

# Synthesis of an Amide/Carboxylate Copolymer for Barium Titanate Suspensions. I. As a Dispersant

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**ABSTRACT:** An anionic copolymer, that is, poly[methacrylamide-co-(ammonium methacrylate)] (PMMN), was synthesized for the purpose of application to barium titanate (BT) suspensions. The chemical structure of the prepared polymer was verified with IR and  $^1\text{H-NMR}$  spectra. PMMN has the potential to have a double function of dispersant and binder for BT suspensions because it contains both amide groups, which are expected to bring a binder contribution, and carboxylate groups, which are expected to bring a dispersant contribution. In this article, the dispersion effects of PMMN with different monomer ratios are

examined and evaluated through viscosity and sedimentation measurements. The results indicate that this polymer could uniformly disperse the particles and make the resulting suspensions less viscous and more stabilized. PMMN with a methacrylamide/ammonium methacrylate ratio of 60/40 appears to be most effective, as this polymer induces sufficient electrostatic forces among particles when it is adsorbed onto BT powder. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2077–2084, 2008

**Key words:** colloids; dispersions; polyelectrolytes; synthesis

## INTRODUCTION

Water-soluble polymers have been applied in many areas such as adhesion, coatings, cosmetics, and water treatment.<sup>1,2</sup> Moreover, they are used as additives, such as dispersing agents and binders, in the preparation of stable ceramic slurries. Consequently, ceramic green parts with a uniform microstructure and enough strength can be prepared, and sintered compacts with good qualities are achieved.<sup>3,4</sup>

Usually ionic polymers, called polyelectrolytes, are used as dispersants. These polymers, when they are dissociated in aqueous solutions and adsorbed onto ceramic particles, will create electrostatic, steric, and/or electrosteric forces.<sup>4–7</sup> Therefore, they could enhance the dispersion of solid particles and cause the resulting suspensions to become less viscous and more stabilized.

Acrylic acid based polymers such as ammonium polyacrylate, poly(acrylic acid)–poly(ethylene oxide), and ammonium polymethacrylate (PMAAN) have widely been used as dispersing agents for barium titanate (BT), alumina, and other ceramic powders in aqueous solutions.<sup>5–14</sup> Moreover, other types of dispersants have also been disclosed. For example,

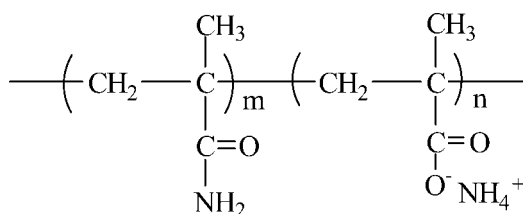
Wang et al.<sup>15</sup> studied the colloidal stability of BT aqueous suspensions with sodium polyaspartate and reported that the amount of sodium polyaspartate required to stabilize BT suspensions decreased as the pH increased. Baklouti et al.<sup>16</sup> examined the effect of sulfonic copolymer dispersants and determined the optimum conditions to ensure stable alumina suspensions. Bouhamed et al.<sup>17</sup> prepared comblike random copolymers from 2-acrylamido-2-methylpropanesulfonic acid sodium salt and methoxypoly(ethylene glycol) methacrylate (MPEG) and indicated that the dispersing effect of the copolymer was controlled by both the ionization level of the copolymer and the length of the MPEG segments.

Separately, water-soluble nonionic polymers such as poly(vinyl alcohol), poly(ethylene glycol), and polyacrylamide are used as ceramic binders. Their function is to confer sufficient strength and hold the ceramic particles of green compacts in the desired shape before and during sintering. In addition, some binders can act as lubricants between the solid particles. Finally, the properties of the sintered ceramics that are finally produced are also significantly affected by the performance of binders.<sup>4,18–21</sup>

Traditionally, dispersants and binders are two different chemicals added to ceramic suspensions. It is then important to evaluate the compatibility between these two chemicals and how the dispersant–binder interactions affect the particulate dispersion in the suspensions and the properties of the resulting green/sintered compacts.<sup>21,22</sup> Alternatively, one could synthesize a copolymer that has two different structural

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**Figure 1** Chemical structure of the PMMN polymer.

units; one plays a dispersing role, and another plays a binding role. By proper adjustment of the fractions of these two structural units, a copolymer with a double function of dispersant and binder is possible.<sup>23,24</sup> Recently, we prepared a copolymer, that is, poly[methacrylamide-*co*-(ammonium methacrylate)] (PMMN), and used it as an additive for BT suspensions. PMMN was prepared from methacrylamide (MAM) and ammonium methacrylate (MAN) through a free-radical polymerization.<sup>25</sup> Figure 1 shows the chemical structure of PMMN. This polymer contains carboxylic groups expected to bring a dispersant contribution and amide groups expected to bring a binder contribution. In this study, PMMN samples with different MAM/MAN ratios were prepared, and their dispersion effects on the BT suspensions were examined and discussed through the viscosity and sedimentation measurements.

