

Synthetic Amphoteric Copolymer as a Dispersant for Aqueous Barium Titanate Slurries

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ABSTRACT: An amphoteric water-soluble copolymer, i.e., poly(methacrylate-co-*N*-(4-vinylbenzyl)-*N,N*-dimethylglycinate) (PMV) was synthesized and used as a dispersion agent for barium titanate (BaTiO₃) (BT) particles. PMV was prepared from methacrylic acid and *N*-(4-vinylbenzyl)-*N,N*-dimethylglycinate in basic conditions through free radical polymerization. The structure of this copolymer was verified by its IR and ¹H-NMR spectra. The dispersing effects of PMV were examined and evaluated through viscosity and sedimentation measurements. The results indicate that

this copolymer could uniformly disperse the particles, make the resulting suspensions less viscous and more stabilized. The dispersing ability of PMV is better than that of a commercial dispersant, ammonium polymethacrylate (PMAAN). Accordingly, the BT compacts with PMV exhibit higher dielectric constant values than those with PMAAN. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1920–1928, 2010

Key words: synthesis; dispersions; polyelectrolytes; colloids

INTRODUCTION

Barium titanate (BaTiO₃) (BT) is a widely used material in making electronic devices.^{1,2} Tape casting is a common wet process in preparing BT green tapes or thin films.^{3–5} 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 suspensions is preferred on the basis of safe, economic, and environmental considerations.^{5,6} Normally, particles will separate each other in aqueous suspension because of electrostatic repulsion when their surfaces contain same ionic charges. However, only manipulating charges on particle surface by controlling pH or adding electrolytes is often not sufficient to obtain a well-dispersed and stabilized system. A more practical way of making a stable dispersion is generally through the use of ionic polymers or polyelectrolytes. These polymers will adsorb onto particles, modify the surface charges, and create electrostatic forces. Furthermore, the extension of adsorbed polymer molecules will induce steric and/or electrosteric forces.^{7,8} Consequently, the agglomer-

ates dissociate into primary particles, and the resulting suspensions become less viscous and more stable.

Acrylic acid-based polymers such as ammonium polyacrylate, sodium polymethacrylate, and ammonium polymethacrylate (PMAAN) are commonly used as dispersants for BT, alumina, and other ceramic powders in aqueous solutions.^{9–13} Besides, other types of dispersants have also been disclosed. For example, Baklouti et al.¹⁴ have prepared a sulfonic copolymer and determined the optimum conditions of the polymer to ensure stable alumina suspensions. Bouhamed et al.¹⁵ have synthesized a copolymer containing 2-acrylamido-2-methyl-propane sulfonic acid sodium salt and methoxypolyethyleneglycol methacrylate and indicated that the dispersing effect of the polymer was controlled by both the ionization level of the polymeric molecules and by the length of the polyethyleneglycol segments.

Generally, polymers containing specific functional groups will adsorb easily onto ceramic particles and create more electrostatic, steric, and/or electrosteric forces. Many studies have been undertaken to find appropriate polymers for this purpose. Kakui and Naito¹⁶ studied the effects of ammonium polyacrylate with different hydrophilic to hydrophobic group ratios for dense Al₂O₃ suspension and discussed the optimum molecular structure of the polymer to achieve a stable suspension. Several articles reported that polymers containing amide groups could interact with the ceramic surface and adsorb more onto the solid particles. Farrokhpay et al.¹⁷ investigated the role of polymer chemical functional groups in

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adsorption onto titania pigment particles and revealed that polymers containing hydroxyl and/or amide functional groups could interact with the pigment surface. Recently, we prepared three copolymers, i.e., poly(acrylamide-*co*-(α -*N,N*-dimethyl-*N*-acryloyloxyethyl)ethanate), poly(acrylamide-*co*-(α -*N,N*-dimethyl-*N*-(3-(β -carboxylate)acrylamino)propyl)ethanate), and poly(acrylamide-*co*-4-carboxylamino-4-oxo-2-butenate), and indicated that they were able to stabilize BT suspensions with particles less agglomerated.^{18–20} In this study, we have synthesized an amphoteric water-soluble copolymer, i.e., poly(methacrylate-*co*-*N*-(4-vinylbenzyl)-*N,N*-dimethylglycinate) (PMV), as a dispersant for BT slurries. PMV was prepared from methacrylic acid (MAA) and *N*-(4-vinylbenzyl)-*N,N*-dimethylglycinate (VBDMG) in basic conditions through free radical polymerization. The dispersion effects of this copolymer were examined by measuring the viscosity and sedimentation of BT suspensions. In addition, a commercial dispersant, i.e., PMAAN, was also tested for comparison.

