

Effect of Molecular Weight of an Anionic Dispersant on the Properties of BaTi₄O₉ Slurries

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ABSTRACT: The colloidal stability of BaTi₄O₉ (BT₄) aqueous suspensions with poly(acrylamide-co-4-carboxylamino-4-oxo-2-butenate) (PAC) of different molecular weights at pH 9 has been investigated by means of zeta potential, adsorption, sedimentation, and particle size measurements. The results indicate that PAC could improve the dispersion of the particles from agglomeration. The resulting suspensions became more stabilized, and contained powder with smaller particle size. Consequently, the compacts with PAC exhibited better properties in terms of density and dielectric constant than those

without any polymer present. The performance of PAC increased with decreasing polymer molecular weight. Clearly, PAC1 ($M_w = 1.8 \times 10^4$) was most effective in dispersing the BT₄ particles, and stabilizing the ceramic suspensions. This is attributed to the highest adsorption of this polymer onto BT₄ powder, and causes strongest electrostatic repulsions among solid particles. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1598–1604, 2012

Key words: anionic polymer; molecular weight; dispersion; adsorption; BaTi₄O₉

INTRODUCTION

Barium titanates are important electronic ceramics which have good dielectric properties and are extensively used in the production of electronic devices. For example, BaTiO₃ (BT) is used in making multi-layer capacitors and piezoelectric sensors; BaTi₄O₉ (BT₄) is used in making resonators and filters for microwave communications.^{1–5} Tape casting is a common wet process in preparing the green tapes or thin films of barium titanates.^{6,7} To produce these ceramic green tapes with a uniform microstructure and high packing density, the preparation of well-dispersed slurries is a prerequisite. Traditionally, organic solvents are used to disperse the powder. Nowadays, the preparation of aqueous suspensions is preferred on the basis of safety, economic, and environmental considerations.^{8,9}

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 sta-

ble 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.^{10,11} Consequently, the agglomerates dissociate into primary particles, the suspensions become less viscous and more stable, and the resulting green and sintered compacts show higher packing densities and greater strength or other properties.

Acrylic acid-based polymers such as ammonium polyacrylate, sodium polymethacrylate, and ammonium polymethacrylate (PMAAN) are commonly used as dispersants for barium titanate, alumina, and other ceramic powders in aqueous solutions.^{12–17} Besides, other types of dispersants have also been disclosed. For example, Baklouti et al.¹⁸ have prepared a sulfonic copolymer and determined the optimum conditions of the polymer to ensure stable alumina suspensions. Bouhamed et al.¹⁹ have synthesized a copolymer containing 2-acrylamido-2-methyl-propane sulfonate and methoxypoly(ethylene glycol) 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 poly(ethylene glycol) segments. In our laboratory, we have prepared two amphoteric copolymers and shown that the polymers with proper reactant ratios and molecular weights were effective in dispersing BT particles in aqueous solutions.^{20,21} Finally, Versluis et al.²² indicated that carrageenans which were negatively charged biopolyelectrolytes containing sulfate

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TABLE I
Basic Properties of the BT₄ Powder

BaO (%)	29.5
ZnO (%)	6.8
Nb ₂ O ₅ (%)	3.3
TiO ₂ (%)	59.5
Median (<i>d</i> ₅₀) particle size (μm)	0.723
Compressed density (g/cm ³)	2.43
Theoretical density (g/cm ³)	4.6
BET specific surface area (m ² /g)	5.13

groups could suspend and stabilize CaCO₃ particles in neutral systems by absorbing on the particle surface and providing charge and steric stabilization that prevented reaggregation of the dispersed particles.

It is clear that dispersant is an essential chemical in the processing of ceramic slurries. Therefore, new and more effective dispersants are worth developing. Previously, we synthesized an anionic copolymer, i.e., poly(acrylamide-co-4-carboxylamino-4-oxo-2-butenate) (PAC). This polymer was found to be effective in dispersing BT particles in aqueous media.²³ In this study, the effects of PAC on the dispersion properties of BT₄ in solutions were further investigated. It is well recognized that polymer molecular weight is one of the important factors that control the conformation of polymer and the adsorption behavior onto particle surface, and govern the dispersing properties of the resulting ceramic slurries.^{16,24,25} In this work, the effect of molecular weight of PAC on the dispersion properties of BT₄ suspensions was examined and discussed.