## EXPERIMENTAL

### Materials

MAM (98%), ammonia (30%), and ammonium persulfate (98%) from Acros Organics (Morris Plains, NJ), methacrylic acid (99%, stabilized with 0.03% hydroquinone) from Showa Chemical Industry Co. (Tokyo, Japan), and 2-methyl-2-propene-1-sulfonic acid sodium salt (>98%) from Tokyo Chemical Industry Co. (Tokyo, Japan) were used without further purification. PMMN was prepared from the chemicals mentioned previously. The prepared PMMN samples had three MAM/MAN molar ratios, and their weight-average molecular weights were close to one another and fell between  $5.2 \times 10^4$  and  $5.5 \times 10^4$ . In addition, PMAAN (30% solid), a common dispersant supplied by R.T. Vanderbilt Co. (Norwalk, CT), was used for comparison. PMAAN had a weight-average molecular weight of  $1.3 \times 10^4$ . The molecular weight of the polymers was measured by the gel permeation chromatography method, which has been reported in detail elsewhere.<sup>26</sup>

The ceramic powder used was a high-purity BT (Prosperity Dielectrics, Taoyuan, Taiwan). The powder had a Ba/Ti ratio of 0.997, an average particle size of 0.94  $\mu\text{m}$ , and a Brunauer–Emmett–Teller specific surface area of 2.51  $\text{m}^2/\text{g}$ . Deionized and dis-

tilled water was used, and the pH was adjusted by the addition of either aqueous HCl or aqueous NaOH.

### Preparation of the PMMN resins

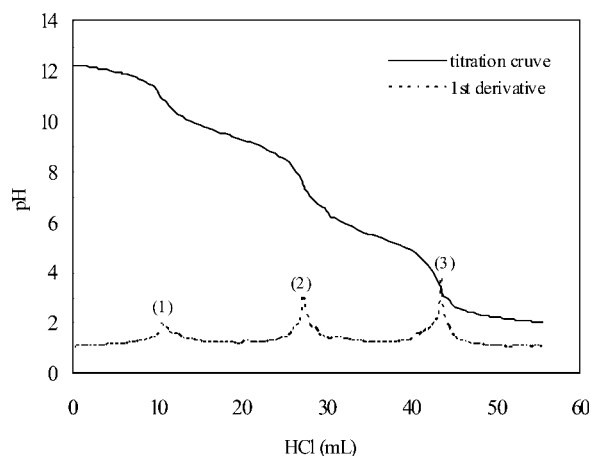
The PMMN samples with different MAM/MAN ratios were prepared through free-radical polymerization. Ammonium persulfate was used as the initiator, and 2-methyl-2-propene-1-sulfonic acid sodium salt was used as a chain-transfer agent. An example of preparing PMMN with a MAM/MAN molar ratio of 1/1 in the feed was as follows. Methacrylic acid (43 g) was dissolved in 86 mL of deionized water, the pH of the solution was adjusted to 10 with 1N  $\text{NH}_4\text{OH}$ , and MAM (42.5 g) was dissolved in 150 mL of deionized water; both solutions were then added to a 500-mL stirred reactor. The reactor was purged with  $\text{N}_2$  gas. Ammonium persulfate (3.99 g) and 2-methyl-2-propene-1-sulfonic acid sodium salt (3.12 g) were added to the reactor, and the polymerization was carried out at 40°C for 8 h. The product was precipitated thereafter and purified with acetone twice. The acetone was removed in a vacuum oven at room temperature for 24 h. A yellowish, dried precipitate (62.4 g), that is, PMMN, was then obtained.

### Identification of the prepared resins

The dried PMMN resin was ground into a powder before the determination of the structure or other procedures. In identifying the chemical structure, the proper amount of the powder samples was mixed with predried KBr and pressed into disks. Transmission IR spectra of the disks were obtained with a PerkinElmer (Waltham, MA) Paragon 500 Fourier transform infrared spectrometer. Moreover, some powder samples were also dissolved in  $\text{D}_2\text{O}$ , and  $^1\text{H-NMR}$  spectra were obtained with a JOEL (Tokyo, Japan) JNM-ECX 400 NMR spectrometer.

### Potentiometric titration of the polymers in aqueous solutions

PMMN and PMAAN were the two polymers used in this study. PMMN contains two functional groups, that is, amide ( $-\text{CONH}_2$ ) and carboxylate ( $-\text{COO}^-$ ), with an ammonium counterion ( $\text{NH}_4^+$ ); PMAAN contains one carboxylate group with an ammonium counterion. These groups will form their conjugated acids or bases under the proper pH conditions. The dissociation behavior and the fraction of each dissociated functional group at various pH values can be determined from potentiometric titrations of the polymer solutions.<sup>5,8</sup>



**Figure 2** Titration curve for PMMN and its corresponding first-derivative plot.

A known amount of a polymer was diluted with deionized water, and the pH value was adjusted to 12 to ensure that the carboxylic groups in the polymeric molecules were fully dissociated. Titrations were then carried out with 0.5N aqueous HCl with a TitroLine Alpha Plus automatic titrator (Schott-Geräte GmbH, Mainz, Germany). Titrations were also conducted on a blank solution. The difference between the amounts of HCl added to the blank solution and the sample at a specified pH corresponded to the amount of HCl that reacted with a certain functional group of the sample. With this information, the fraction of each dissociated functional group could be determined.