EXPERIMENTAL

Materials

N-(4-Vinylbenzyl)-*N,N*-dimethylamine (90%, stabilized with 0.1% *P*-tertbutyl catechol), chloroacetic acid sodium salt (98%), ammonia (30%), and ammonium persulfate (98%) from Acros Organics (Morris Plains, NJ), MAA (99%, stabilized with 0.03% hydroquinone) from Showa Chemical Industry (Tokyo, Japan), and 2-methyl-2-propene-1-sulfonic acid sodium salt (>98%) from Tokyo Chemical Industry (Tokyo, Japan) were used without further purification. PMV was prepared from the chemicals mentioned previously and a weight-average molecular weight of 3.3×10^4 . In

addition, PMAAN, a common dispersant supplied from R. T. Vanderbilt (Norwalk, CT), was also used. The weight-average molecular weight of PMAAN is 1.3×10^4 .

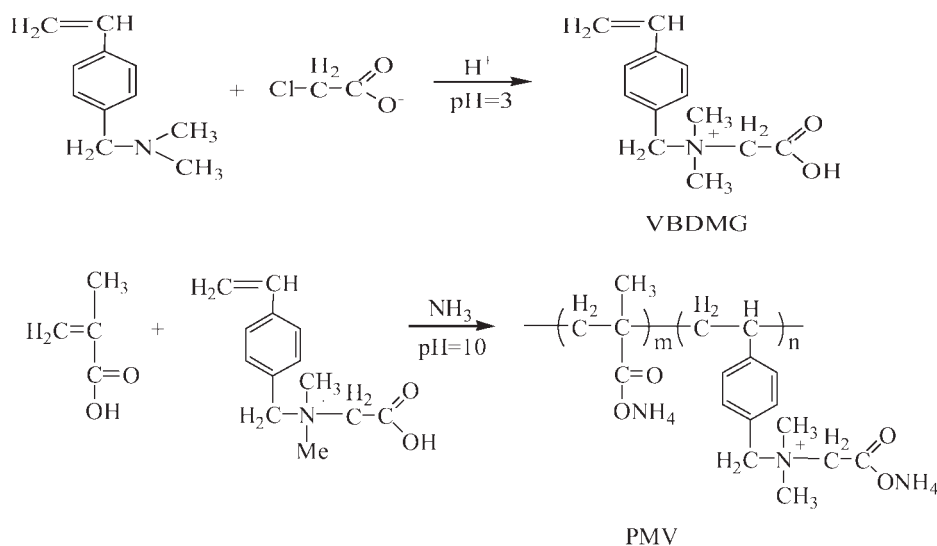
The ceramic powder used was a high purity BT (Prosperity Dielectrics, Taoyuan, Taiwan). The powder has a Ba/Ti ratio of 0.997, an average (d_{50}) particle size of 0.94 μm , and a Brunauer-Emmett-Teller specific surface area of 2.51 m^2/g . Deionized and distilled water were used, the pH of suspensions was adjusted by the addition of either $\text{HCl}_{(\text{aq})}$ or $\text{NaOH}_{(\text{aq})}$.

Preparations of PMV resins

PMV was prepared from MAA and VBDMG through free radical polymerization. VBDMG was prepared from *N*-(4-vinylbenzyl)-*N,N*-dimethylamine and chloroacetic acid sodium salt. The reaction equations for the preparation of VBDMG and PMV are shown in Scheme 1.

VBDMG and PMV were prepared as follows: sodium chloroacetate (0.3 mol) dissolved in 200 g deionized water, the solution was adjusted to a pH of about 3, followed by addition of *N*-(4-vinylbenzyl)-*N,N*-dimethylamine (0.3 mol). Thereafter, the mixture was added to a 500-mL stirred reactor. The reaction proceeded at 70°C for 12 h. After the reaction, a majority of the solvent was removed in a vacuum condenser, the product was precipitated and purified with acetone. The acetone was removed in a vacuum oven at 85°C for 30 min. A brownish precipitate (62.5 g), i.e., VBDMG, could be collected.

MAA (0.1 mol) was dissolved in 20 g deionized water, the solution was adjusted to a pH of about 10 using 1N $\text{NH}_{3(\text{aq})}$, and then 0.1 mol of VBDMG dissolved in 100 g deionized water was added dropwise



Scheme 1 Synthesis of VBDMG and PMV.

into a 250-mL stirred reactor, followed by ammonium persulfate (1.37 g) was added as the initiator. After mixing in a nitrogen atmosphere for 30 min, 2-methyl-2-propene-1-sulfonic acid sodium salt (0.95 g) was then added as a chain-transfer agent. The polymerization was carried out at 70°C for 8 h. The mixture was vacuum filtered, washed with acetone, and the precipitate was dried in a vacuum oven at 85°C for 30 min, a reddish product (22.7 g), i.e., PMV, was then obtained.