EXPERIMENTAL

Materials

The ceramic powder used was BT₄ from Prosperity Dielectrics (Taoyuan, Taiwan). The powder had a Ba/Ti ratio of about 1/4, an average size of 0.72 μm, and a Brunauer–Emmett–Teller (BET) specific surface area of 5.13 m²/g. Table I lists the basic properties of the BT₄ powder.

PAC was evaluated as a dispersant for BT₄ slurries. PAC was prepared from acrylamide (AM) and 4-carboxylamino-4-oxo-2-butenate (COB) through free-radical polymerization. Details of the preparation procedure were reported previously.²³ Figure 1 shows the chemical structure of PAC. The prepared polymer samples had a fixed AM/COB ratio of 1/1 and four different molecular weights, as listed in Table II. The molecular weight of polymer was determined by gel permeation chromatography, as described elsewhere.²³

Preparations of BT₄ suspensions

Aqueous suspensions containing either 20 or 60 wt % BT₄ were prepared. They contain 0–1.5 wt % PAC

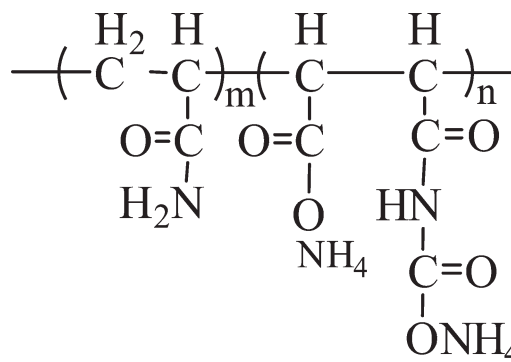


Figure 1 The chemical structures of PAC polymer.

with respect to the weight of the dry BT₄ 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 to attain a dispersed state homogeneously. After ball-milling, the BT₄ suspensions were adjusted to various pH values by the addition of either aqueous HCl or NaOH. Unless specified otherwise, the pH value of the suspensions was fixed at 9 in this study.

Measurements of dispersion properties

The dispersion properties were determined by observing the sedimentation behavior of BT₄ powder and measuring the particle size in the suspension. Experimentally, 20 wt % BT₄ suspensions were prepared and poured into 50-mL graduated cylinders. These suspensions were left in the cylinders for 30 days, and the change of the dispersion volume along with the time were measured and recorded. Besides, the particle size of the solid particles in 20 wt % BT₄ slurries was determined with a Mastersizer 2000 particle size analyzer (Malvern, Worcestershire, UK).

Separately, 20 wt % BT₄ suspensions at various pH values were prepared. 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 zeta potential of the remaining powder in the supernatant was measured with a Malvern Zetasizer 3000HSA. Furthermore, the residual dispersant concentration in the supernatants was analyzed and determined by a

TABLE II
Molecular Weights of PAC Samples

Polymer	<i>M_w</i>	<i>M_n</i>
PAC1	1.8×10^4	1.0×10^4
PAC2	6.0×10^4	1.8×10^4
PAC3	1.0×10^5	2.3×10^4
PAC4	2.8×10^5	7.4×10^4

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

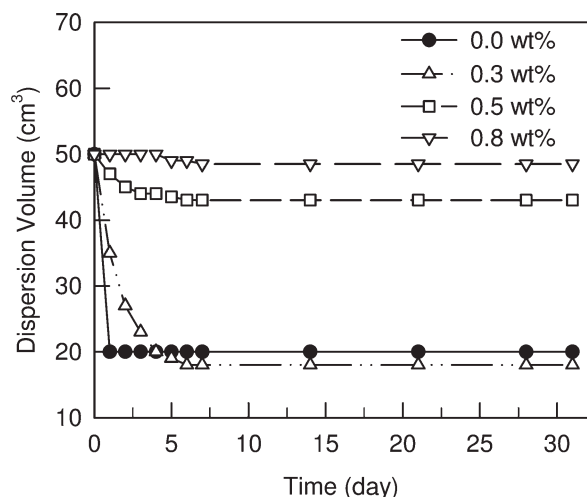


Figure 2 The sedimentation behavior of 20 wt % BT_4 suspensions with PAC1.

titration procedure from the literature.²⁶ The amount of dispersant adsorbed on BT_4 was calculated from the difference in the dispersant concentration before and after adsorption.

