

Effect of pH on the Properties of Barium Titanate Slurries with an Anionic Dispersant

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ABSTRACT: The colloidal stability of barium titanate (BT) aqueous suspensions with poly(acrylamide/4-carboxylamino-4-oxo-2-butenate) (PAAM/COB) at pH 7, 9, and 12 has been investigated by means of ζ potential, adsorption, sedimentation, and particle size measurements. The isoelectric point of BT powder is at pH 4.6 and the value of ζ potential decreases as the pH of suspensions increases. The adsorption of PAAM/COB onto BT particles follows the Langmuir adsorption isotherm. The saturated amount of adsorbed polymer decreases with increasing pH. In general, BT particles in basic solutions with PAAM/COB are more

stabilized, and less agglomerated than those without any dispersant present. As pH is increased, the resulting ζ potential becomes more negative, although lower polymer concentration is required for monolayer coverage of particle surface. Consequently, the resulting suspensions become more stabilized, and contain powder with smaller particle size. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1082–1088, 2006

Key words: PAAM/COB; pH; dispersion; adsorption; Ba-TiO₃

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.

Polymeric surfactants adsorbed at the surface of ceramic particles can stabilize colloidal suspensions through electrostatic, steric, or electrosteric effect of the adsorbed polymer.^{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 (BT), 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 continue to be developed.^{13–17} Previously, we synthesized an anionic water-soluble copolymer, i.e., poly(acrylamide/4-carboxylamino-4-oxo-2-butenate) (PAAM/COB). This polymer was found to be effective in dispersing Ba-TiO₃ (BT) particles in aqueous media.¹⁸ It is well recognized that pH of aqueous media is an influential factor on the charged state of particle surface and governing the dispersing properties of a dispersant. The number of dissociated ionic groups depends on the pH and their chemical nature. For example, ammonium salt of poly(methacrylic acid) (PMAAN) molecules will dissociate and contain anionic carboxylate groups; their conformation becomes stretched in basic solutions and they adsorb in a flat conformation on ceramic particle surface.^{19,20} In this article, the effect of pH of PAAM/COB on the dispersion of BT colloids was examined and discussed.

EXPERIMENTAL

Materials

The ceramic powder used was high purity BT from Prosperity Dielectrics (Taoyuan, Taiwan). The powder had a Ba/Ti ratio of 1/1, an average size of 0.45 μm , and a Brunauer-Emmett-Teller (BET) specific surface area of 4.53 m²/g. Table I lists the basic properties of the BT powder.

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TABLE I
Basic Properties of the BT Powder

Ba/Ti	1/1
Purity (%)	99.8
SrO (%)	0.022
Nb ₂ O ₅ (%)	0.001
Al ₂ O ₃ (%)	0.033
SiO ₂ (%)	0.016
Average particle size (μm)	0.45
Moisture (%)	0.25
Ignition loss (%)	0.6
Compressed density (g/cm ³)	3.269
BET specific surface area (m ² /g)	4.53

PAAM/COB was prepared and used as a dispersant for BT slurries. Details of the preparation procedure are reported in our first article.¹⁸ Figure 1 shows the chemical structure of PAAM/COB. This prepared polymer has a fixed AAM/COB ratio of 5/1 and a weight-average molecular weight of 2.8×10^5 . The molecular weight of polymer was determined with a gel permeation chromatography, which was described elsewhere.¹⁶

Preparations of BT suspensions

Aqueous suspensions containing either 20 or 60 wt % BT were prepared. They contain 0–1.5 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 attaining a homogeneously dispersed state. After ball-milling, the BT suspensions were adjusted to various pH values by the addition of either aqueous HCl or NaOH.

ζ potential measurements

BT aqueous suspensions (20 wt %) at various pH values with or without dispersants present were prepared. After 24-h ball-milling and mixing, the suspensions were centrifuged at a speed of 4×10^4 rpm for 15 min to obtain supernatants. The ζ potential of remaining powder in the supernatant was measured with a PenKem Laser ZeeMeter Model 501 (Bedford Hills, NY).