Identification of prepared resins

The dried monomer or PMV resin was ground into powder before the determination of the structure or other procedures. In identifying the chemical structure, proper amount of powder samples was mixed with predried KBr and pressed into disks. Transmission infrared spectra of the disks were obtained with a PerkinElmer Paragon 500 Fourier transform infrared spectrometer (Boston, MA). Moreover, some powder samples were also dissolved in D₂O, and ¹H-NMR spectra were obtained with a NMR spectrometer (BRUKER AVANCE, 500 MHz, Rheinstetten, Germany). The dissociation behavior and the fraction of dissociated carboxylate groups for polymers at various pH values can be determined from potentiometric titrations of the polymer solutions.^{21,22} The molecular weight of the polymers was measured by the gel permeation chromatography method, which has been reported in detail elsewhere.²⁰

Preparation of the BT suspensions

Aqueous suspensions containing 10 or 60 wt % BT were prepared. They contained 0–0.5 wt % dispersant 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. The 24-h period of milling was believed to be long enough for a homogeneously dispersed state to be reached.

Viscosity measurements of BT suspensions

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

Zeta potential measurements of BT particles

A total of 60 wt % BT aqueous suspensions at pH 9 with dispersants were prepared. After ball-milled, 1.5 μ L suspensions were taken and diluted in 100 mL deionized water, which was adjusted to pH 9 previ-

ously. Samples were measured with a ζ -Meter 3.0+ (ζ -Meter, Staunton, VA).

Adsorption of the polymers onto BT particles

A total of 60 wt % BT suspensions with different concentrations of polymers were prepared at pH 9. After ball-milling, the suspensions were centrifuged at a speed of 8000 rpm for 60 min to obtain supernatants. A known volume of the supernatant was diluted with distilled water to 60 mL, the pH value adjusted to 12, and then the polymer concentration could be determined by titrating the diluted supernatant using 0.1N HCl_(aq) in a TitroLine Alpha Plus automatic titrator (Schott-Geräte GmbH, Mainz, Germany). The amount of polymer adsorbed onto BT was calculated from the difference in the dispersant concentration before and after adsorption.²²

Sedimentation tests of BT suspensions

A total of 10 wt % BT aqueous suspensions 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 dispersion volume along with the time was measured and recorded.

Microstructure observation of BT green compacts

BT compacts were made through the gravitational settlement and consolidation of 60 wt % BT suspensions with or without the presence of dispersants. The microstructures of BT green compacts were observed with a JSM-6500F scanning electron microscope (SEM) (JEOL, Tokyo, Japan).

Dielectric properties of BT sintered compacts

A totals of 60 wt % BT slurries with different concentrations of polymers were prepared at pH 9. The green disc samples were formed after the BT slurries were subjected to drying, grinding, and compacting. Thereafter, disc specimens were sintered at 1280°C for 6 h. The dielectric properties of sintered samples at room temperature were measured at a frequency of 1 kHz using an impedance analyzer (HP 4284, Palo Alto, CA).

RESULTS AND DISCUSSION

Structure of prepared resins

The structure of the prepared monomer or polymer was verified from its IR and ¹H-NMR spectra. Figure 1 shows the IR spectrum of VBDMG. The OH band appears in the region of 3600–3200 cm⁻¹. The adsorption peaks in the region of 1700–1500 cm⁻¹

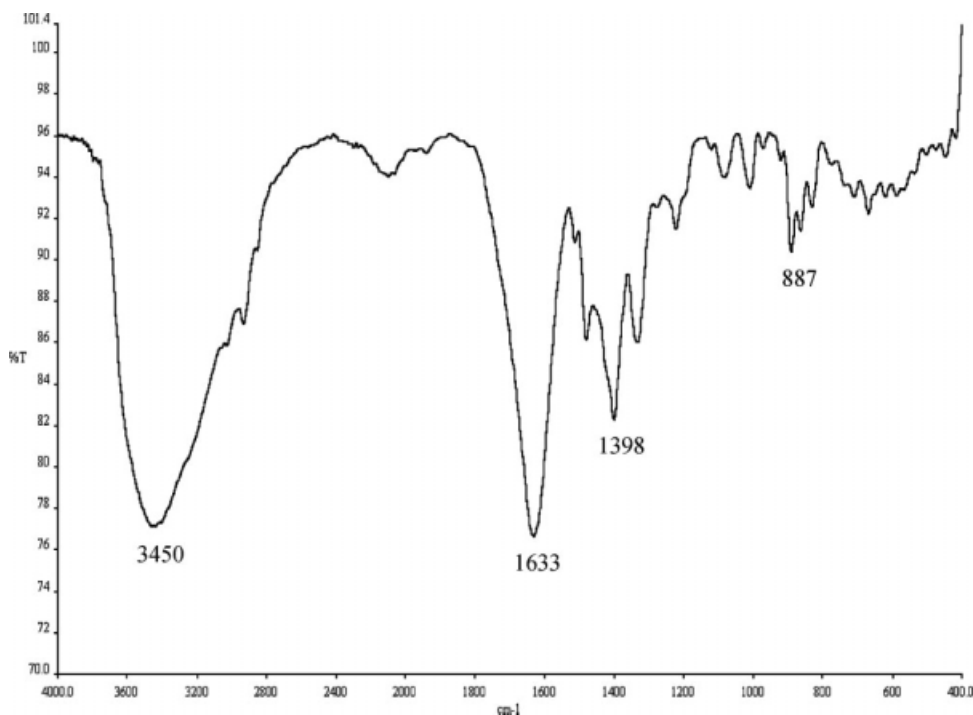


Figure 1 The IR spectrum of VBDMG.

