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Dispersion of $BaTi_4O_9$ powders in aqueous solutions with PAMCOB copolymer

Tzu-Min Chung, Kung-Chung Hsu *

Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan, ROC

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Abstract

An anionic water-soluble copolymer, i.e., poly(acrylamide-co-4-carboxylamino-4-oxo-2-butenate) (PAMCOB) was used as a novel dispersant for aqueous $BaTi_4O_9$ (BT_4) slurries. The dispersing property of this copolymer was examined by means of rheology, sedimentation, and leached Ba^{2+} concentration measurements. The dielectric properties of BT_4 compacts were also measured. The results indicated that this copolymer can reduce the viscosity and stabilize the BT_4 slurries. Compared to a commercial dispersant, ammonium salt of polymethylacrylic acid (PMAAN), PAMCOB was as effective in preparing stabilized suspensions. More importantly, PAMCOB reduced the leached Ba^{2+} concentration. Consequently, the BT_4 compacts with this polymer showed higher dielectric constant and lower dielectric loss than those without any dispersant present.

Keywords: $BaTi_4O_9$; Anionic polyelectrolytes; Dispersion; Leached barium ions

1. Introduction

Barium titanates are important electronic ceramics with good dielectric properties. Therefore, they are extensively used in the production of electronic devices. For example, $BaTiO_3$ (BT) is used in making multilayer capacitors and piezoelectric sensors; $BaTi_4O_9$ (BT_4) and $Ba_2Ti_9O_{20}$ are used in making resonators and filters for microwave communications [1–7]. The electronic properties of barium titanate compacts are clearly dependent on the microstructural characteristics. In turn, the microstructural characteristics depend on the manufacturing processes. Tape casting is a common wet process in the preparation of barium titanate green tapes or thin films. To produce these ceramic green tapes with a uniform microstructure and high packing density, the preparation of well-dispersed slurries is a prerequisite. Practically, either organic or aqueous solvents have been used to disperse the powder. Currently, the preparation of water-based suspensions is attracting a great deal of attention for safety, economic, and environmental reasons [8,9].

Usually, well-dispersed ceramic slurries can be prepared by adding organic dispersing agents or polyelectrolytes in the aqueous system because the added chemicals can enhance the dispersion of solid particles and stabilize the resulting suspensions. Among commercial dispersants, acrylic acid-based polymers such as ammonium polyacrylate, poly(acrylic acid)–poly(ethylene oxide) and ammonium polymethacrylate (PMAAN), are often used for barium titanate, alumina and other ceramic powders in aqueous solutions [9–22]. Although these polyelectrolytes have been proven to be effective dispersants, there are still some aspects which need to be improved. Specifically, barium titanate powder is known to be thermodynamically unstable in water. A substantial amount of Ba^{2+} ions leach out from solid particles to solutions, especially in an acidic condition [23–25]. The leached Ba^{2+} ions redeposit onto the particle surfaces upon drying, which may lead to deviation in stoichiometry, exaggerated grain growth, inhomogeneous microstructure, and degradation of the dielectric properties of the final product [26–29]. Therefore, new and more effective dispersants continue to be developed [30–32].

Previously, an anionic copolymer, i.e., poly(acrylamide-co-4-carboxylamino-4-oxo-2-butenate) (PAMCOB), was prepared and applied to disperse BT suspensions [33]. In this study the dispersion properties of PAMCOB on BT_4 powder in aqueous

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* Corresponding author. Tel.: +886 2 29309088; fax: +886 2 29324249.
E-mail address: kchsu@ntnu.edu.tw (K.-C. Hsu).

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solutions were investigated. Furthermore, the Ba^{2+} concentrations in the resulting suspensions were measured. The dielectric properties of BT_4 compacts were also determined. The results were compared to those using PMAAN.

2. Experimental

2.1. Materials

The BT_4 powder, supplied by Prosperity Dielectrics (Taoyuan, Taiwan) with a median (d_{50}) particle size of 0.72 μm and a BET specific surface area of 5.13 m^2/g was used in this work. Two dispersants, i.e., PAMCOB and PMAAN, were used. PAMCOB was prepared from acrylamide (AM) and 4-carboxylamino-4-oxo-2-butenate (COB) through a free radical polymerization. The detailed preparation procedure of PAMCOB can be found elsewhere [33]. The prepared PAMCOB polymer had a fixed AM/COB molar ratio of 1/1, and a weight-average molecular weight (Mw) of 1.8×10^4. PMAAN with $Mw = 1.0 \times 10^4$ was supplied by the R.T. Vanderbilt Company. The molecular weights of these two polymers were measured by the GPC mentioned elsewhere [33]. Fig. 1 shows the chemical structures of these two polymers.