Adsorption measurements

BT aqueous suspensions (60 wt %) with different concentrations of PAAM/COB were prepared at pH 7–12. After 24-h ball-milling and 15-min centrifugation at a speed of 4×10^4 rpm, a small amount of supernatant was taken. 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.

Sedimentation tests

BT aqueous suspensions (20 wt %) with or without dispersants present were prepared and poured into 50 mL graduated cylinders. The initial height of the suspension in the graduated cylinder was measured. These graduated cylinders were kept still for 30 days, and the height of the cloudy suspensions at different settled time was measured.

Particle size measurements

BT aqueous suspensions (60 wt %) at various pH values with or without dispersants present was 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. The green density of compacts was determined by the Archimed's method.

RESULTS AND DISCUSSION

Dissolution and ζ potential

It is clear that the dispersion property of a dispersing agent is controlled by the adsorption of this chemical onto ceramic powders. As the adsorption of PAAM/COB onto BT powder is significantly affected by the surface state of BT particles, understanding the surface chemistry of BT powder is essential. Figure 2 shows the effect of milling time on the pH value of 60 wt % BT suspensions. For the BT suspension with initial pH value of 3, the pH value increases very quickly with

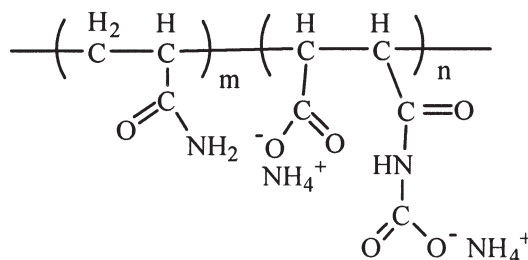


Figure 1 Chemical structure of PAAM/COB.

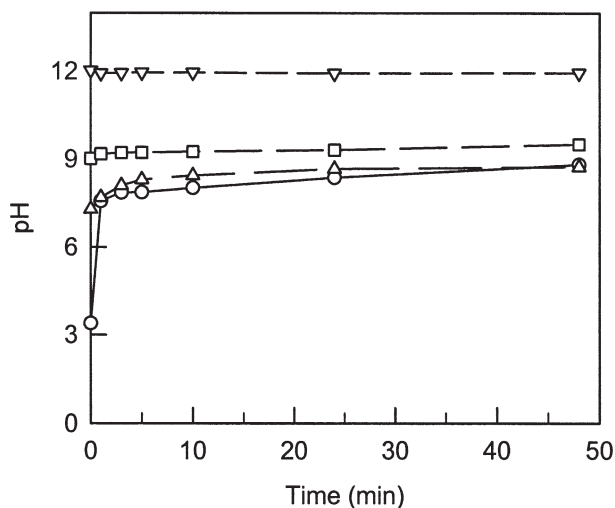


Figure 2 Effect of milling time on pH of 60 wt % BT suspensions.

milling time, and then approaches a plateau. The pH value at plateau is about 8.5. The increase of pH value is mainly because the dissolution of barium ion from BT powder.^{8,21} As the total amount of barium ion leached decreases with increasing pH, the change of pH was observed to be insignificant for the BT suspension milled at $\text{pH} > 7$.

Figure 3 shows the ζ potential of particles in 20 wt % BT suspensions as a function of pH. The surface charge or ζ potential of particles is positive at low pH values, and becomes negative at high pH values. The isoelectric point occurs at about pH 4.6 that is below the reported value for BT powder, i.e., pH 8.5.²² Instead, this value is comparable to that of TiO_2 , i.e., pH 4–6.³ The shift of the isoelectric point provides another evidence of barium ion leached from BT pow-