are attributed to the overlapping of C=C, C=O, and aryl functional groups. The peak at 1398 cm⁻¹ represents the C—N band and that near 887 cm⁻¹ represents the C—H of aromatic ring. The ¹H-NMR spectrum in Figure 2 gives signals at $\delta = 7.5\text{--}7.7$ (Ar), 6.8 (1H), 6.0 (2H), 5.5 (3H), 4.7 (4H), 3.7 (5H), and 3.2 ppm (6H). Figure 3 displays the IR spectrum of PMV. The broad peak in the region of 3600–

2800 cm⁻¹ was caused by OH stretching and the peak at 1656 cm⁻¹ was assigned to the C=O stretching vibration band of the carboxylate group. The absorption band appears at 1200 cm⁻¹ results from the C—H bending of the aromatic ring. The presence of peak at 1399 cm⁻¹ indicates the C—N band. The ¹H-NMR spectrum of PMV shown in Figure 4 gives signals at $\delta = 7.0\text{--}7.5$ (Ar), 3.6–3.8 (1H), 3.0–3.3 (2H),

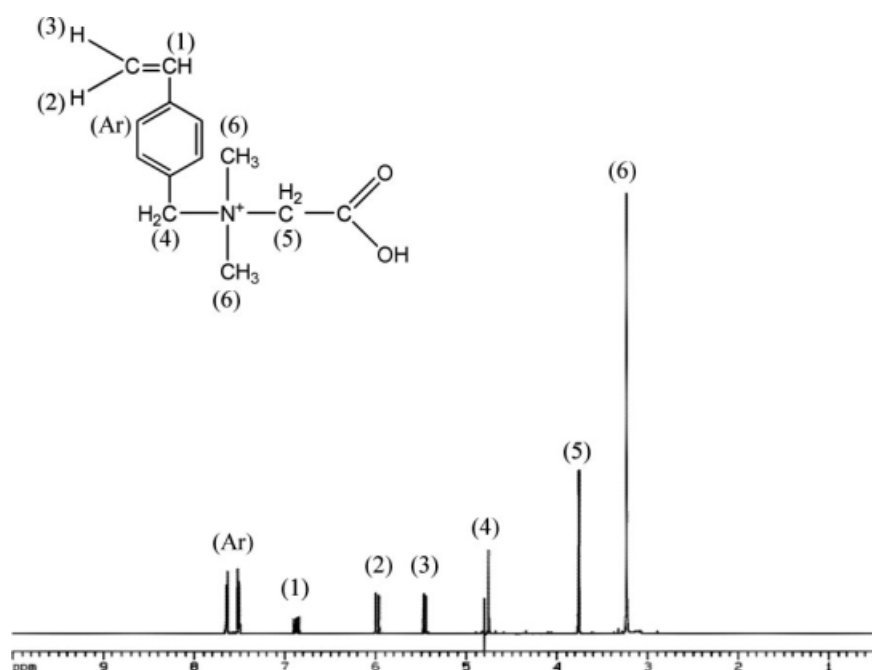


Figure 2 The ¹H-NMR spectrum of VBDMG.

