Three acrylamide-based copolymers were prepared and tested as new dispersants for aqueous BaTiO$_3$ (BT) suspensions. The results indicated that they could make the suspensions to be less viscous, BT particles to be less agglomerated. Compared with polymethacrylate, these polymers are as effective or even better in the dispersion performance. More importantly, these polymers could lessen the leached Ba$^{2+}$ concentration. This is related to their interaction with BT particles.

**Keywords:** Polymer; Dispersant; Barium Titanate; Barium Ions Dissolution.

1. **Introduction**

Tape casting is a common wet process in preparing barium titanate (BT) green tapes or thin films. Traditionally, organic solvents are used to disperse the powder. Nowadays, the preparation of aqueous suspensions has been given more attention because of safety, economic, and environmental reasons.[1,2]

In preparing well-dispersed ceramic slurries, dispersants are usually required. Among commercial dispersants, acrylic acid-based polymers such as polymethacrylate (P0), are often used.[3,4] Although good results have been reported, some aspects can still be improved. Normally BT slurries were suggested to be processed in basic conditions because of substantial amount of Ba$^{2+}$ leached out from the particles to the solutions at pH < 7.[2] Clearly P0 would enhance Ba$^{2+}$ leaching due to its interactions with Ba$^{2+}$ ions.[5] This would cause a change in the Ba/Ti ratio on the particle surface and a variation of properties of BT compacts.[2]

In this study, three acrylamide-based copolymers were prepared as dispersants for BT powder. Their dispersing effects on BT suspensions were examined. In addition, the concentration of Ba$^{2+}$ leached from the particles was also measured and discussed.

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2. Experimental

2.1. Materials

Acrylate (AA), methacrylate (MAA), acrylamide (AM), 2-acrylamido-2-methylpropane-1-sulfonate (AMP), 4-(2-octadecyloxy-poly(ethoxy))-4-oxobut-2-enoate (OPE), 4-(3-((carboxylatomethyl)(dimethyl)amino)propylamino)-4-oxobut-2-enoate (CDA), and 4-(2-hydroxy-poly(ethoxy))-4-oxobut-2-enoate (HPE) were the monomers used. Fig. 1 shows the chemical structure of these monomers. Three copolymers used as dispersants were prepared from these monomers through a free radical polymerization. Table I lists the characteristics of these polymers. A commercial dispersant, P0, was also used for comparison. The BT powder used had a Ba/Ti ratio of 0.995, an average (d50) particle size of 0.82 μm, and a Brunauer-Emmett-Teller specific surface area of 4.0 m²/g.

2.2. Preparations and tests of the BT suspensions

Aqueous suspensions containing either 20 or 60 wt % BT particles were prepared. They contained 0–1.0 wt % dispersant relative to the dry weight of BT powder. The suspensions were milled for 24 h to assure a homogeneously dispersed state. The pH value was fixed at 9. The viscosity of 60 wt % BT suspensions was determined with a Brookfield LVDV-II viscometer (Middleboro, MA) with a #1 or #4 spindle at a rotation speed of 60 rpm. The particle size of the powder in suspensions was determined with a Malvern Mastersizer 2000 analyzer (Worcestershire, UK). The amount of dispersant adsorbed on BT particles in BT suspensions was determined.[5] Finally, the Ba²⁺ concentration in BT suspensions was measured by ICP-AES (JOBIN YVON JY24, France).

Table 1. The characteristics of these polymers.

<table>
<thead>
<tr>
<th>Polymer symbol</th>
<th>Monomer ratio</th>
<th>Mn*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>MAA = 1</td>
<td>6.9x10⁴</td>
</tr>
<tr>
<td>P1</td>
<td>AM/OPE = 9/1</td>
<td>1.4x10⁵</td>
</tr>
<tr>
<td>P2</td>
<td>AM/CDA = 5/1</td>
<td>8.1x10⁴</td>
</tr>
<tr>
<td>P3</td>
<td>AMP/MAA/HPE = 2/3/1</td>
<td>3.1x10⁴</td>
</tr>
</tbody>
</table>

*Number-average molecular weight.
3. Results and Discussion

3.1 Rheological behavior of BT suspensions

Figure 2 shows the effect of dispersant concentration on the viscosity of 60 wt % BT suspensions. The viscosity of suspensions without dispersant was high. It became smaller when polymer was incorporated. As Pn(n=0-3) concentration was increased, the viscosity of suspensions decreased sharply at first, reached a minimum value, and then increased slightly. Although the required amount to achieve the lowest viscosity was different for different polymer, the achieved minimum viscosity of the suspension with each one was close to each other. This suggests that each Pn(n=0-3) could disperse BT particles in solutions.