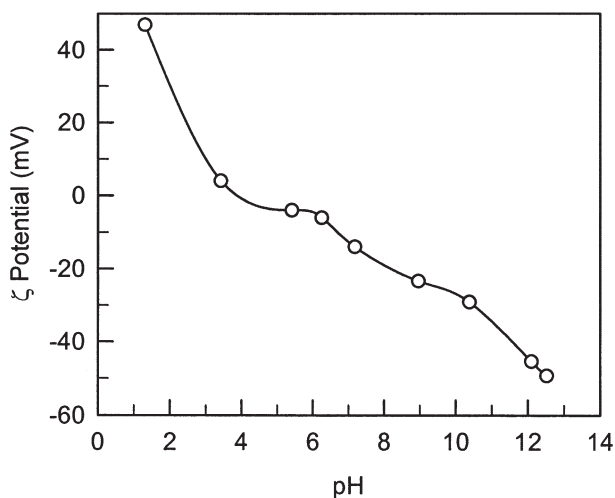


Figure 3 Effect of pH on the ζ potential of 20 wt % BT suspensions.

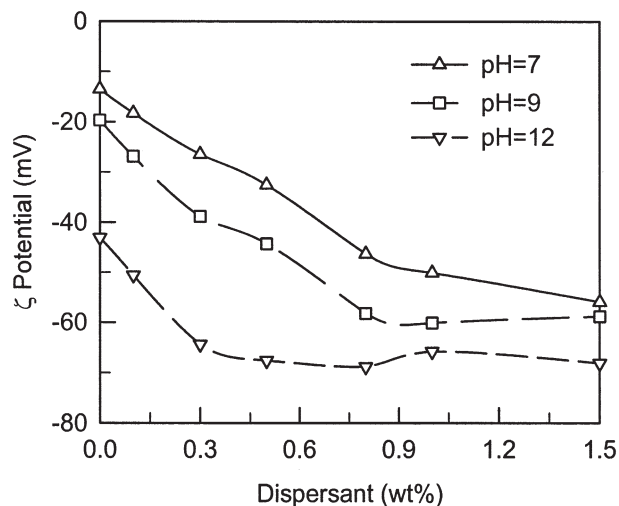


Figure 4 Effect of PAAM/COB concentration on the ζ potential of 20 wt % BT suspensions.

der, which causes the particle surface to become depleted in barium and enriched in TiO_2 .^{21,23} Furthermore, the absolute ζ potential value was found in Figure 3 to be lower than 50 mV in the pH range 7–12. Therefore, the electrostatic repulsion between particles is insufficient to keep the system stable without the presence of any dispersant.^{7,24}

Figure 4 shows the effect of PAAM/COB concentration on the ζ potential of 20 wt % BT suspensions at different pH values. As BT powder is stable in basic solutions,^{8,21} only those conditions with $\text{pH} \geq 7$ were investigated in the following study. When dispersant is present in suspensions, the ζ potential decreases. This change in ζ potential is a consequence of the adsorption of the dispersant. Generally, the ζ potential decreases rapidly and approaches a level-off value. At lower pH, the initial decreasing rate is slower and a higher PAAM/COB concentration is required to attain the level-off. Moreover, the difference between the initial ζ potential for the suspensions without any dispersant present and the level-off value decreases as the pH increases.

Dissociation and adsorption

Figure 5 shows the adsorption amount of polymer on the BT surface in aqueous suspensions at different pH values as a function of initial polymer concentrations. For all the pH values investigated, the amount of adsorbed polymer was found to increase with dispersant concentration initially, and then reach a characteristic plateau. The plateau corresponds to the saturated amount of polymer required for a monolayer coverage. The initial PAAM/COB concentration to reach the plateau decreases with increasing pH, i.e., about

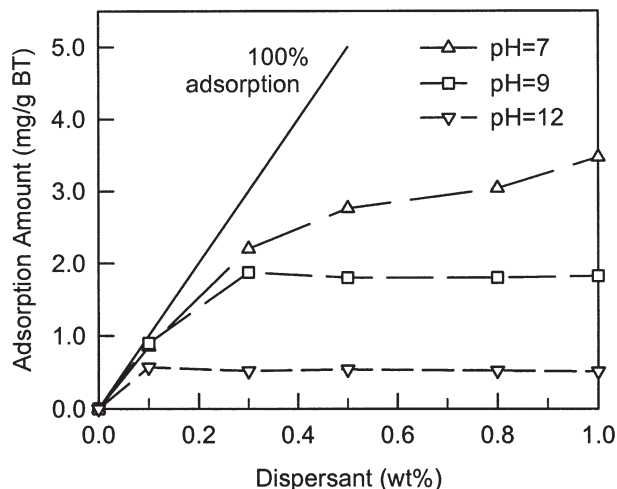


Figure 5 Effect of PAAM/COB concentration on the adsorption amount of polymer on BT surface.