Measurements of compact properties

Green compacts were made from the gravitational settlement and consolidation of 60 wt % BT_4 suspensions with or without the presence of dispersants. Furthermore, sintered samples were made from sintering the green compacts in air, with heating and cooling rate of 10 °C/min and 6 h soaking time at 1150°C. Both the green density and sintered density of compacts were determined by the Archimede's method. Besides, the dielectric constant of sintered samples was measured at a frequency of 1 kHz using an impedance analyzer (HP 4284A, Agilent, Santa Clara, CA).

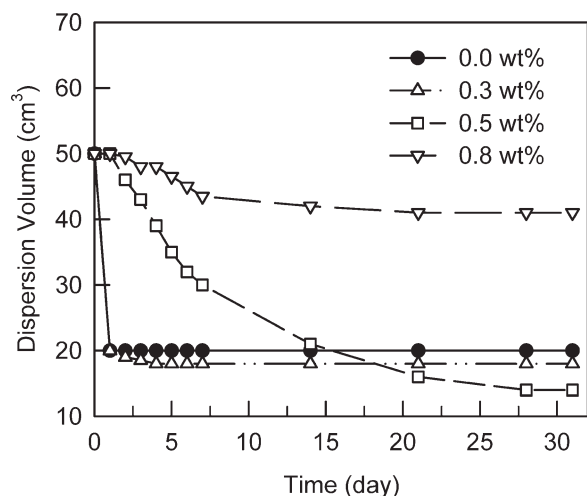


Figure 3 The sedimentation behavior of 20 wt % BT_4 suspensions with PAC2.

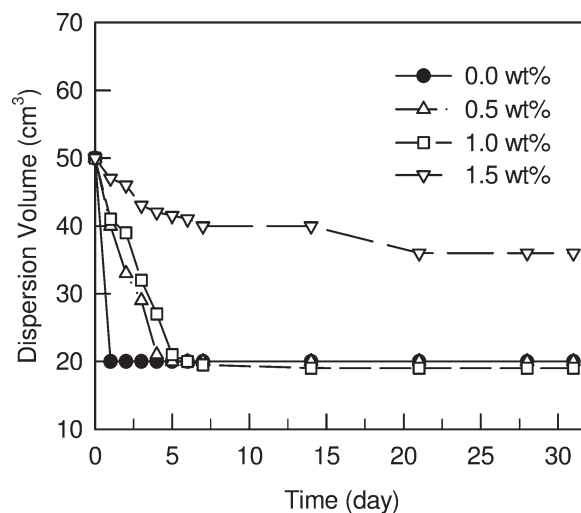


Figure 4 The sedimentation behavior of 20 wt % BT_4 suspensions with PAC3.

RESULTS AND DISCUSSION

The dispersion properties of BT_4 suspensions

Ceramic particles in the solutions often agglomerate each other because of attractive van der Waals forces. The smaller the particles, the easier they agglomerated together. Addition of dispersants could disperse the particles, reduce the agglomerated size, and stabilize the resulting suspension.^{21,25} In this study, the colloidal stability and the effectiveness of a dispersant were determined by observing the sedimentation behavior of BT_4 suspensions and measuring the particle size of particles in aqueous solutions.