Figure 2 shows a typical titration curve and its corresponding first derivative plot of a PMMN solution at pH 12 initially and titrated with aqueous HCl. As explained later, peaks 1, 2, and 3 are associated with NaOH,  $\text{NH}_3$ , and carboxylate groups, respectively.<sup>8</sup> The carboxylic acid group of PMMN starts to dissociate at peak 3 and dissociates completely at peak 2. The fraction of the dissociated carboxylic acid group ( $\alpha$ ) at a specified pH can be calculated from the ratio of the distance from peak 3 to that between peaks 2 and 3.

Furthermore, the composition of the prepared PMMN samples could also be determined with the titration method mentioned previously. For an aqueous solution with the same polymer concentration, the amount of HCl that reacted with the carboxylate group of the polymer depended linearly on the MAN content of the titrated sample.

### Preparation of the BT suspensions

Aqueous suspensions containing 10 or 60 wt % BT were prepared. They contained 0–0.5 wt % polymer with respect to the dry weight of the BT powder. The suspensions were milled and mixed in a ceramic

jar with a fixed number of zirconia balls for 24 h to ensure a homogeneously dispersed state.

### Viscosity measurements

The viscosity of 60 wt % BT aqueous suspensions at pH 9 with or without any dispersant present was determined with a Brookfield LVDV-II viscometer (Brookfield Engineering Laboratories, Middleboro, MA) with several spindles or an adapter at a rotation speed of 60 rpm.

### Zeta potential measurements

BT aqueous suspensions (60 wt %) at pH 9 with or without any dispersant present were prepared. After ball milling, 1.5- $\mu\text{L}$  suspensions were taken and diluted in 100 mL of deionized water, which was adjusted to pH 9 previously. Samples were measured with a Zeta-Meter 3.0+ (Zeta-Meter, Staunton, VA).

### Adsorption of the polymers

BT suspensions (60 wt %) with different concentrations of the polymers were prepared at pH 9. After ball milling, the suspensions were centrifuged at a speed of 3000 rpm for 30 min to obtain supernatants. A known volume of the supernatant was diluted with distilled water to 60 mL, the pH value was adjusted to 12, and then the polymer concentration was analyzed with the potentiometric titration method previously mentioned.<sup>5</sup> The amount of the polymer adsorbed onto BT was calculated from the difference in the dispersant concentration before and after adsorption.

### Sedimentation tests

BT aqueous suspensions (10 wt %) at pH 9 with or without any dispersant present were prepared and poured into 50-mL graduated cylinders. These suspensions were left in the cylinders for 14 days, and the change of the sedimentation volume along with the time was measured and recorded.

## RESULTS AND DISCUSSION

### Structure of PMMN

The structure of the prepared polymer was verified from its IR and  $^1\text{H-NMR}$  spectra. Figure 3 shows the IR spectrum of PMMN. The peaks in the region of 3500–2800  $\text{cm}^{-1}$  were caused by OH stretching overlapped with NH stretching. The peak at 1680  $\text{cm}^{-1}$  was due to the C=O stretching vibration band of the carboxylate group. The presence of the peak at 1557  $\text{cm}^{-1}$  represents the asymmetric stretching

