adsorption in a dense conformation with a highly adsorbed amount.

As listed in Table II, the DAE fractions in PAD are 10, 29, and 41% for PAD(10), PAD(29), and PAD(41), respectively. The PAD molecules with higher DAE fraction contain more cationic amine groups, which would promote the adsorption of the polymer onto BT particles. However, DAE has certain chain length, which provides some steric effect and hinders the adsorption. The amount of adsorbed polymer with more DAE content would become less because of stronger steric hindrance. As shown in Figure 2 and Table III, the results show that the adsorbed amount decreases with increasing DAE content, and it indicates that the latter factor is more influential than the former one.

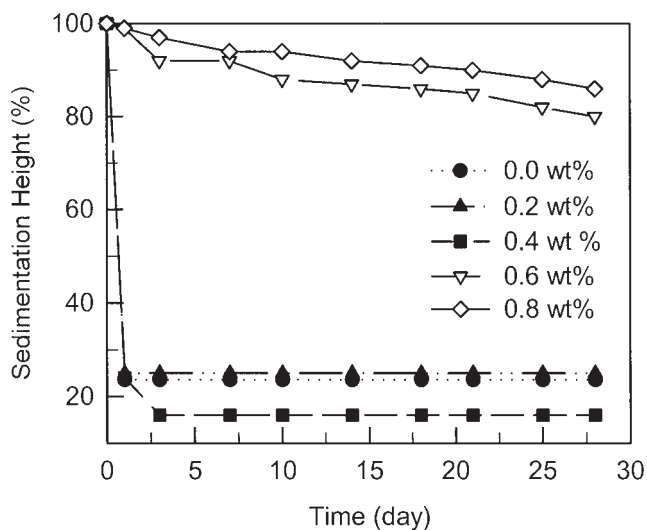
### $\zeta$ potential of BT suspensions

Figure 6 shows the effect of dispersant concentration on the  $\zeta$  potential of 20 wt % BT suspensions at pH 9. The  $\zeta$  potential of the suspension without any dispersant is about  $-29$  mV. With the addition of PAD to the suspension, the potential value becomes more negative, as a consequence of polymer adsorption. As the polymer concentration increases, the  $\zeta$  potential decreases initially, and then approaches a plateau. At lower polymer concentration, that is, 0.2 wt %, the  $\zeta$  potential of particles with adsorbed PAD(29) or PAD(41) is more negative than that of particles with PAD(10). This is because of PAD(10) containing lower fraction of ionic group. Besides, lower polymer concentration is required for PAD with higher DAE



**Figure 6** Effect of PAD concentration on the  $\zeta$  potential of 20 wt % BT suspensions at pH 9.



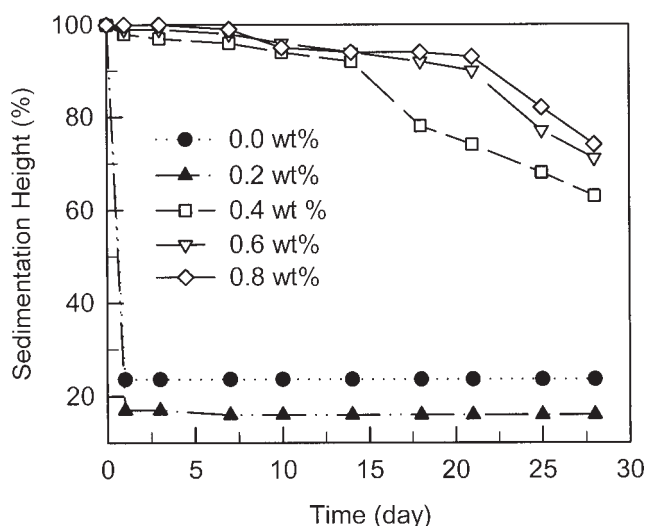


**Figure 7** Sedimentation of 20 wt % BT suspensions with PAD(10).

fraction to attain the plateau, which agrees with the adsorption result in Figure 2. Nevertheless, the approached potential values at plateau for the BT suspension with either PAD(10) or others are close to each other.