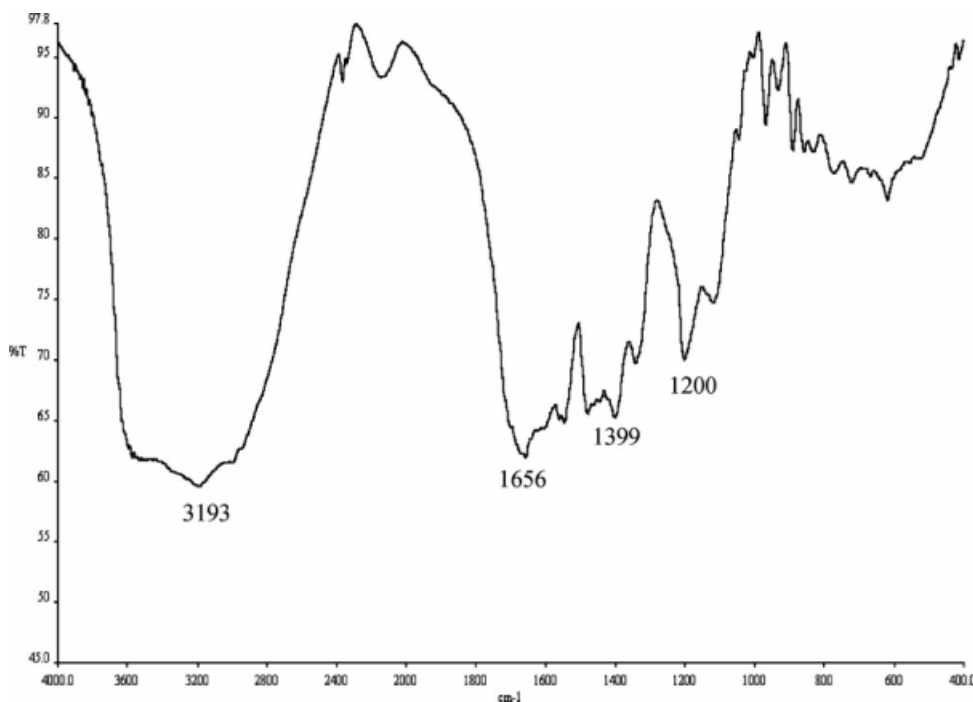


Figure 3 The IR spectrum of PMV.

1.5–2.0 (3H), 1.1–1.3 (4H), and 0.8–1.1 ppm (5H).²³ The ¹H-NMR spectrum of the copolymer shows that there are no double bonds that appear between 5.5 and 6.8 ppm in the monomer spectrum. This indicates the formation of copolymer from its two monomers. Furthermore, the amphoteric monomer content in copolymer is calculated from the ratio of peak area of the aromatic ring (Ar) to that of the CH₃ group (5H) in the polymer backbone. The pK_a of PMV is close to that of poly(methacrylic acid) reported by Kirby et al.,²⁴ the dissociation behavior of PMV was believed to be similar to that of PMAAN. Table I lists the characteristics of PMV polymer.

Rheological behavior of BT suspensions

The viscosity measurement is applied to evaluate the degree of powder dispersion in concentrated suspensions and the effectiveness of a dispersing agent.^{12,25} Usually, the viscosity of a concentrated suspension is higher if powder was agglomerated. The viscosity of a suspension could be decreased when a suitable dispersant was incorporated. The extent of decrease in viscosity depends on the effectiveness of the dispersant in reducing the agglomerate size. Figure 5 shows the viscosity of 60 wt % BT suspensions at pH 9 as a function of dispersant concentration. The viscosity of BT suspension without dispersant is about 2000 mPa s. The suspensions become less viscous when PMV is added, indicating that this polymer could enhance the dispersion of BT particles. As the polymer con-

centration is increased, the viscosity of suspensions decreases first, reaches a plateau, and then increases slightly afterward. The critical polymer concentration to achieve the lowest viscosity value is about 0.2 wt %. A similar trend was also observed from Figure 5 for the BT suspensions containing PMAAN. The amount of PMAAN required to achieve the lowest viscosity is about 0.1 wt %, which is less than that of PMV required.

Although similar rheological behavior was observed for 60 wt % BT suspensions containing either PMV

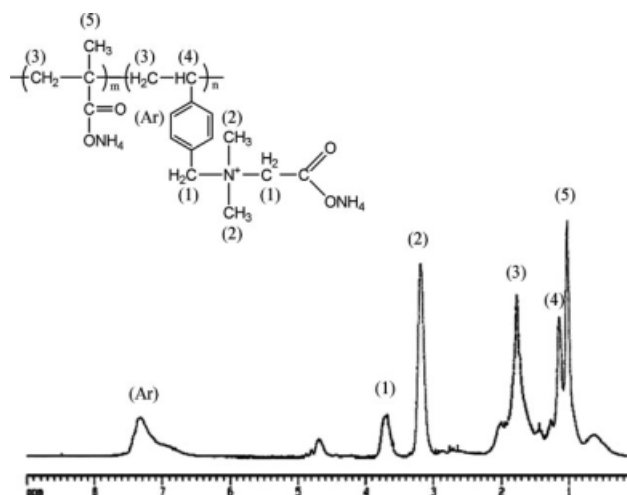


Figure 4 The ¹H-NMR spectrum of PMV.

TABLE I
Properties of the PMV Polymer

Composition MAA/VBDMG	Weight-average molecular weight	Number-average molecular weight	pH of fully dissociated	pKa	Yield (%)
57 : 43	3.3×10^4	2.6×10^4	7.7	4.9–6.0	59