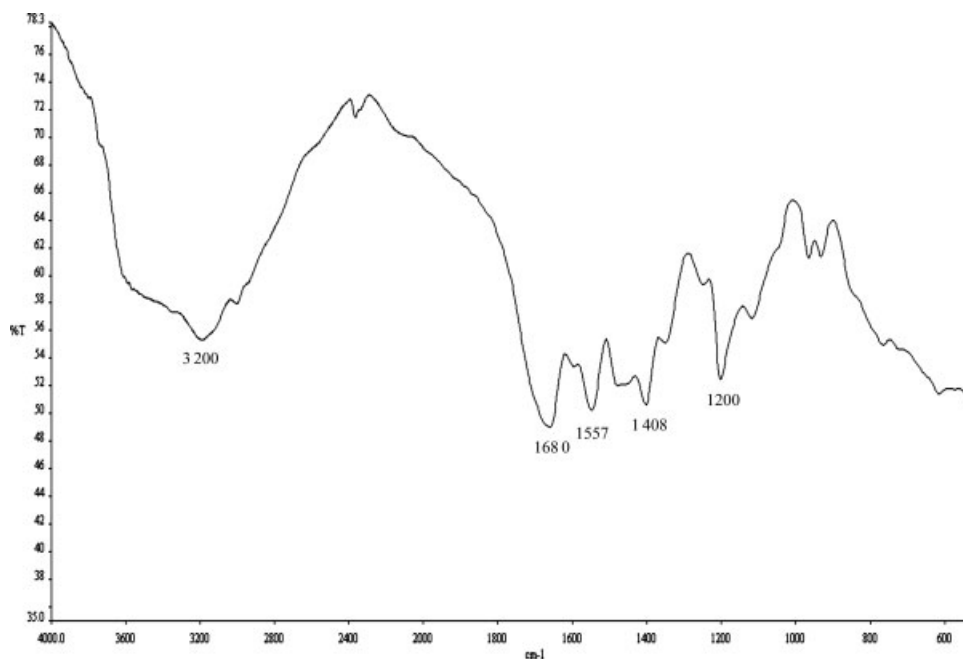
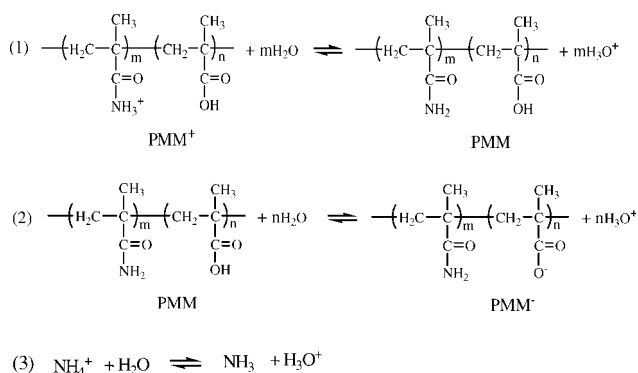


Figure 3 IR spectrum of PMMN.

band of the carboxylate group. The band occurs in the  $1408\text{-cm}^{-1}$  region because of the C—N stretching of the amide group. The  $^1\text{H-NMR}$  spectrum of PMMN shows three signals. The signal at  $\delta = 1.7\text{--}1.9$  ppm represents the  $-\text{CH}_2$  proton in the polymer backbone; two signals at  $\delta = 1.0\text{--}1.1$  and  $1.1\text{--}1.3$  ppm are related to the  $-\text{CH}_3$  proton of MAN and the  $-\text{CH}_3$  proton of MAM, respectively.<sup>27</sup>

### Dissociation of PMMN

PMMN contains amide and carboxylate functional groups with an ammonium counterion, which will form their conjugated acids or bases under different pH conditions and have the following dissociation reactions:



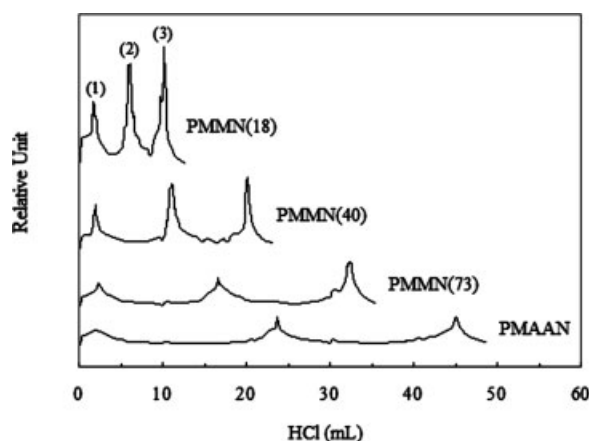
A typical titration curve and its corresponding first derivative plot of a PMMN solution at pH 12 initially and titrated with aqueous HCl are shown in Figure 2. The  $\text{p}K_a$  value of the functional groups is in the fol-

lowing order:  $-\text{CONH}_3^+ > -\text{COOH} > \text{NH}_4^+$ . The acid, having a higher  $\text{p}K_a$  value, will dissociate into its conjugated base at a lower pH value. Peak 1 in Figure 2 represents the excess NaOH in the solution that was neutralized with HCl. Peaks 2 and 3 represent all the  $\text{NH}_3$  and carboxylate groups (or  $\text{PMM}^-$ ) that were converted into  $\text{NH}_4^+$  and carboxylic acid groups (or PMM), respectively. The peak related to the complete conversion of PMM to  $\text{PMM}^+$  was not observed in Figure 2; it would appear at  $\text{pH} < 0$  because amides are very weak bases and  $\text{p}K_a$  of their conjugate acids is about 0.<sup>28</sup>

On the basis of Figure 2, the carboxylic acid group of PMMN starts to dissociate at peak 3 and dissociates completely at peak 2.  $\alpha$  at a specified pH can be calculated from the ratio of the distance from peak 3 to that between peaks 2 and 3. In general, the carboxylic acid group of PMMN was found not to dissociate at a pH of about 3.5. It starts to dissociate at pH 3.5, and the  $\alpha$  value increases with increasing pH value. At the pH value of about 8, the carboxylic acid groups are dissociated completely, and PMMN molecules become effectively anionic. The  $\alpha$  values of PMMN with different MAN contents at the same pH value were observed to be slightly different from one another. Finally, the dissociation behavior of PMAAN was found to be similar to that of PMMN.