0.5 wt % at pH 7, 0.3 wt % at pH 9, and 0.1 wt % at pH 12.

The saturated amount of dispersant can be determined using the following Langmuir adsorption equation:²⁵

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

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 6 shows the relationship of C_e/A_s and C_e for PAAM/COB at pH 7–12. A linear relationship was observed for each curve in Figure 6, indicating the adsorption

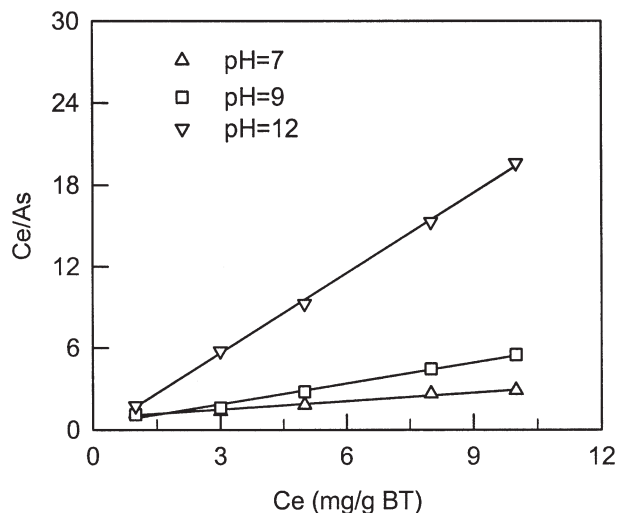


Figure 6 Relationship between C_e/A_s and C_e for PAAM/COB on BT surface.

TABLE II
Saturated Adsorption Amount of PAAM/COB on Particle Surface

pH	C_m (mg/g BT)
7	4.88
9	1.97
12	0.51

behavior of PAAM/COB 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 6, C_m could be determined. Table II summarizes the results. The C_m values are 4.88, 1.97, and 0.51 mg/g of BT at pH 7, 9, and 12, respectively; they decrease as the pH increases.

The adsorption of PAAM/COB is related to the interaction between polymer molecules and BT surface. As shown in Figure 1, the PAAM/COB molecules contain COONH_4 functional groups, which change to anionic (COO^-) groups when they are dissociated in an aqueous solution. Figure 7 shows the fraction dissociated of dispersant molecules in aqueous solutions at various pH values. The fraction dissociated, defined as the ratio of the number of COO^- groups to the number of initial COONH_4 groups in the molecules, was determined by a titration method reported elsewhere.⁵ The polymer molecules were observed in Figure 7 to be unassociated at $\text{pH} < 4.5$. They start to dissociate at $\text{pH} > 4.5$, and are more dissociated at higher pH value. At $\text{pH} > 9$, PAAM/COB molecules are dissociated completely.

At pH 7, the particle surface should be negative because the isoelectric point of BT powder is about 4.6; the PAAM/COB molecules are about 50% dissociated, and contain anionic groups ($-\text{COO}^-$) and polar

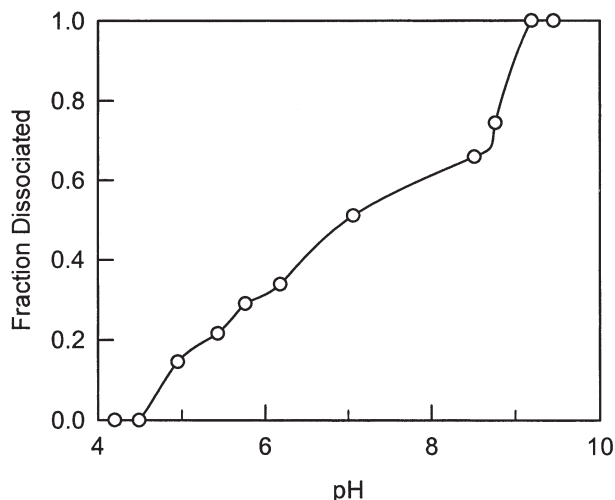


Figure 7 Effect of pH on the fraction dissociated of PAAM/COB in aqueous solutions.