or PMAAN, the dispersing mechanism was believed to be somewhat different for these two polymers. PMAAN molecules are anionic polyelectrolytes, which cause mainly electrostatic repulsions when they were adsorbed onto BT particles. In contrast, PMV molecules also cause electrostatic repulsions when adsorbed onto BT particles. However, the effect would be less than that by PMAAN molecules because they belong to amphoteric polyelectrolytes. Figure 6 shows the effect of the dispersant concentration on the ζ potential of 60 wt % BT suspensions at pH 9. Generally, the ζ potential becomes more negative when dispersants are present in the suspensions. The ζ potential decreases with increasing PMV concentration initially, approaches a minimal value, and then increases afterward. For suspensions with PMAAN, the initial decreasing rate of the ζ potential is greater, and the potential value at a certain polymer concentration is more negative than that of suspensions with PMV. This confirms that PMAAN causes stronger electrostatic forces among particles than PMV. Nevertheless, PMV is expected to produce more steric effect than PMAAN. This is because PMV molecules have higher molecular weight and their VBDMG moieties possess certain side chain length. Steric stabilization of particles is imparted by polymers that are adsorbed onto the surfaces of the particles. For many common carbon backbone polymers, the chain dimensions, R , can be estimated using the following equation^{24,26}:

$$R(\text{nm}) = 0.06(M_w)^{1/2} \quad (1)$$

where M_w is the weight-average molecular weight of the polymer. The dimensions of polymer molecules in solution when adsorbed on colloid surfaces influence the ability of polyelectrolyte to stabilize suspensions. These values of R calculated from Eq. (1) were about 10.9 nm for PMV and 6.8 nm for PMAAN, respectively. The spatial extension of PMV molecules attached to the surfaces of the particles is greater than that of PMAAN. In addition, PMV whose molecular structure contains $-\text{NR}_3^+$ and aromatic ring that would be adsorbed easier onto negatively charged surface of BT particles than PMAAN because of charge neutralization and aryl hydrophobic characteristics. Figure 7 shows the adsorption amount of polymers onto BT powder in suspensions at pH 9 as a function of the initial polymer concentrations. The adsorbed amount increases with increasing polymer concentration, then reaches a plateau. The plateau corresponds to the saturated amount of polymer required for a monolayer coverage. The amount of PMV adsorbed onto BT is three times greater than that of PMAAN. Thicker and denser adsorption layer will create more steric force than PMAAN among particles.

Sedimentation behavior of BT suspensions

The sedimentation observation and measurement is another way for examining the colloidal stability. A

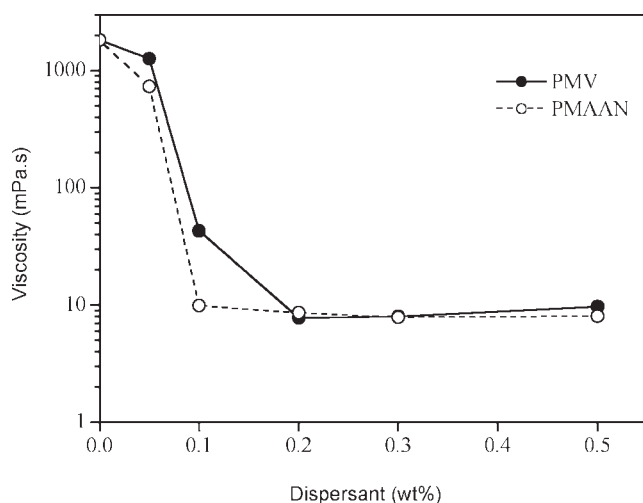


Figure 5 Effect of the dispersant concentration on the viscosity of 60 wt % BT suspensions at pH 9.

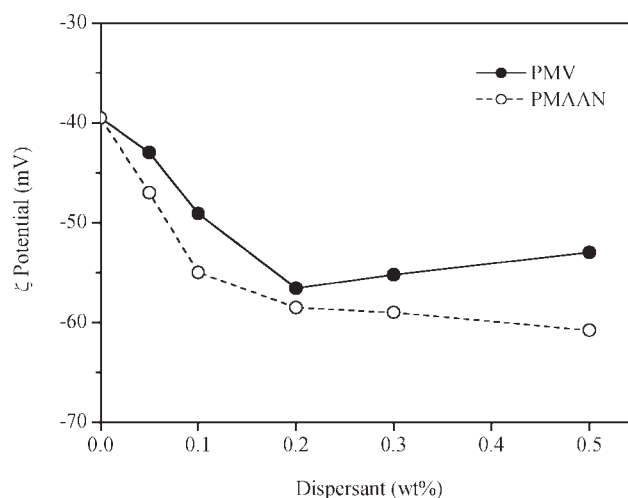


Figure 6 Effect of the dispersant concentration on the ζ potential of 60 wt % BT suspensions at pH 9.