### Sedimentation of BT particles in suspensions

The sedimentation behavior of BT particles in the slurry is appropriate in determining the colloidal stability and examining the effectiveness of the incorporated dispersant.<sup>15,16,22</sup> Figure 7 shows the sedimentation of particles in 20 wt % BT suspensions with various amounts of PAD(10). For suspensions without any dispersants present, two distinct layers were observed after 1-day sedimentation. These two layers



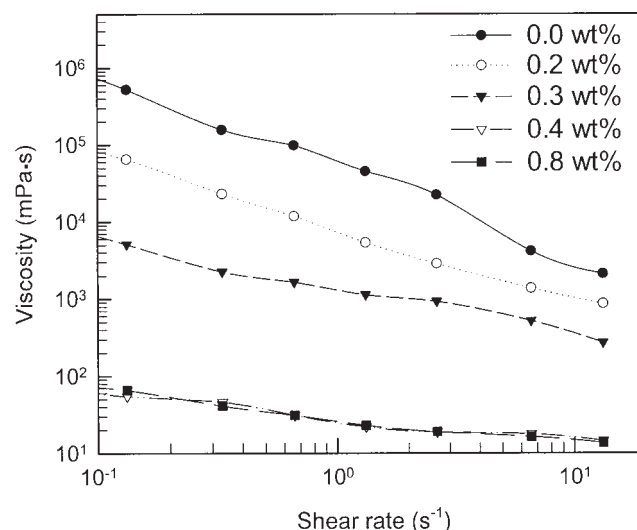
**Figure 8** Sedimentation of 20 wt % BT suspensions with PAD(29).

are a clear aqueous layer on the top and a sediment layer. When PAD(10) was added, improvement of the stability in the resulting suspension was found to be limited at low polymer concentration, that is, <0.4 wt %. This is a consequence of insufficient adsorption of the polymer and the resulted  $\zeta$  potential not high enough to stabilize the suspension. When the polymer concentration is more than 0.6 wt %, the resulting suspension becomes stable and remains cloudy after settling for 30 days. In addition, a clear aqueous layer forms gradually above the cloudy layer and becomes thicker in suspensions along with elapsed time or decreasing polymer content.

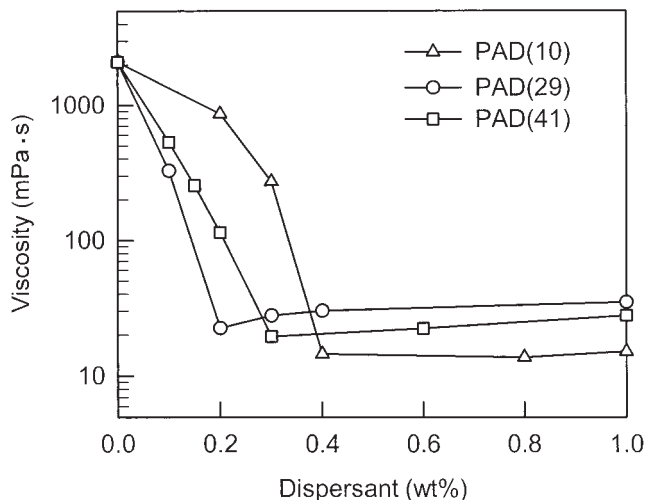
Similar sedimentation behavior was observed for the BT suspension with either PAD(29) or PAD(41). One typical example is shown in Figure 8. However, the required amount of polymer to stabilize the suspension is less, that is, 0.4 wt %. From Figure 5, the  $\zeta$  potential of the colloid with 0.6 wt % PAD(10) or 0.4 wt % PAD(29) is about  $-40$  mV, which is not enough to provide sufficient electrostatic repulsions.<sup>23</sup> This implies that the adsorbed polymer should contribute steric effect in addition to electrostatic repulsion to stabilize the BT suspensions.

### Rheological behavior

Figure 9 shows the viscosity of 60 wt % BT suspensions with different PAD(10) content at different shear rates at pH 9. The viscosity of suspensions decreases as shear rate increases, and all tested samples display shear-thinning behaviors. The viscosity of the BT suspension without any dispersant present is very high, that is,  $\sim 2100$  mPa s. Addition of the polymer decreases the degree of particle agglomeration and greatly reduces the viscosity of the suspension. The



**Figure 9** Viscosity of 60 wt % BT suspensions with different PAD(10) concentration at pH 9.



**Figure 10** Effect of PAD concentration on the viscosity of 60 wt % BT suspensions at pH 9.

viscosity reaches a minimum value when 0.4 wt % PAD(10) was added in the colloidal system.