### Composition of the PMMN resins

The composition of PMMN or its MAN content can also be determined from the first derivative of the titration curve of the polymer. Figure 4 shows the first



**Figure 4** First-derivative plots of the titration curves of PMMN(*n*) and PMAAN.

derivatives of the titration curves of PMMN(*n*) and PMAAN. As mentioned earlier, the distance between peaks 2 and 3 represents the amounts of HCl required to reach the end point and is linearly dependent on the number of carboxylate groups of the titrated polymer. By the comparison of the distance between peaks 2 and 3 of PMMN(*n*) to that of PMAAN, the MAN content of each PMMN(*n*) can be calculated. The MAN content in PMAAN is assumed to be 100% because this polymer contains one carboxylate group in its structural unit. The result is listed in Table I; the three PMMN polymers have MAN contents of 18, 40, and 73, and they are named PMMN(18), PMMN(40), and PMMN(73), respectively. PMMN molecules with more MAN units contain more negative charges and would be more effective in dispersing ceramic particles. Besides, Table I shows that the production yield is lower for PMMN with a higher fraction of the MAN moiety. This implies that MAM is more reactive than MAN during polymerization. According to the mechanism of copolymerization, the composition of a copolymer prepared from two monomers,  $M_1$  and  $M_2$ , can be expressed as follows:<sup>29</sup>

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (1)$$

where  $F_1$  is the molar fraction of  $M_1$  in the produced copolymer;  $f_1$  and  $f_2$  are the molar fractions of  $M_1$

and  $M_2$  in the feed, respectively; and  $r_1$  and  $r_2$  are the respective reactivity ratios of  $M_1$  and  $M_2$ . The reactivity ratio is defined as the ratio of the self-propagation rate constant to the cross-propagation rate constant. In this study, the reactive ratio of the two monomers was determined with a nonlinear least-square method to fit the experimental data in Table I; the determined  $r_1$  and  $r_2$  values are 0.94 and 0.41, respectively, with MAM and MAN designated as  $M_1$  and  $M_2$ . These values are close to those [ $r_1$  (acrylamide) = 1.11,  $r_2$  (acrylate) = 0.32] of poly (acrylamide-*co*-sodium acrylate) reported by Kelen and Tudos.<sup>30</sup> The fact that both  $r_1$  and  $r_2$  are less than 1 indicates that MAM and MAN have some tendency toward alternation in the PMMN molecules. Accordingly, the anionic charges along the polymeric molecules would be somewhat uniformly distributed.

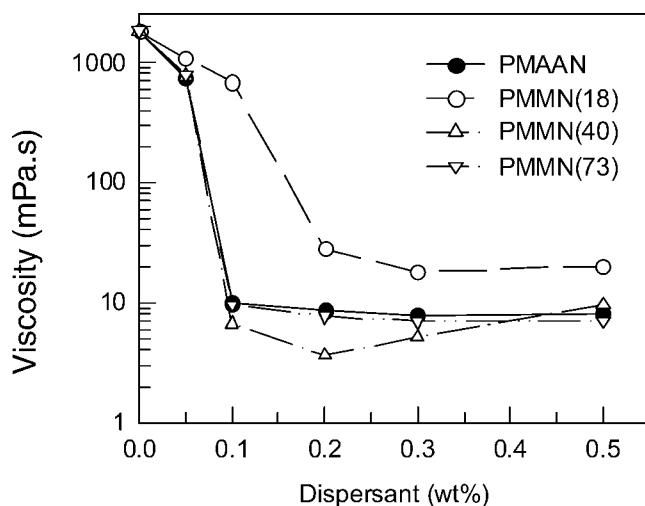
### Rheological behavior

The viscosity measurement is commonly applied to evaluate the degree of powder dispersion in concentrated suspensions. Usually, a concentrated suspension is viscous, especially when particles agglomerate to one another. The viscosity of a suspension could be decreased if a dispersant were incorporated. The extent of the decrease in viscosity depends on the effectiveness of the dispersant in reducing the agglomerated size. Figure 5 shows the effect of the dispersant concentration on the viscosity of 60 wt % BT suspensions at pH 9. The viscosity of BT suspensions without a dispersant is more than 1000 mPa s. The incorporation of PMMN reduces the viscosity of the resulting BT suspensions, and this indicates that this polymer could enhance the dispersion of BT particles. Along with increasing polymer concentration, the viscosity of the suspensions decreases first, reaches a minimum, and increases slightly afterwards. At a certain polymer content, the suspension with PMMN(40) is less viscous than that with either PMMN(18) or PMMN(73). This suggests that PMMN(40) is more effective in reducing the viscosity of BT slurries than the other two PMMN samples. The critical polymer concentration to achieve the lowest viscosity value is about 0.15, 0.15, and 0.25 wt % for PMMN(73), PMMN(40), and PMMN(18), respectively. A similar trend was also