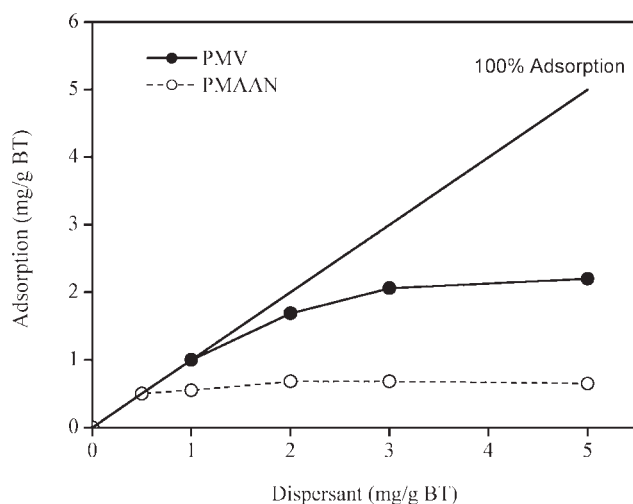


Figure 7 Effect of the initial dispersant concentration on the adsorption amount of the polymer onto BT particles.

good dispersant will make suspensions to remain cloudy for a long time and result in a small final sediment volume.^{27,28} Figure 8 shows the sedimentation behavior of 10 wt % BT suspensions with various amount of PMV at pH 9. The higher the dispersion volume, the more stable the suspension. For the suspension without any dispersant present, it is not stable and separates into two layers after 1-day sedimentation; a clear boundary exists between a sediment layer and an upper clear aqueous layer. When 0.1 wt % PMV was added, the resulting suspension also separated into two layers after 2-day sedimentation. However, the final sediment volume is less than that of the BT suspension without any dispersant, as an indication of denser packing of par-

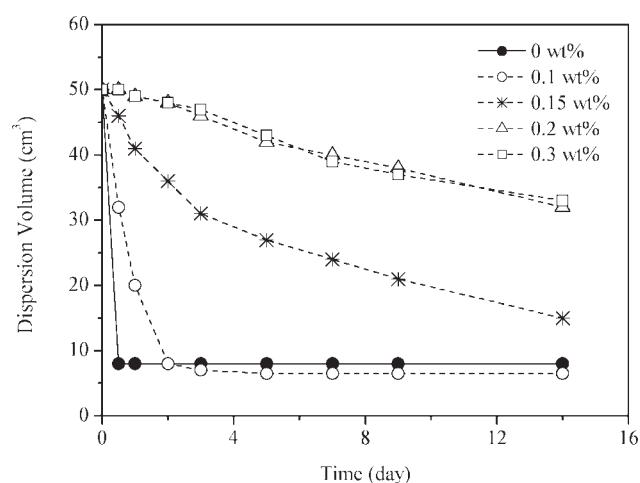


Figure 8 Effect of the PMV concentration on the sedimentation of 10 wt % BT suspensions at pH 9.

ticles. When the amount of incorporated PMV is greater than 0.15 wt %, the resulting suspensions become stable and maintain cloudy partly for 14 days. A similar trend can be observed in Figure 9 for the sedimentation behavior of 10 wt % BT suspensions with PMAAN at pH 9. Apparently, when PMAAN was added, the stability of suspensions improved. The resulting suspensions become more stable and remain cloudy longer if incorporating more PMAAN. 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 0.15 wt % PMV. This suggests that PMV is more effective than PMAAN in stabilizing BT particles in aqueous solutions.

SEM observation of green BT compacts

Figure 10 shows SEM micrographs of the green compacts obtained from the gravitation, sedimentation, and consolidation of 60 wt % BT suspensions with or without the presence of 0.2 wt % dispersant. The compact with no dispersant appears to be more porous, and the particles are more agglomerated. In contrast, the suspensions with the dispersant show lower viscosity and form denser and more consolidated compacts. Apparently, the particles in the compacts with PMV appear to be dispersed more uniformly than those with PMAAN. This proves that PMV is better than PMAAN in dispersing BT particles.

Dielectric constant of sintered BT compacts

Figure 11 shows the effect of the dispersant concentration on the dielectric constant of the BT samples sintered at 1280°C. The dielectric constant of BT

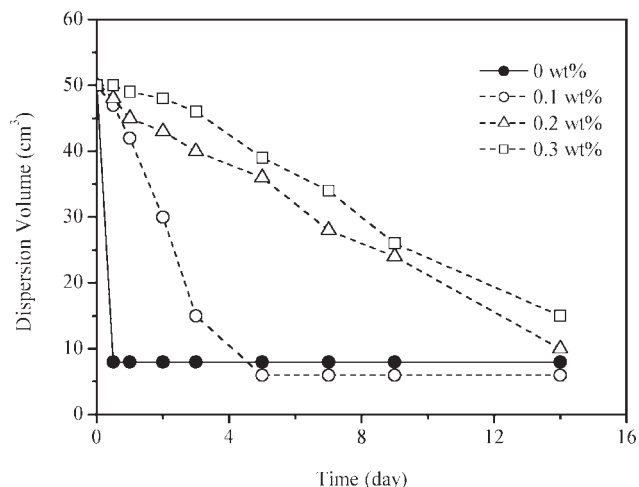


Figure 9 Effect of the PMAAN concentration on the sedimentation of 10 wt % BT suspensions at pH 9.