Figure 2 shows the sedimentation behavior of 20 wt % BT_4 suspensions with various amounts of PAC1. For the suspension without any dispersants present, two distinct layers were observed after the

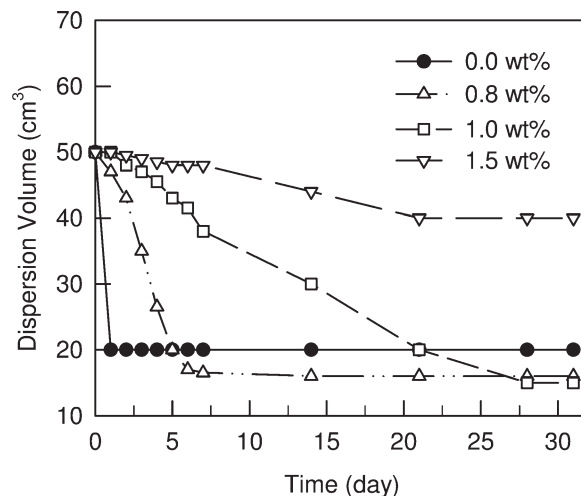


Figure 5 The sedimentation behavior of 20 wt % BT_4 suspensions with PAC4.

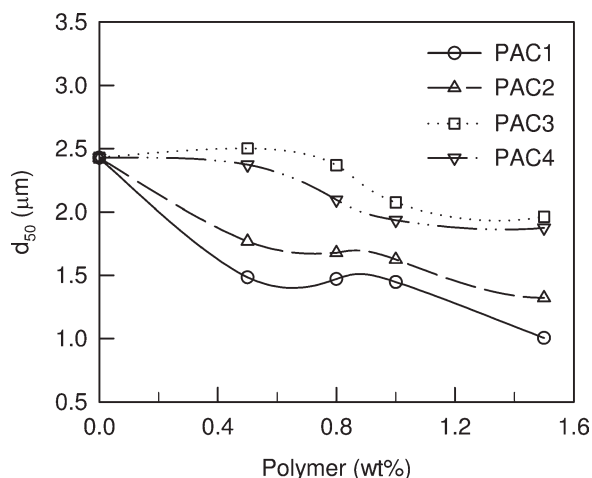


Figure 6 The d_{50} particle size of 20 wt % BT₄ suspensions with PAC.

sedimentation of 1 day. These two layers were a clear aqueous layer on the top and a sediment layer. Addition of PAC1 improved the colloidal stability. When 0.3 wt % polymer was added, the resulting suspension remained cloudy longer, and separated into two layers after 5-day sedimentation. Besides, the volume of the final sediment layer was less than that of the BT₄ suspension without the presence of any polymer, as an indication of denser packing of particles.^{21,27} If more than 0.5 wt % PAC1 was added, the resulting suspensions became more stabilized and remained cloudy even settled after 30 days. Similar sedimentation behaviors were observed for the BT₄ suspensions with other three PACs, as are shown in Figures 3–5. However, greater amount of polymer was required to make the suspensions remaining cloudy for 30 days. The required amount of PAC2 was 0.8 wt %; that of either PAC3 or PAC4 was 1.5 wt %.

Figure 6 shows the median (d_{50}) particle size of 20 wt % BT₄ suspensions with PAC of different molecu-

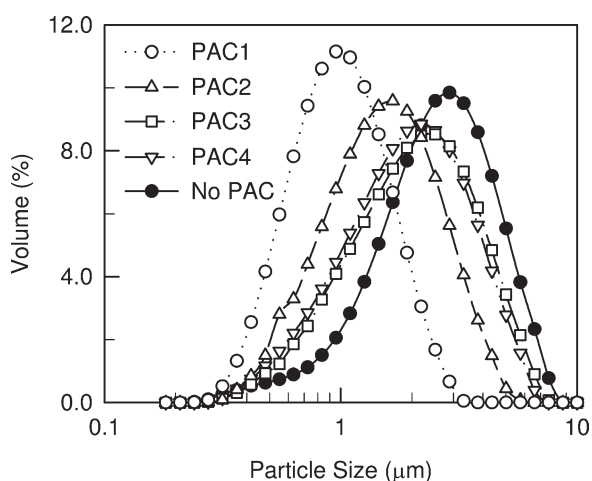


Figure 7 The particle size distribution of 20 wt % BT₄ suspensions with 1.5 wt % PAC.