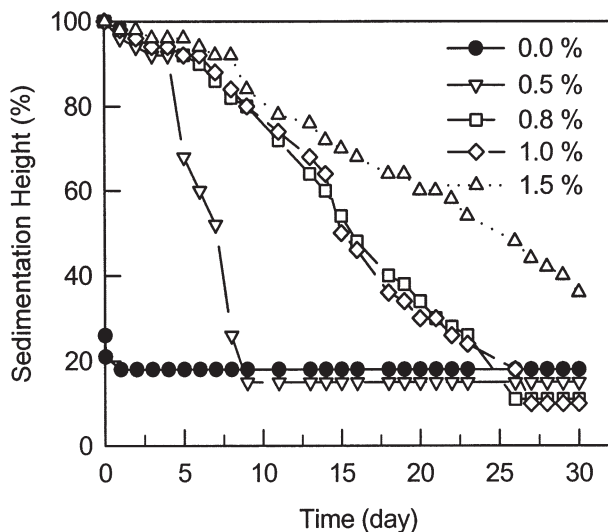


Figure 8 Sedimentation height of 20 wt % BT suspensions with different PAAM/COB concentrations at pH 7.

groups ($-\text{NH}_2$, $-\text{COONH}_4$). PAAM/COB adsorption on BT surface is due to the attraction between the polar groups and the particle surface by hydrogen bonding. In addition, there are some positively charged sites, which are due to the redeposition of dissolved barium ions on BT surface to interact with the anionic groups of polymer molecules. A similar argument was proposed to explain the adsorption behavior of ammonium salt of PMAAN onto BT particles in basic solutions.⁸

As pH is increased, the PAAM/COB molecules become more dissociated and contain more $-\text{COO}^-$ groups. Furthermore, the polymer would become more stretched in molecular conformation. The increased electrostatic repulsive forces between particles and the free polymer molecules in the solution, and the more extended PAAM/COB conformation prevent more polymer molecules from adsorbing onto BT powder. As a result, the adsorption amount decreases with increasing pH.

Sedimentation

The sedimentation observation and measurement is appropriate in indicating the colloidal stability. A good dispersant will make suspensions to remain cloudy and result in a small final sediment height.^{7,8} Figure 8 shows the sediment height of 20 wt % BT suspensions with different amount of PAAM/COB at pH 7. 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, particles settled very quickly, and they separate into two layers after 1-day sedimentation; a clear boundary exists between a sed-

iment layer and an upper clear aqueous layer. This agrees with the results of ζ potential measurement in Figure 4. That is, the ζ potential in BT suspensions at pH 7 is only -13.5 mV. The resulting electrostatic forces are not sufficient to produce suspension with good dispersion and stability. When PAAM/COB is added, the stability of suspensions improves. The resulting suspensions become more stable and remain in a cloudy state longer if more polymer is incorporated. Besides, the final sediment height is less than that of the BT suspension without any dispersant as an indication of denser packing of particles.

Similar results were observed for suspensions with other pH values. For convenience of discussion, only the sedimentation results of 20 wt % BT suspensions at various pHs with 1.0 wt % dispersant are shown in Figure 9. For the suspension at pH 7, it becomes unstable and separate into two layers when the sedimentation time is more than 26 days. BT suspensions at higher pH exhibit improved dispersions; they remain cloudy for 30 days. This can be attributed to higher absolute ζ potential of the suspensions, as is indicated in Figure 4.