sample without any dispersant present is 1512. The dielectric constant of sample increases as polymer concentration is increased first, reaches a maximal value, and then decreases slightly afterward. The dielectric constant of sample with PMV is slightly higher than that with PMAAN when the added polymer dosage is more than 0.2 wt %. This indicates that PMV indeed provides a better dispersion

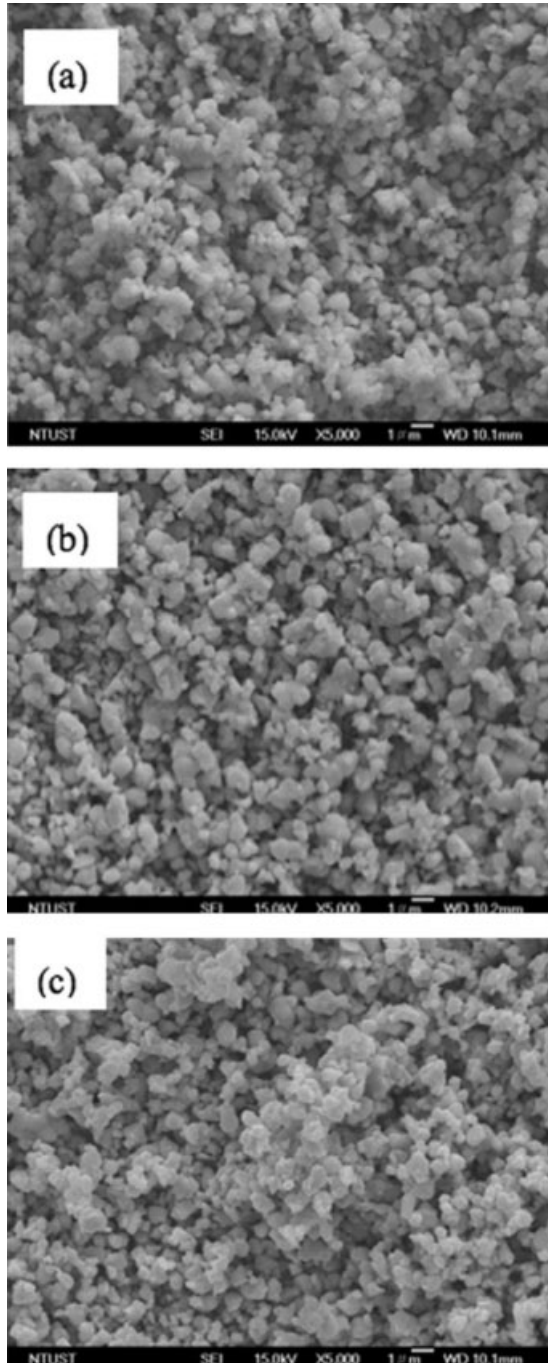


Figure 10 SEM micrographs of the green compacts from 60 wt % BT suspension with (a) no dispersant, (b) 0.2 wt % PMV, and (c) 0.2 wt % PMAAN.

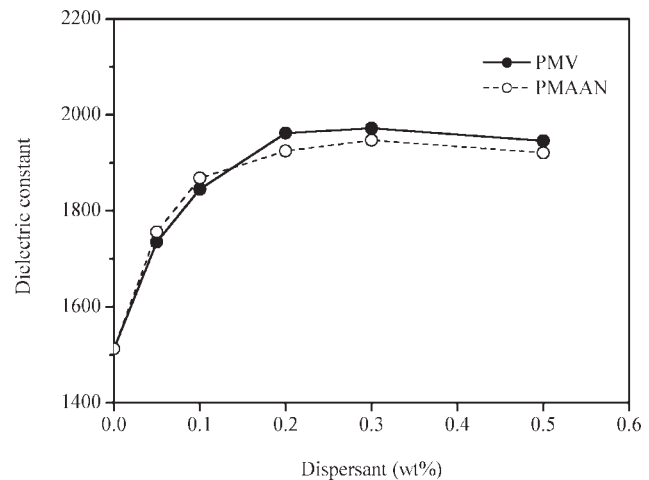


Figure 11 Effect of the dispersant concentration on the dielectric constant of sintered BT samples.

effect than PMAAN, causes BT particles to be more densely packed, and thus increases the dielectric constant of the resulting sintered BT sample.

CONCLUSIONS

In this study, an amphoteric water-soluble copolymer, i.e., PMV, was synthesized, and the chemical structure was verified by the IR and ¹H-NMR spectra. As PMV could uniformly disperse the BT particles, the resulting suspensions with this polymer become less viscous and more stabilized. This is because the adsorbed PMV molecules cause not only electrostatic repulsions but also some steric effect. Apparently, PMV is more effective than PMAAN in dispersing BT particles. As a result, the BT sintered compacts with PMV show higher dielectric constant values than those with PMAAN.

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