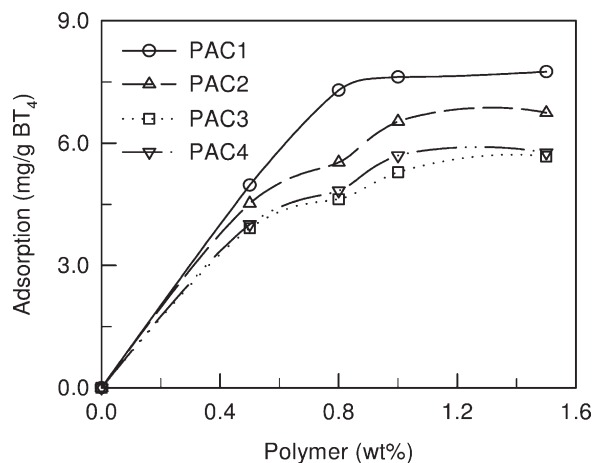


Figure 8 The adsorbed amount of PAC on BT₄ particles as a function of the initial polymer concentration.

lar weights. For the suspension without any dispersant present, the d_{50} value was about 2.4 μm , which was much greater than the true median particle size (0.9 μm) provided by the supplier. This indicates that particles in the slurry were not stable and agglomerated with each other. When PAC was added, the particle sizes shifted to smaller values. Along with increasing polymer concentration, the d_{50} value decreased gradually. Different molecular weight of PAC caused different effect in shifting the particle size. Among the four tested polymers, PAC1 appeared to be most effective and the d_{50} value was smallest, followed by PAC2, PAC4, and PAC3.

Figure 7 shows the particle size distribution of 20 wt % BT₄ suspensions with 1.5 wt % PAC of different molecular weights. Regardless of which polymer incorporated, the suspensions with 1.5 wt % PAC were stable and remained cloudy for 30 days, as are indicated in Figures 2–5. Compared to the suspension without any polymer present, addition of PAC

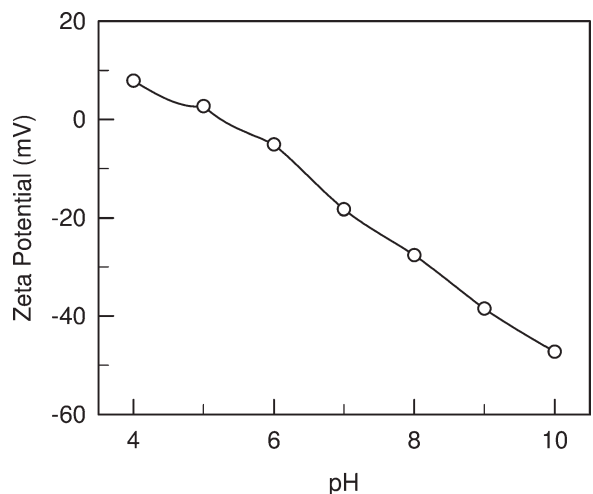


Figure 9 The zeta potential of particles in 20 wt % BT₄ suspensions at various pH values.

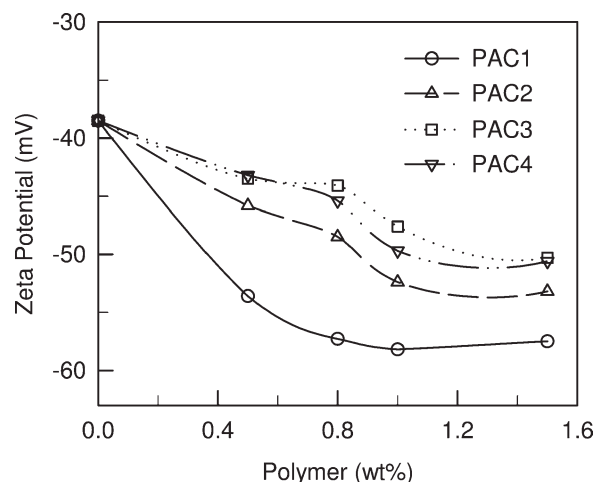


Figure 10 Effect of polymer concentration on the zeta potential of 20 wt % BT_4 suspensions.

could shift the particle size to smaller values. The degree of shifting increased in the following order: PAC1 > PAC2 > PAC3 \approx PAC4. It is clear that PAC1 ($M_w = 1.8 \times 10^4$) was most effective in dispersing BT particles and resulted in smallest particle sizes.