2.2. Preparations of BT_4 suspensions

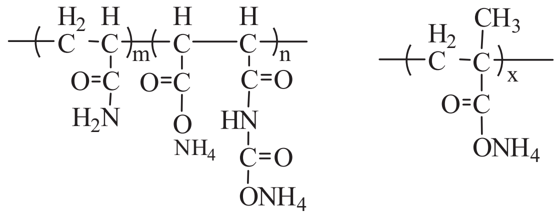
Either 20 wt% or 60 wt% BT_4 aqueous suspensions were prepared. They contained 0–1.5 wt% dispersant relative to the dry weight of BT_4 powder. The suspensions were milled and mixed in a ceramic jar with a fixed amount of zirconia balls for 24 h. In this study, deionized and distilled water was used and the pH value of prepared suspensions was adjusted by the additions of either $HCl_{(aq)}$ or $NaOH_{(aq)}$. Unless specified otherwise, the pH value of suspensions was controlled at 9.

2.3. Viscosity measurements

The viscosity of 60 wt% BT_4 aqueous suspensions was determined by a viscometer (DV-II, Brookfield Engineering Lab.) using several spindles at a rotation speed of 60 rpm.

2.4. Sedimentation test

20 wt% BT_4 aqueous suspensions were prepared and poured into 50 mL graduated cylinders. These suspensions were left in the cylinders for 30 days, and the changes of sedimentation volumes along with elapsed time were measured and recorded.



(a) PAMCOB (b) PMAAN

Fig. 1. The chemical structures of (a) PAMCOB and (b) PMAAN polymers.

2.5. Particle size measurement

20 wt% BT_4 aqueous suspensions were prepared. After ball-milling, the particle size of the solid particles in aqueous slurries was determined by a particle size analyzer (Malvern Mastersizer 2000).

2.6. Zeta potential measurement

20 wt% BT_4 aqueous suspensions were prepared. After ball-milling, the suspensions were centrifuged at a speed of 9000 rpm for 30 min to obtain supernatants. The zeta potential of remaining particles in the supernatant was measured by a zetasizer (Malvern Zetasizer 3000HSA).

2.7. Ba^{2+} concentration analysis

20 wt% BT_4 aqueous suspensions were prepared. After ball-milling and centrifugation, a small amount of supernatant was taken and the Ba^{2+} concentration in the supernatant was measured by inductively coupled plasma-mass spectrometry (ICP-MS HP4500).

2.8. Adsorption of dispersants

20 wt% BT_4 aqueous suspensions were prepared. After ball-milling and centrifugation, a small amount of supernatant was taken. The residual dispersant concentration in the supernatants was analyzed and determined by the aforementioned GPC [33]. The amount of dispersant adsorbed on BT_4 was calculated from the difference in dispersant concentration before and after adsorption.

2.9. Dielectric properties measurements

60 wt% BT_4 aqueous suspensions were prepared. After ball-milling, the suspensions were dried, ground, and pressed into disks. The disk samples were sintered at 1150 °C for 6 h and both sides were coated with silver paste. The dielectric constant and dielectric loss were measured using a HP 4284A LCR Meter (Agilent Technologies) at a frequency of 1 kHz.

3. Results

3.1. Rheological behavior

Viscosity measurement is a common way to evaluate the degree of dispersion in concentrated suspensions. Fig. 2 shows the effect of dispersant concentration on the viscosity of 60 wt% BT_4 suspensions. The viscosities of suspensions without dispersant were more than 3500 mPa s. The value decreased when PAMCOB was added. Along with increasing polymer concentration, the viscosity of suspensions was found to decrease first, and then approach a minimum value at the

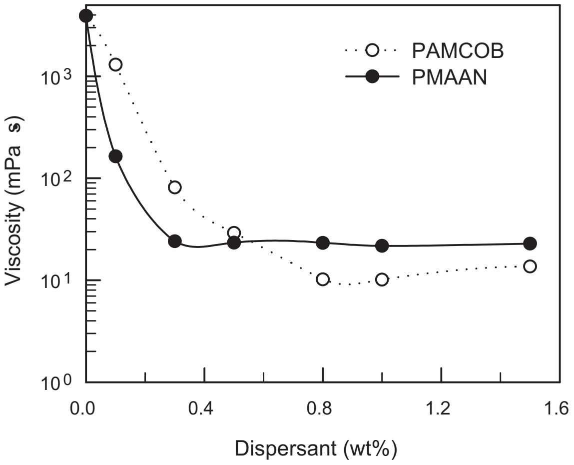


Fig. 2. The effect of dispersant concentration on the viscosity of 60 wt% BT_4 suspensions at 60 rpm.