**TABLE I**  
Properties of the PMMN Polymers

Polymer	MAM/MAN in the feed	MAM/MAN in the polymer	MAN (%)	$M_w$	$M_n$	Yield (%)
PMMN(18)	83.3/16.7	82/18	0.18	$5.2 \times 10^4$	$2.5 \times 10^4$	80
PMMN(40)	50/50	60/40	0.40	$5.2 \times 10^4$	$2.4 \times 10^4$	73
PMMN(73)	16.7/83.3	27/73	0.73	$5.5 \times 10^4$	$2.5 \times 10^4$	72

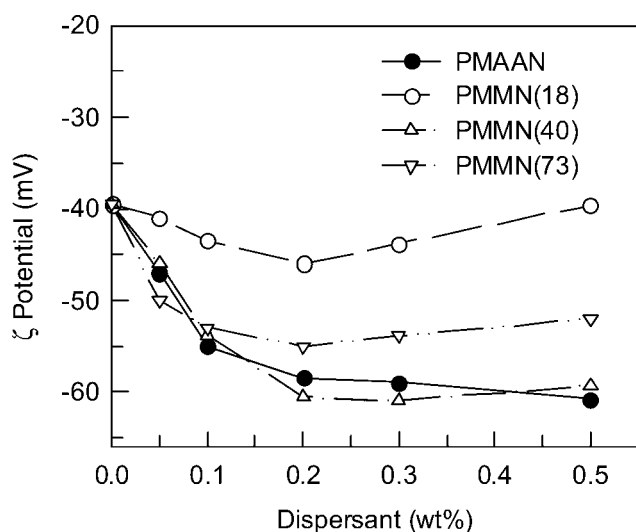
$M_n$ , number-average molecular weight;  $M_w$ , weight-average molecular weight.



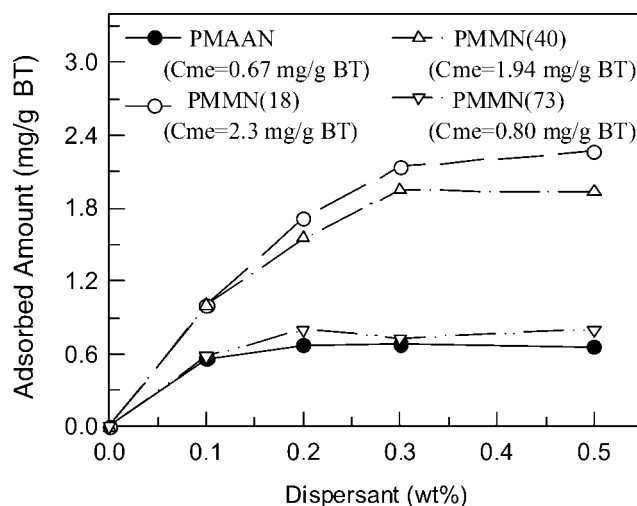
**Figure 5** Effect of the dispersant concentration on the viscosity of 60 wt % BT suspensions at pH 9.

observed in Figure 5 for the BT suspension containing PMAAN. The critical PMAAN concentration to achieve the minimum viscosity value is about 0.12 wt %. However, the achieved minimal value is slightly higher than that of the suspension with PMMN(40). Therefore, PMMN(40) appears to show better performance than PMAAN in dispersing BT powder in aqueous solutions.

It is clear that both PMMN and PMAAN contain the carboxylic acid group that will dissociate completely and convert into carboxylate. Accordingly, both chemicals become anionic polyelectrolytes at pH 9, and their dispersion mechanism is expected to be mainly electrostatic repulsions. Figure 6 shows the effect of the dispersant concentration on the  $\zeta$  potential of 60 wt % BT suspensions at pH 9. Gener-



**Figure 6** Effect of the dispersant concentration on the  $\zeta$  potential of 60 wt % BT suspensions at pH 9.



**Figure 7** Effect of the initial dispersant concentration on the adsorption amount of the polymer onto BT particles.

ally, the  $\zeta$  potential becomes more negative when dispersants are incorporated. The  $\zeta$  potential decreases with increasing PMMN concentration initially, approaches a minimal value, and then increases slightly afterwards. At a certain polymer content, the suspension with PMMN(40) has a lower potential value and thus stronger electrostatic forces among particles than that with either PMMN(18) or PMMN(73). Furthermore, the minimum potential value of the PMMN(40) suspension is slightly less than that of the PMAAN suspension. This is consistent with the results of the viscosity measurements.