Particle size

The measurement of particle size in ceramic slurry is another way in determining the colloidal stability and examining the effectiveness of the incorporated dispersant. A good dispersant will stabilize suspensions and result a smaller particle size. Figure 10 shows the effect of PAAM/COB concentration on the particle size of 60 wt % BT at pH 7. The d_{10} , d_{50} , and d_{90} particle sizes in the suspension with the absence of any dispersant are 0.60, 1.95, and 4.1 μm , respectively. The average (d_{50}) particle size of BT powder in suspensions is greater than that from supplier, as listed in Table I.

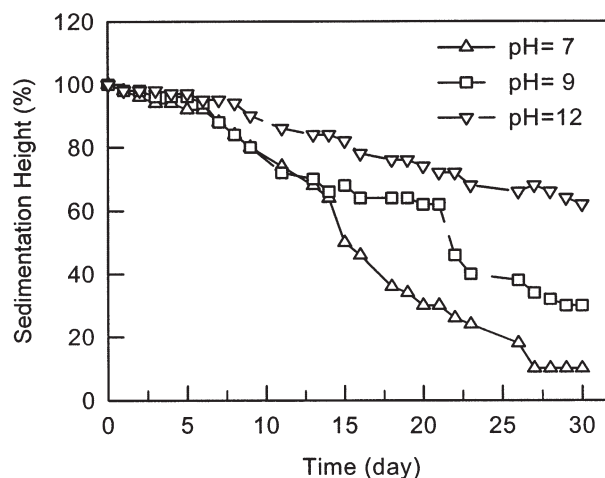


Figure 9 Sedimentation height of 20 wt % BT suspensions with 1 wt % PAAM/COB.

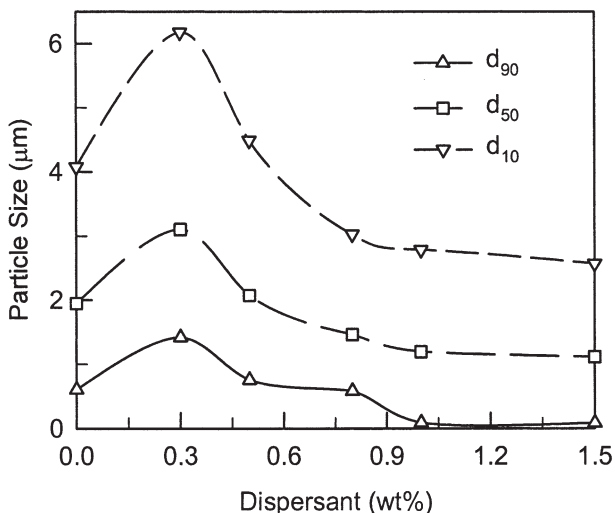


Figure 10 Effect of PAAM/COB concentration on the particle size of 60 wt % BT suspensions at pH 7.

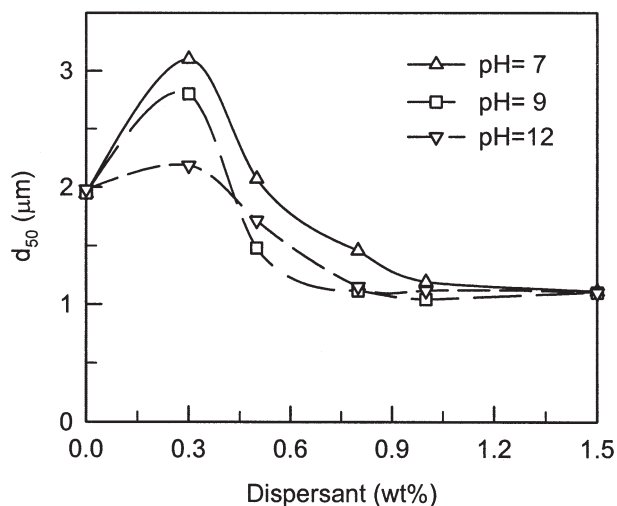


Figure 11 Effect of PAAM/COB concentration on the d_{50} particle size of 60 wt % BT suspensions.