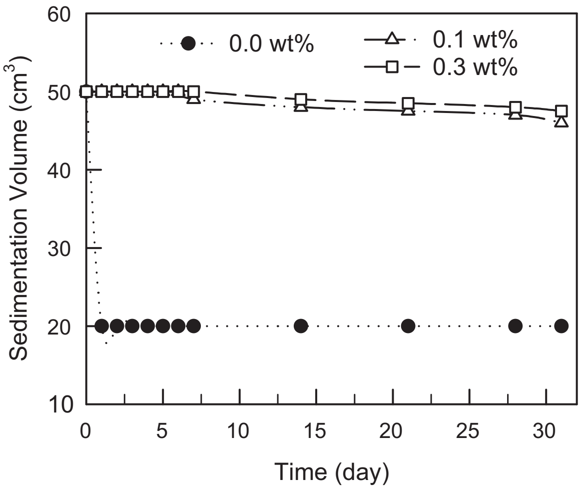


Fig. 4. The sedimentation behavior of 20 wt% BT_4 suspensions with PMAAN.

polymer concentration of about 0.8 wt%. The suspension with PMAAN showed a similar rheological behavior. The required amount of PMAAN to achieve the lowest viscosity was about 0.3 wt%, which was lower than that of PAMCOB. However, the minimum viscosity of the suspensions with PMAAN was slightly higher than that with PAMCOB.

3.2. Sedimentation

Alternatively, colloidal stability can be examined through the sedimentation observation and measurement. A good dispersant will keep a cloudy state in the suspensions for long time [9,12]. Fig. 3 shows the sedimentation behavior of 20 wt% BT_4 suspensions with various amounts of PAMCOB. For suspensions without any dispersants present, two distinct layers were observed in the sedimentation after 1 day. These two layers included a clear aqueous layer on the top and a sediment layer. When 0.1 wt% or 0.3 wt% PAMCOB was added, the resulting suspensions remained cloudy for 5 days, indicating the stability was improved. If the added polymer concentration was 0.5 wt% or greater, the resulting suspensions became more stable and remained cloudy after 30 days. Fig. 4 shows the sedimentation behavior of 20 wt% BT_4 suspensions with the presence of PMAAN. The suspensions became stable and remained cloudy for 30 days when they contained 0.1 wt% polymer or more.

Although the sedimentation behavior of the BT_4 suspension with 0.3 wt% PAMCOB was similar to that with 0.1 wt% polymer, the sediment velocity in the former suspension was found to be faster than that in the latter as the sedimentation curve with 0.1 wt% PAMCOB is higher than the one with 0.3 wt% polymer. It is clear that sediment velocity is affected by the particle size of BT_4 powder and the viscosity of the suspension. When the powder has larger particle size or the suspension is more viscous, the sediment velocity will be faster. The particle size of BT_4 powder in 20 wt% suspensions with various amount of PAMCOB was measured using a particle size analyzer. The d_{10}, d_{50}, and d_{90} of BT_4 powder in the suspension with 0.1 wt% PAMCOB were measured as 0.689 μm, 1.483 μm, and 2.952 μm, respectively. The d_{10}, d_{50}, and d_{90} of BT_4 powder in the suspension with 0.3 wt% PAMCOB were measured as 0.709 μm, 1.47 μm, and 2.807 μm, respectively. The suspension with 0.1 wt% polymer contained particles which showed smaller d_{10} and greater d_{90} than that with 0.3 wt% polymer. This implies that the former suspension comprised BT_4 powder of wider particle size distribution than the latter suspension. Although the median particle size of the ceramic powder in the 0.3 wt% PAMCOB suspension was smaller than that in the 0.1 wt% polymer suspension, the observed sediment velocity in the former suspension appeared to be faster. This is because the 0.3 wt% polymer suspension had lower viscosity and contained particles with higher d_{10} than the 0.1 wt% polymer suspension.

3.3. Ba^{2+} dissolution

Barium titanate powder is not thermodynamically stable in water. When BT_4 powder was dispersed in aqueous solutions, Ba^{2+} ions leached out from the surface of the solid particles.