The  $\zeta$  potential value of BT particles with an adsorbed dispersant is clearly related to the amount of the carboxylate groups in the adsorbed polymer, which in turn is determined by the amount of the adsorbed polymer, the content of the carboxylate group, and its dissociated fraction. Figure 7 shows the adsorption amount of each polymer on BT powder in aqueous suspensions at pH 9 as a function of the initial polymer concentrations. For all the polymers investigated, the amount of adsorbed polymer was found to increase with the dispersant concentration initially and then reach a characteristic plateau. The plateau corresponds to the saturated amount of the polymer ( $C_{mc}$ ) required for a monolayer coverage.<sup>8,23</sup> The estimated  $C_{mc}$  values of PMMN(18), PMMN(40), and PMMN(73) are 2.30, 1.94, and 0.80 mg/g of BT, respectively.

The saturated amount of the dispersant can also be determined with the following Langmuir adsorption equation:<sup>31</sup>

$$C_e/A_s = C_e/C_{mc} + 1/(K \times C_{mc}) \quad (2)$$

where  $C_e$  is the equilibrium concentration of the polymer in solution (mg/g of BT),  $C_{mc}$  is the satu-

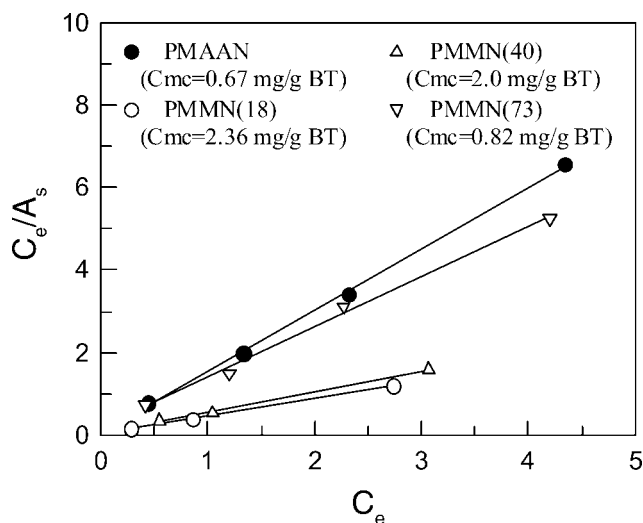


Figure 8 Relationship of  $C_e/A_s$  and  $C_e$ .

rated amount of the adsorbed polymer (mg/g of BT),  $A_s$  is the amount of the adsorbed polymer (mg/g of BT), and  $K$  is an adsorption constant. Figure 8 shows the existence of a linear relationship between  $C_e/A_s$  and  $C_e$  for each polymer, indicating that the adsorption behavior of PMMN indeed follows the Langmuir adsorption model. From the slope of each line,  $C_{mc}$  could be determined. The  $C_{mc}$  values of PMMN(18), PMMN(40), and PMMN(73) are 2.36, 2.0, and 0.82 mg/g of BT, respectively; these values are close to those ( $C_{me}$ ) determined experimentally. The  $C_{mc}$  value increases as the MAN content in the polymer decreases. This may be attributed to a lower repulsion between ionic carboxylate groups that allows a denser packing of the polymeric chains onto the particle surface. In addition, the loop conformation of the adsorbed polymer will be more favored as the MAM content increases or MAN con-

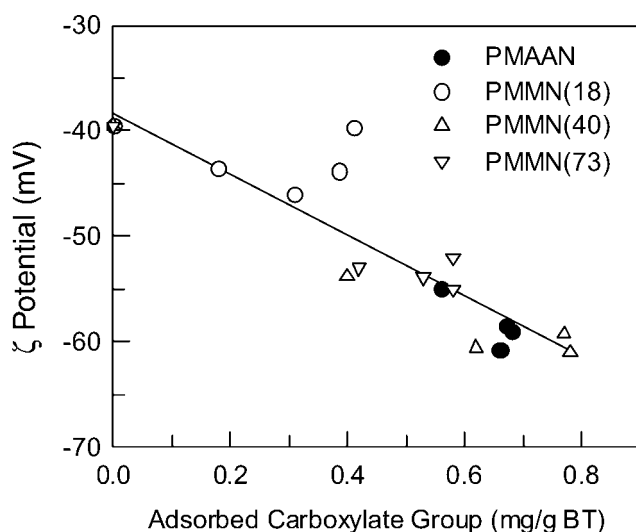


Figure 9 Relationship between the  $\zeta$  potential and adsorbed carboxylate groups.

tent decreases. A similar argument was made by Ben Romdhane et al.<sup>23</sup> in their study on dispersion properties of poly(sodium acrylate/vinyl alcohol) in alumina suspensions.

Figure 9 shows the relationship between the  $\zeta$  potential value of BT particles and the total amount of carboxylate groups of the adsorbed polymer on the BT surface. The total amount of carboxylate groups is the product of the amount of the adsorbed polymer by the content of the carboxylate group and its  $\alpha$  value. In fact, the  $\alpha$  value equals 1 for each polymer in aqueous solutions at pH 9, for all carboxylic acid groups convert into carboxylates completely under this condition. Except for a few data points, a linear relationship can be observed in Figure 9, confirming that the  $\zeta$  potential indeed depends linearly on the total amount of adsorbed carboxylate groups. Among the three PMMN( $n$ ) samples, PMMN(40) has the greatest value of the total amount of adsorbed carboxylate groups. This explains why PMMN(40) is most effective in reducing the viscosity of the resulting BT suspension.

