Effects on aqueous barium titanate tape properties of passivation of barium ion leaching by using dispersants

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Abstract

To passivate a barium titanate ($BaTiO_3$) ceramic powder surface from Ba^{2+} ion leaching in water, passivation agent layer (PAL) was formed by drying the slurry after adding a commercial polymeric dispersant. By following the several characteristic steps of actual MLCC production process, slip and green properties were compared for two different polymer-adding modes; one is the PAL and the other is the conventional dispersant mode. Compared to the conventional dispersant adding method, PAL mode was the only effective way in reducing the amount of Ba^{2+} leaching. However, slip viscosity and green body properties were not a function of adding mode but a function of dispersant itself, which means using PAL did not deteriorate any of slip and green properties of $BaTiO_3$.
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1. Introduction

Most of multilayer ceramic capacitor (MLCC) industries are currently using solvent-based slip systems for the production of green tapes.[1] On the other hand, water-based slip formulations have been receiving increasing attention due to the reduced health and environmental hazards coupled with a lower cost compared to the solvent-based ones. One of the important obstacles to be solved for using water-based slip systems, however, is the leaching of Ba^{2+} due to the thermodynamic instability of $BaTiO_3$ in water.[2–4] An inconsistent Ba/Ti ratio of the powder in a slip system results in the variations of slip viscosity, sintered density and dielectric properties.[3,5] Therefore, control or reduction of the amount of Ba^{2+} leaching is essential in order to use the water-based slip system in the MLCC industry with high reliability.

One possible concept to reduce the amount of Ba^{2+} leaching is the creation of a passivation agent layer (PAL or primer) which covers the $BaTiO_3$ surface and acts as a surface diffusion barrier. It has been reported[6] that oxalic acid PAL can be used for the prevention of Ba^{2+} leaching in water considering the fact that an alkaline earth oxalate is easily formed on $BaTiO_3$ surface and quite insoluble. This concept with the same oxalic acid was further applied for yttria-stabilized zirconia system.[7] It was hypothesized that the oxalate formed on the surface of both powders remained and acted as a diffusion barrier. However, it is doubtful whether this oxalate layer still remains at the powder surface under a high-energy milling process which is widely performed for powder dispersion. Moreover, once this insoluble barium oxalate is formed and precipitated from the reaction between oxalic acid and Ba^{2+}, it is very difficult to determine precisely the amount of Ba^{2+} leaching in solution because most of the quantitative analysis methods use a clean supernatant.[4,8–10]

As an alternative method to passivate the powder from Ba^{2+} leaching, three kinds of commercial dispersants were used for two different adding modes. In general, a dispersant is added to a liquid medium directly to enhance the slurry dispersion without any drying process. After adding dispersant, however, slurry was dried to make a PAL which adsorbs on the powder surface and acts as a polymeric diffusion barrier for Ba^{2+} leaching in this experiment. The aim of this study is to investigate the differences in Ba^{2+} dissolution, slurry, slip, and green tape properties between dispersant and PAL modes. Here slurry is defined as a ceramic suspension with particles in a liquid medium with

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a dispersant, and a slip as ceramic particles in a liquid medium with all the processing additives including binder, dispersant, plasticizer, surfactant, and defoamer.

2. Experimental procedure

The ceramic powder used in this study was a hydrothermal BT-8 (Cabot Performance Materials, Boyertown, PA) with a mean particle size of 0.24 μm, specific surface area of 8.50 m^2/g, and a Ba/Ti ratio of 0.998. Three kinds of dispersants and oxalic acid were tested as PALs. Dispersants used were a modified polymethylmethacrylate with polyethylene glycol side chains (PMMA/PEG) (Hypermer KD-6, Uniqema, New Castle, DE), an ammonium salt of polyacrylic acid (APA) (Geosperse 644A, GEO Chemicals, Horsham, PA), and a sodium salt of polyaspartic acid (PApA-Na) (Amisorb, Donlar Corp., Bedford Park, IL). More detailed information on these dispersants can be found in the literatures.[11,12]

As a first test, aqueous slurries of 55 wt.% $BaTiO_3$ with different dispersant concentrations were prepared to decide the adequate amount of each dispersant for monolayer adsorption. The slurries were milled for 2 h and stabilized for 24 h without agitation in air atmosphere. To acquire a clean supernatant, slurries were centrifuged at a speed of 13,000 rpm for 20 min. The adsorption isotherms of the PALs were determined by a gravimetric method after drying the supernatant. Based on these results, the amount of dispersant in this experiment was fixed at 0.5 wt.% with respect to the ceramic powder.

As a second test, a PAL-coated powder was made by adding a dispersant. After dispersing the powder in water containing the dispersant, this mixture was immediately dried at 120 °C for overnight to minimize the Ba^{2+} leaching at this step. To maintain the overall Ba/Ti ratio constant in the slurry, no portion of the liquid was discarded but removed by drying. The rheological behaviors of the slurries were compared using a programmable rheometer (DV-III, Brookfield, Stoughton, MA) for the two different modes; dispersant and PAL. EDTA titration was performed with the supernatant obtained from the slurry to measure the amount of Ba^{2+} leaching after 24 h ball-milling and 1-day aging at pH = 8. Detailed description of the EDTA titration method can be found in the literature.[2]

As a third test, slips were prepared with an acrylic formulation binder solution (WB40B, Polymer Innovations, San Marcos, CA), 60 g of ceramic powder, and other processing additives. Dispersant in 0.5 wt.% was added to the dispersant mode slip, but PAL-coated powder was directly used without adding any dispersant because it already contained the dispersant. The amount of acrylic binder resin added was 8 wt.% with respect to the ceramic powder. Surfactant (S465, Air Products and Chemicals, Allentown, PA) in 0.5 wt.% and defoamer (DF001, Polymer Innovations, San Marcos, CA) in 0.2 wt.% with respect to the total slip were added.