This indicates particles in the slurry are not stable and agglomerate with each other. The higher extent the powder agglomerated, the greater is the difference in particle size. When PAAM/COB is added, the resulting suspensions become more stable and particle size shifts to smaller value if the polymer concentration is more than 0.5 wt %.

Apparently, BT suspensions with 0.3 wt % dispersant show greater d_{10} , d_{50} , and d_{90} particle size than those without dispersant. It is interesting that this is not in agreement with the results of ζ potential, as is shown in Figure 4. The reason can be attributed to the incomplete surface coverage of adsorbed PAAM/COB when the initial PAAM/COB concentration is 0.3 wt %. Under this situation, BT particles may flocculate into clusters to reach complete surface coverage between the available surface and the corresponding dispersant amount in the suspension. Besides, the prepared PAAM/COB has a weight-average molecular weight of 2.8×10^5 , which is quite high. Its molecules may also form interparticle bridges and cause some flocculation among particles. The bridging effect occurs when the polymer size or molecular weight is large enough to overcome the interparticle electrostatic forces.¹⁰ For BT suspensions containing more than 0.5 wt % PAAM/COB, the particle size was found (in Fig. 10) to decrease with dispersant concentration initially, and approaches a minimum when the added polymer is greater than 1.0 wt %.

Similar results are observed at other pH values. Nevertheless, different pH causes different degree of shift in particle size, as is shown in Figure 11. The required dispersant concentration to attain the minimal d_{50} particle size appears to decrease with increasing pH, which is in accordance with the adsorption measurement.

Compact density

The relative green density of the powder compact obtained from gravitation sedimentation and consolidation of the suspension is shown in Figure 12. For BT compacts without any dispersant present, the green density is 45% theoretical density (TD). The density value is increased when PAAM/COB was incorporated in the compact. Furthermore, the value increases with increasing polymer concentration up to a maximum of about 59% TD. As expected, the pH value affects the critical polymer concentration required to stabilize BT powder in suspensions, to attain smaller particle size, and to achieve maximal green density of the resulting compact. The greater the pH value, the lower is the critical polymer concentration required,

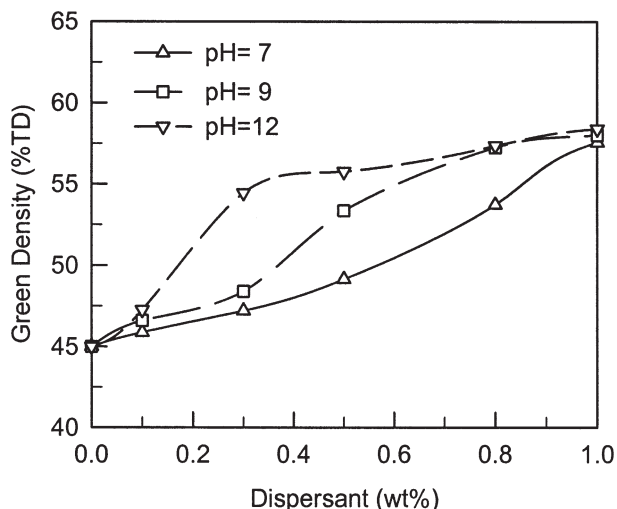


Figure 12 Effect of PAAM/COB concentration on the green density of BT compacts.

and the higher is the maximal green density. The trend is consistent with that determined by adsorption and ζ potential measurements.

CONCLUSIONS

In this study, the effect of pH on the colloidal stability of BT powder in aqueous solutions with amphoteric copolymer, i.e., PAAM/COB, at pH 7–12 has been investigated. The adsorption of this polymer on particle surface follows the Langmuir adsorption isotherm. Although the critical amount for monolayer coverage of particles decreases with increasing pH, the resulting ζ potential becomes more negative. This is related to interaction between the polymer, having different degrees of dissociation and molecular conformation, and BT particles, at different pH values. Consequently, the resulting suspensions become more stabilized, contain particles less agglomerated, and the resulting compacts are more consolidated and show higher green densities.

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