Figure 2. Effect of dispersant concentration on the viscosity of 60 wt% BT suspensions.
3.2 Particle size of BT particles

Figure 3 shows the effect of dispersant concentration on the d50 size of the BT suspensions. For BT suspensions with P0 or P3, the d50 value was found to decrease with increasing dispersant concentration quickly, and reach a minimum. For BT suspensions with P1 or P2, the d50 value was found to increase slightly with the dispersant concentration initially up to a maximum, then decrease afterwards and reach a minimum. Nevertheless, these trends indicate that particles became less agglomerated and particle sizes shifted to smaller values when proper amount of dispersants were added in the suspensions.

![Figure 3. Effect of dispersant concentration on the d50 size of powder in 20 wt% BT suspensions.](image)

3.3 Adsorption of polymer on BT particles

Figure 4 shows the adsorption amount of Pn(n=0-3) onto the BT surface in suspensions as a function of the initial dispersant concentration. For all tested polymer samples, the adsorbed amount was shown to increase with dispersant concentration initially, and then reach a characteristic plateau. The value at the plateau accounts for the amount of polymers (Cm) required for the formation of monolayer on the particle surface. The Cm values are about 1.4, 3.6, 2.2, and 1.7 mg/g BT for P0, P1, P2, and P3, respectively. Apparently, Pn(n=1, 2, 3) shows higher Cm value than P0.

Clearly the structural unit of P0 molecules contains one functional group, i.e., carboxylate (-CO2). The structural unit of P1 molecules contains two functional groups, i.e., carboxylate and amide (-CONH2). The structural unit of P2 molecules contains two functional groups: cationic amine (-N+(CH3)2-) and amide. The structural unit of P3 molecules contains two functional groups; i.e., carboxylate, amido (-CONH-), and sulfonate (-SO3). Therefore, P0, P2, and P3
molecules are anionic, and only P1 molecules are amphoteric. It was reported that the BT surface is negative at pH 9, and \(-\text{CO}_2^–\) and \(–\text{SO}_3^–\) groups in Pn molecules would generate repulsive forces with the negative sites of particle surface and hinder the adsorption of polymer onto BT particles. In contrast, the cationic amine group, and amide or amido group in Pn molecules would interact with the negatively charged BT particles by electrostatic interactions and hydrogen bonding. This promotes the adsorption of polymer onto ceramic particles. Therefore, Pn(n=1-3) shows higher Cm value than P0.

![Figure 4](image)

Figure 4. Adsorption amount of dispersants as a function of the initial dispersant concentration.

### 3.4 \(\text{Ba}^{2+}\) dissolution

Figure 5 shows the effect of dispersant concentration on \(\text{Ba}^{2+}\) dissolution concentration of 20 wt\% BT suspensions. The suspension with P0 contains higher [\(\text{Ba}^{2+}\)] than that without. The more the polymer added, the greater \(\text{Ba}^{2+}\) is leached. In contrast, Pn(n=1-3) causes an opposite trend. It is known that dispersants contain anionic (-\(\text{CO}_2^–\)) group could interact with \(\text{Ba}^{2+}\) ions. When P0 was in the suspensions, the interaction between the \(-\text{CO}_2^–\) groups of polymer and \(\text{Ba}^{2+}\) ions will promote the leaching of \(\text{Ba}^{2+}\) ions from the particles. As a result, [\(\text{Ba}^{2+}\)] in the slurries with P0 was higher than that without. Although Pn(n=1-3) can also enhance the dissolution of \(\text{Ba}^{2+}\) from the powder, an appreciated fraction of released \(\text{Ba}^{2+}\) ions would redeposit and chemically link with the adsorbed polymer on the particle surface because this polymer has stronger interactions with BT particles and the adsorbed amount is higher than that of P0. Consequently, addition of Pn(n=1-3) causes a decrease in the leached [\(\text{Ba}^{2+}\)] in the BT suspension.
4. Conclusions

Three acrylamide-based copolymers were synthesized. Incorporation of them could reduce the viscosity and stabilize the resulting slurries. They also help to obtain smaller particle sizes. Compared with polymethacrylate, they are as effective or even better. In additions, these polymers could be adsorbed more onto BT particles and interact stronger with Ba$^{2+}$ ions. As a result, they could reduce Ba$^{2+}$ ions dissolution from BT suspensions.

References