Figure 10 shows the effect of dispersant concentration of PAD on the viscosity of 60 wt % BT suspensions at a shear rate of  $13.2 \text{ s}^{-1}$ . Again, the viscosity of BT suspensions without addition of any dispersant is high. The suspension becomes less viscous when PAD was incorporated. Along with increasing polymer concentration, the viscosity was found to decrease first, and then reach a minimum at critical polymer content. Further incorporation of this dispersant will increase the viscosity slightly because of the occurrence of bridging between particles and the compression of the double electric layer. When compared with Figure 6, it can be noticed that these results correspond well with the  $\zeta$  potential curves. The critical dispersant concentration, that is, the amount, which gives the lowest viscosity, is about 0.4, 0.2, and 0.2 wt %, for PAD(10), PAD(29), PAD(41), respectively. In addition, the lowest viscosity for suspensions with different PAD polymers was found to be close to each other. This means that all three tested PAD polymers are effective in dispersing BT powder and reducing the viscosity.

## CONCLUSIONS

In this study, PAD copolymers with different DAE fractions were synthesized. These polymers have

proved to be effective in reducing the viscosity and stabilizing the resulting BT slurries. The adsorption of PAD onto BT particles follows the Langmuir adsorption isotherm. Along with increasing DAE fraction, both the adsorbed amount and the amount of the polymer required to reach the minimal  $\zeta$  potential decrease. The dispersing mechanisms of PAD include both electrostatic repulsion and steric hindrance. The BT suspensions with PAD polymers whatever the DAE fraction in the polymer could become stabilized and less viscous when saturated amount of polymer was adsorbed on particle surface.

## References

- Molyneux, P. *Water-Soluble Synthetic Polymers: Properties and Behavior*; CRC: Boca Raton, FL, 1984.
- Piirma, I. *Polymeric Surfactants*; Marcel Dekker: New York, 1992.
- Reed, J. S. *Introduction to the Principles of Ceramic Processing*, 2nd ed.; Wiley: New York, 1995.
- Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: New York, 1983.
- Cesarano, J., III; Aksay, I. A.; Blier, A. *J Am Ceram Soc* 1988, 71, 250.
- Cesarano, J., III; Aksay, I. A. *J Am Ceram Soc* 1988, 71, 1062.
- Chen, Z. C.; Ring, T. A.; Lemaitre, J. *J Am Ceram Soc* 1992, 75, 3201.
- Jean, J. H.; Wang, H. R. *J Am Ceram Soc* 1998, 81, 1589.
- Shih, C. J.; Hon, H. M. *Mater Chem Phys* 1998, 57, 125.
- Das, K. K.; Somasundaran, P. *Colloids Surf A* 2003, 223, 17.
- Mahdjoub, H.; Roy, P.; Filiatre, C.; Bertrand, G.; Coddet, J. *J Eur Ceram Soc* 2003, 23, 1637.
- Shen, Z. G.; Chen, J. F.; Zou, H. K.; Yun, J. *J Colloid Interface Sci* 2004, 275, 158.
- Kirby, G. H.; Harris, D. J.; Li, Q.; Lewis, J. A. *J Am Ceram Soc* 2004, 87, 181.
- Wang, X.; Lee, B. I.; Mann, L. *Colloids Surf A* 2002, 202, 71.
- Hsu, K. C.; Ying, K. L.; Chen, L. P.; Yu, B. Y.; Wei, W. C. *J Am Ceram Soc* 2005, 88, 524.
- Chen, L. P.; Ying, K. L.; Hsu, K. C. *J Appl Polym Sci* 2005, 96, 1443.
- Baklouti, S.; Romdhane, M. R. B.; Boufi, S.; Pagnoux, U.; Chartier, T.; Baumard, J. F. *J Eur Ceram Soc* 2003, 23, 905.
- Ben Romdhane, M. R.; Boufi, S.; Baklouti, S.; Chartier, T.; Baumard, J. F. *Colloids Surf A* 2003, 212, 271.
- Ben Romdhane, M. R.; Baklouti, S.; Bouaziz, J.; Chartier, T.; Baumard, J. F. *J Eur Ceram Soc* 2004, 24, 2723.
- Langmuir, L. *Science* 1938, 88, 450.
- Walter, H.; Harrats, C.; Muller-Buschbaum, P.; Jerome, R.; Stamm, M. *Langmuir* 1999, 15, 1260.
- Gomez-Yanez, C.; Balmori-Ramirez, H.; Martinez, F. *Ceram Int* 2000, 26, 609.
- Vallar, S.; Houivet, D.; El Fallah, J.; Kervadec, D.; Haussonne J. M. *J Eur Ceram Soc* 1999, 19, 1017.