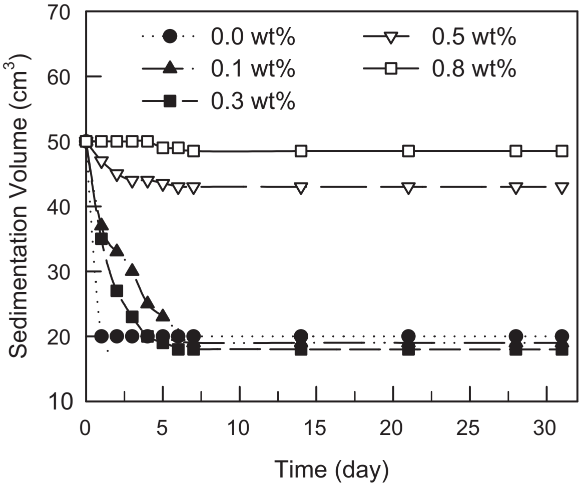


Fig. 3. The sedimentation behavior of 20 wt% BT_4 suspensions with PAMCOB.

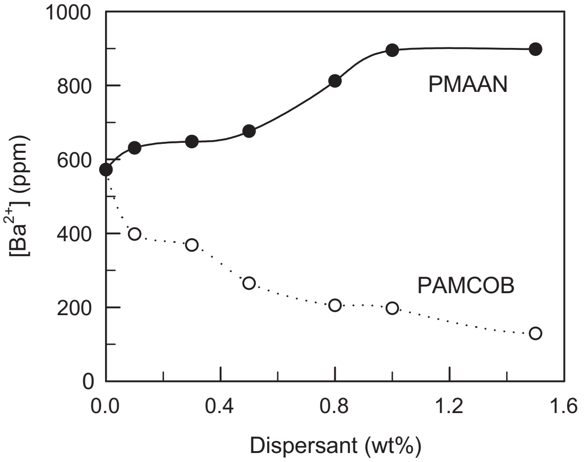


Fig. 5. The effect of dispersant concentration on Ba^{2+} dissolution concentration of 20 wt% BT_4 suspensions.

Addition of dispersants affects the leaching behavior of Ba^{2+} ions. Fig. 5 shows the effect of dispersant concentration on the leached Ba^{2+} concentration of 20 wt% BT_4 suspensions. The Ba^{2+} concentration was found to decrease with PAMCOB content. The more the polymer was incorporated, the less the amount of leached Ba^{2+} ions measured. In contrast, the leached Ba^{2+} ions were found to increase with increasing PMAAN concentration.

3.4. Dielectric properties

Fig. 6 shows the effect of dispersant concentration on the dielectric constant of BT_4 compacts. For the compact without any dispersant incorporated, the dielectric constant was 31.3. The dielectric constant increased when dispersants were present. Along with increasing dispersant content, the dielectric constants also increased. Furthermore, the compacts with PAMCOB showed slightly higher dielectric constant than those with PMAAN, when the polymer concentration was more than 0.3 wt%. Fig. 7 shows the effect of dispersant concentration on the dielectric loss of BT_4 compacts. Addition of dispersants reduced the dielectric loss of the resulting compacts. The more the dispersant added, the less the dielectric loss. Furthermore, the compacts with PAMCOB showed slightly lower dielectric loss than those with PMAAN, when the polymer concentration was more than 0.3 wt%. The trend was just opposite to that of dielectric constant.

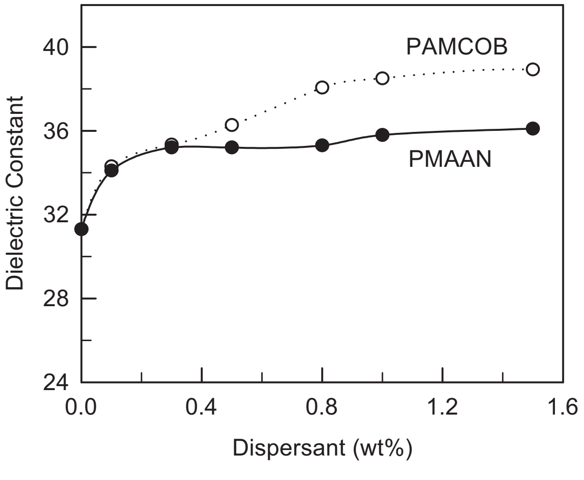


Fig. 6. The effect of dispersant concentration on the dielectric constant of BT_4 compacts.