### Sedimentation

Sedimentation observation and measurement constitute another way of examining the colloidal stability. A good dispersant will make suspensions remain cloudy and result in a small final sediment volume. Figure 10 shows the sedimentation behavior of 10 wt % BT suspensions with various amount of PMMN(40) at pH 9. For the suspension without any dispersant present, it is not stable and separates into two layers after 1 day of sedimentation; a clear boundary exists between a clear aqueous layer and a lower sediment layer. When 0.1 wt % PMMN(40) is

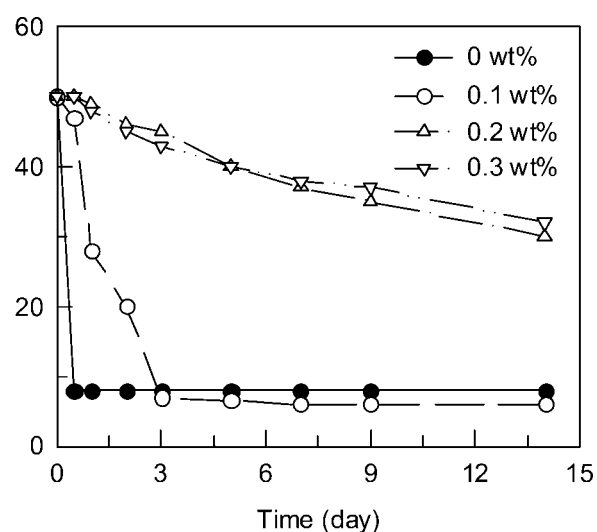
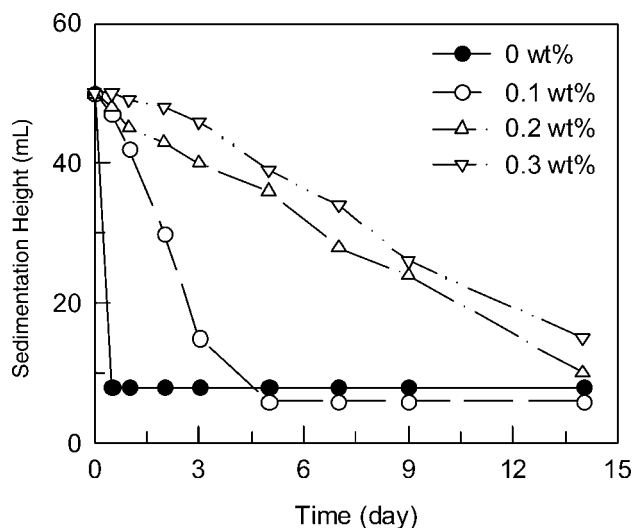


Figure 10 Effect of the PMMN(40) concentration on the sedimentation of 10 wt % BT suspensions at pH 9.



**Figure 11** Effect of the PMAAN concentration on the sedimentation of 10 wt % BT suspensions at pH 9.

added, the resulting suspension also separates into two layers after 1 day of sedimentation. However, the final sediment volume is less than that of the BT suspension without any dispersant present; this is evidence of denser packing of particles. When the incorporated PMMN(40) concentration is greater than 0.2 wt %, the resulting suspension becomes stable and remains cloudy for more than 14 days. A similar trend can be observed in Figure 11 for the sedimentation behavior of 10 wt % BT suspensions with PMAAN at pH 9. However, the thickness of the cloudy layer of BT suspensions with 0.2 wt % PMAAN after 14 days was observed to be lower than that with 0.2 wt % PMMN(40). This suggests that PMMN(40) is more effective than PMAAN in stabilizing BT particles in aqueous solutions.

## CONCLUSIONS

In this study, anionic water-soluble copolymers, that is, PMMNs with three MAM/MAN ratios, were synthesized and applied as additives for BT suspensions. By the use of the potentiometric titration method, the dissociation behavior and composition of PMMN were determined. The addition of PMMN could improve the dispersion of the BT particles; the resulting suspensions became less viscous and more stabilized. With the fraction of MAN increasing in PMMN, the amount of the carboxylate groups in the polymer increased, and the adsorbed amount of the polymer decreased. As a result, the BT suspensions incorporating PMMN with a MAM/MAN ratio of 60/40 appeared to have the greatest adsorbed amount of carboxylate groups and lowest  $\zeta$  potential value and became most effective in dispersing solid particles and making stable suspensions.

Amide groups in PMMN are expected to act as binders for ceramic suspensions. The effect of this polymer on the cohesion and strength of the resulting green compact is under investigation.

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