The above results indicate that PAC could disperse BT_4 particles, stabilize the suspensions, and lead to smaller particle sizes. Apparently, PAC of higher molecular weight became less effective in preventing BT_4 powder from agglomeration. This could be explained by the adsorption behavior of the polymer onto the ceramic particles. Figure 8 shows the adsorption amount of four PACs on the particle surface in aqueous solutions at different initial polymer concentrations. Generally, the amount of adsorbed polymer increased with polymer content initially, and then reached a characteristic plateau. The plateau corresponded to the saturated amount of polymer required for a monolayer coverage.^{25,26} The saturated amount increased in the following order: PAC1 > PAC2 > PAC3 \approx PAC4. It indicated that the saturated amount increased with decreasing polymer molecular weight.

The adsorption of polymer was related to the interaction between the particle surface and the functional groups of PAC. Figure 9 shows the relationship between the zeta potential of particles and the pH value of 20 wt % BT_4 suspensions. The surface charge or zeta potential of particles was found to decrease monotonically with increasing pH. The isoelectric point occurred at pH of about 5.3. Therefore, the particle surface was negative at pH 9. As shown in Figure 1, PAC molecules would dissociate and contained anionic carboxylate ($-\text{COO}^-$) groups and polar amide ($-\text{CONH}_2$) groups under this basic condition. The adsorption of the polymer onto BT_4 surface was believed mainly due to the dipole-ionic

attraction between the amide groups, and the surface sites of the ceramic particles. For PAC of higher molecular weight, the polymeric molecules had greater dimension and contained more negative charges at pH 9. It would cause stronger electrostatic repulsions and prevent other polymeric molecules from approaching and anchoring on the particle surface. As a result, the saturated amount of PAC decreased with increasing molecular weight.

Figure 10 shows the effect of polymer concentration on the zeta potential of particles in 20 wt % BT_4 suspensions at pH 9. The zeta potential of suspensions without any dispersant present was -38.5 mV. It was reported that a minimum potential value of 50 mV was required to have sufficient electrostatic repulsions between ceramic particles and to achieve stable suspensions.²⁸ Therefore, the BT_4 suspension without any dispersant present was not stable and separated into two layers after 1-day sedimentation. When PAC was added in the suspensions, the potential value became more negative. Addition of more polymer resulted in higher absolute potential value. Regardless of which PAC was incorporated, the suspensions with 1.5 wt % polymer became stable for 30 days, as the absolute potential values of particles were greater than 50 mV. It is clear that the adsorption amount of PAC1 on BT_4 particles was highest and the corresponding zeta potential was most negative. Consequently, PAC1 was more effective in stabilizing the ceramic particles than other polymers with higher molecular weight.

The material properties of BT_4 compacts

The relative green density of the ceramic compacts obtained from gravitation, sedimentation, and consolidation of 60 wt % BT_4 suspensions is shown in Figure 11. The green density of the compact without

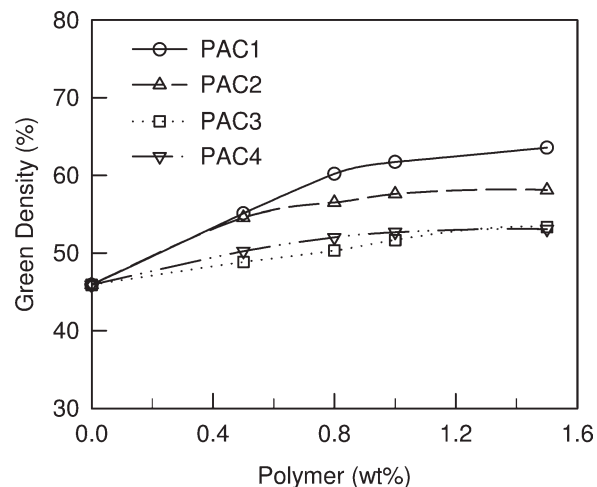


Figure 11 Effect of polymer concentration on the relative green density of BT_4 compacts.