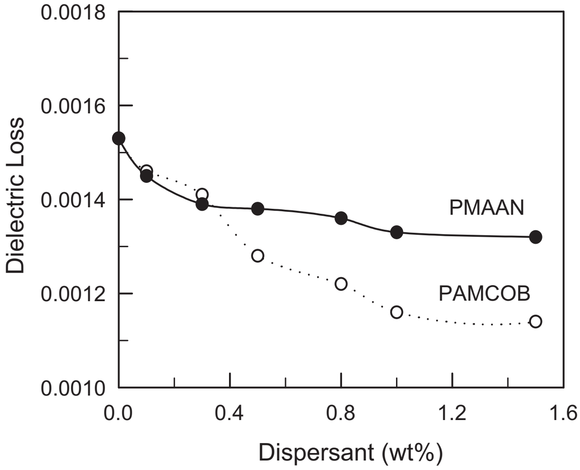


Fig. 7. The effect of dispersant concentration on the dielectric loss of BT_4 compacts.

4. Discussion

From the above results, it is clear that the BT_4 suspensions with either PAMCOB or PMAAN show similar rheological behaviors, and their viscosities are significantly lower than those without any dispersant present. Furthermore, both polymers can stabilize the BT_4 particles in aqueous solutions at pH = 9. This indicates that PAMCOB, like PMAAN, is an effective dispersant for BT_4 slurries. However, the amount of PAMCOB required to make the ceramic suspensions to reach a minimum viscosity and became stable was greater.

As is shown in Fig. 1, both PAMCOB and PMAAN molecules contain carboxylate groups and become anionic polyelectrolytes in basic solutions, which cause mainly electrostatic repulsions when adsorbed on ceramic particles [15]. The electrostatic repulsions generated by PAMCOB are expected to be lower than those generated by PMAAN, as PAMCOB contains fewer charge groups per unit weight of polymer. However, there is a short side chain linked with the carboxylate group in the structural unit of PAMCOB molecules. Therefore, the dispersing effect generated by the copolymer is not only caused by electrostatic repulsion (due to carboxylate groups) but also slightly by steric hindrance (due to short side chains). This explains why a greater amount of PAMCOB was required, as compared to PMAAN to make the resulting suspensions less viscous and stabilized. Fig. 8 shows the effect of dispersant content on the zeta potential of 20 wt% BT_4 suspensions at pH = 9. The zeta potential of suspensions without dispersant was −38.5 mV. Zeta potential becomes more negative when dispersant is present in the suspensions. For suspensions with PAMCOB, the zeta potential becomes more negative with increasing polymer concentration, and

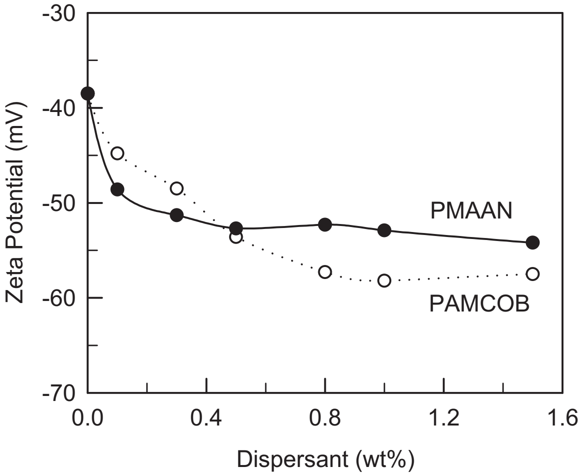


Fig. 8. The effect of dispersant content on the zeta potential of 20 wt% BT_4 suspensions.

approaches a constant value of about −58 mV. It has been reported that well-dispersed slurries can be achieved if the zeta potential of ceramic particles is greater than 50 mV in absolute value [34]. For suspensions with PMAAN, the change of the zeta potential with polymer concentration was similar, and the final constant value was about −54 mV. In addition, the amount of the copolymer to achieve the constant value was greater than that of PMAAN; according the previous results of both viscosity and sedimentation measurements.

It is noted that suspensions incorporating different dispersant showed different trend in the changes of leached Ba^{2+} concentration with polymer content. For suspensions with PAMCOB, the Ba^{2+} concentration was found to decrease with increasing polymer content. For suspensions with PMAAN, the opposite trend was observed. The different trend could be attributed to different adsorption and interaction behaviors of these two chemicals on solid particles.