any dispersant was about 45.4% of the theoretical density. The density increased when PAC was incorporated. Along with increasing polymer concentration, the density increased initially, and then approached a maximal value. At a fixed incorporated amount, the compact containing PAC1 showed higher green density than those containing PAC of higher molecular weight, confirming that the former had better packing efficiency than the latter. Figure 12 shows the relative sintered density of the BT₄ compact with various amounts of PAC of different molecular weights. The trend was similar to that in Figure 11. The results indicate that the effect of polymer in enhancing the green density and sintered density was in the following order: PAC1 > PAC2 > PAC3 ≈ PAC4.

BT₄ is a dielectric material used in making microwave frequency resonators due to its good dielectric properties. Figure 13 shows the effect of dispersant concentration on the dielectric constant of the BT₄ compacts. For the compact without any dispersant incorporated, the dielectric constant was about 31. When PAC was incorporated, the dielectric constant increased. Incorporation of more polymer in the suspension led to higher dielectric constant of the resulting compact. As PAC1 provided a better dispersion effect and caused BT₄ powder to be more densely packed, the sintered compacts showed highest dielectric constant values compared to those with PAC of higher molecular weights.

CONCLUSIONS

In this study, the stability of BT₄ aqueous suspensions with an anionic copolymer, i.e., PAC, at pH 9 has been investigated. The results indicate that PAC could improve the dispersion of the particles, stabilize the resulting suspensions which contained pow-

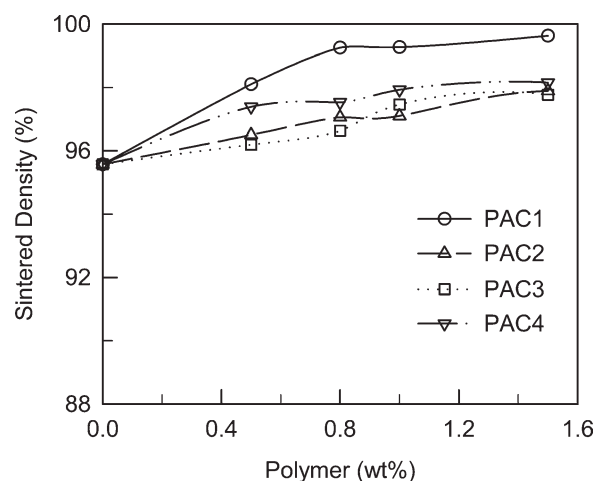


Figure 12 Effect of polymer concentration on the relative sintered density of BT₄ compacts.

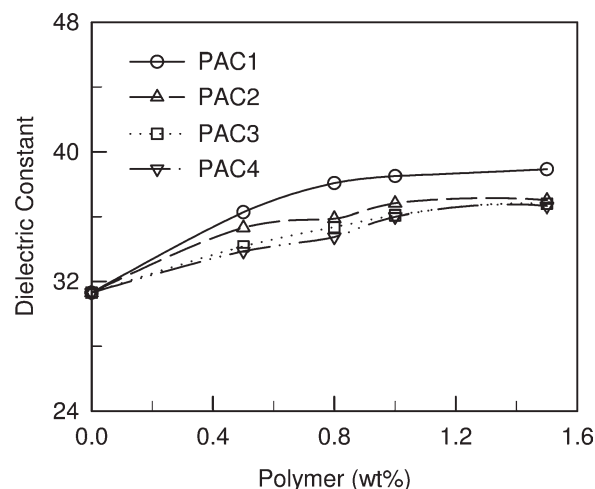


Figure 13 Effect of polymer concentration on the dielectric constant of BT₄ compacts.

der with smaller particle size. Consequently, the BT₄ compact with PAC showed greater green density and sintered density, and higher dielectric constant value than those without any polymer present. As PAC of lower molecular weight adsorbed more onto BT₄ powder, and resulted in stronger electrostatic repulsions among particles, the performance of PAC was found to increase with decreasing polymer molecular weight.

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