Fig. 9 shows the amount of these two dispersants adsorbed on BT_4 particles as a function of the initial dispersant concentration at pH = 9. In general, the amount adsorbed increased quickly with increasing dispersant concentration, and then reached a plateau. The critical value at the plateau accounts for the amount of polymers required for the coverage of the particle surface. The critical value for the suspension with PMAAN occurred at a dispersant concentration of about 0.3 wt%, and the adsorbed amount was about 1.2 mg/g BT_4. The value for the suspension with PAMCOB occurred at dispersant concentration of about 0.8 wt% and the adsorbed amount was about 7.6 mg/g BT_4. The critical value was roughly consistent with that of achieving the minimum viscosity. Furthermore, the adsorbed amount of PAMCOB was greater than that of PMAAN.

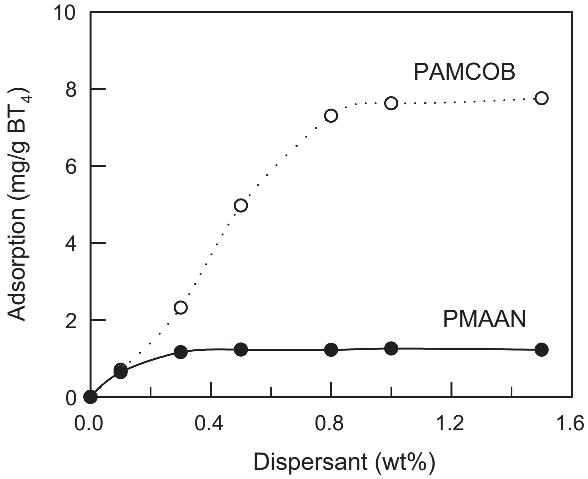


Fig. 9. The amount of the dispersant adsorbed on BT_4 particles as a function of the initial dispersant concentration at pH = 9.

At pH = 9, the surface charge or zeta potential of particles was negative, as shown in Fig. 8. Under this basic condition, PMAAN molecules also effectively became negatively charged because the carboxylic acid groups in polymeric molecules were completely dissociated [9,31]. Therefore, it was difficult for PMAAN molecules to be adsorbed on the particle surface. Similarly, it was also difficult for PAMCOB molecules to be adsorbed onto particles through their dissociated $–COO^-$ groups. However, a PAMCOB molecule contains another amide functional group in the structural unit. The $–CONH_2$ groups enhance this polymer, allowing it to be adsorbed on the particle surface through hydrogen bondings [35]. Moreover, ethylene diamine tetraacetic acid (EDTA) is a known chelating agent which can form coordinate bonds to metal ions with its carboxylate and amino groups [36]. Similarly, PAMCOB can also form coordinate bonds to Ba^{2+} ions on particle surface with its $–CONH_2$ and $–COO^-$ functional groups. Accordingly, the adsorbed amount of PAMCOB molecules was more than that of PMAAN molecules.

When PMAAN was added into the suspensions, it promoted the leaching of barium ions from particles. This is because the $–COO^-$ functional groups of the dissociated polymer interacted with Ba^{2+} ions. As a result, the Ba^{2+} concentrations in the slurries with PMAAN were slightly higher than those in the slurries without any dispersant (Fig. 5). Although PAMCOB also enhances the dissolution of Ba^{2+} from powder, an appreciated fraction of released Ba^{2+} ions is chemically linked with the adsorbed polymer on the particle surface, as the adsorbed amount of this polymer (=7.6 mg/g BT_4) is much higher than that of PMAAN (=1.2 mg/g BT_4). Therefore, addition of PAMCOB caused a decrease of the leached Ba^{2+} concentration in the resulting suspensions. Consequently, the BT_4 compacts with sufficient amounts of this copolymer showed greater dielectric constants and lower dielectric losses than those with PMAAN [28,29].

5. Conclusions

An anionic water-soluble copolymer, i.e., PAMCOB, was used as a dispersing agent for aqueous $BaTi_4O_9$ suspensions. Incorporation of PAMCOB was as effective as PMAAN in reducing the viscosity and stabilizing the resulting slurries. Moreover, suspensions with PAMCOB were found to contain lower Ba^{2+} concentration than those without any dispersant.

This could be related to the greater amount of PAMCOB molecules adsorbed onto particles and the interactions between Ba^{2+} ions and the polymer. As a result, the BT_4 compacts with this copolymer showed higher dielectric constant and lower dielectric loss than those without any dispersant incorporated.

Acknowledgements

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