The slip was adjusted to the pH of 9.7 ± 0.1 by using ammonium hydroxide, and subjected to 24 h ball-milling.

After producing green tapes on moving polypropylene film by means of tape casting (TTC-1000, Richard E. Mistler, Morrisville, PA), the tape surface morphologies were compared using a scanning electron microscope (SEM; Hitachi S-3500N). Small rectangular-shaped chips (K-squares) with the thickness of approximately 1 mm were made from each green tape by stacking, laminating at a pressure of 300 kPa for 5 min at 80 °C, and cutting. Green density of the K-squares was determined using a geometrical method with six samples per each condition. The thickness and length were measured using a micrometer accurate to 0.001 mm, and the weight using a scale accurate to 0.1 mg. More detailed slip composition and experimental procedures can be found in our previous reports.[11,12]

3. Results and discussion

Fig. 1 shows the adsorption isotherms of chemicals used in this experiment. Although the thermodynamic equilibrium is not often attained, and the final amount of adsorption is determined kinetically, adsorption of polymers on ceramic powder is usually fast.[13] The amount adsorbed and conformation strongly depend on the molecular weight, and the charge on the polymer chain and on the powder surface.[13–15] PMMA/PEG shows the highest amount of adsorption and increases gradually with its concentration up to 1 wt.%, which can be attributed to the high molecular weight, surface charge and multi-functional groups of PMMA/PEG as explained in the literatures.[11,12] APA and PApA-Na dispersants show an adsorption plateau at the concentration of approximately 0.5 wt.%, which corresponds to the amount of dispersants for monolayer coverage. Oxalic acid shows a plateau at the concentration of 0.7 wt.% which
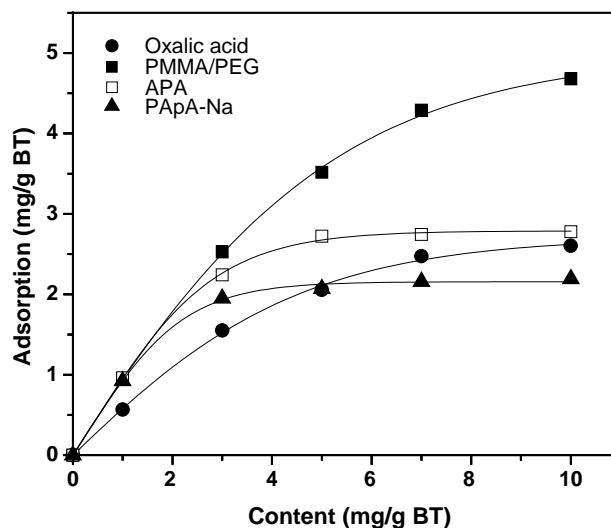

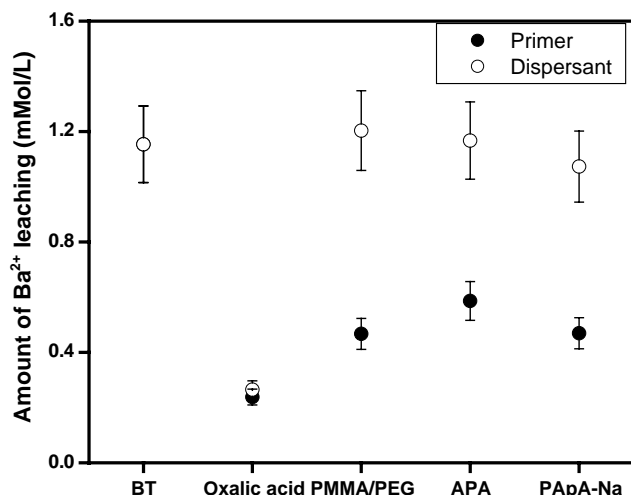Fig. 1. Adsorption isotherms of different chemicals on $BaTiO_3$ surface.

Fig. 2. Comparison of the amount of Ba^{2+} leaching at pH = 8 with two different adding methods of the chemicals used.

Fig. 3. Comparison of slurry viscosity with two different polymeric adding methods.

might include the effect of the enhanced Ba^{2+} leaching due to the formation of Ba-oxalate precipitate. Based on these adsorption isotherm results, the amount of dispersant is fixed at 0.5 wt.% with respect to the ceramic powder, although PMMA/PEG and oxalic acid need slightly higher amount for the adsorption saturation.

Fig. 2 compares the amount of Ba^{2+} leaching between two modes; PAL or primer and dispersant, measured by EDTA titration. According to the previous study on Ba^{2+} ion leaching kinetics with similar condition,[2] more than 90% of total amount of leaching occurs within 48 h. Therefore, 48 h was set as the leaching time in this experiment, although the thermodynamic equilibrium had not been reached. Fig. 2 clearly shows that the degree of leaching depends on the mode of polymer covering the $BaTiO_3$ surface. PAL mode is more effective in passivating $BaTiO_3$ than dispersant mode. More effective passivation with the PAL mode compared to the dispersant mode comes from the stronger bonding between $BaTiO_3$ powder surface and organic dispersant molecules, and more adsorption on the surface of the ceramic powder. According to the adsorption isotherms in Fig. 1, only half of the added polymer adsorbed on the $BaTiO_3$ surface at its saturation concentration for monolayer coverage for the dispersant mode. On the other hand, the entire added polymer adsorbed on the powder surface due to the drying process for the PAL mode. Oxalic acid does not show any difference with its adding mode, where it shows the smallest amount of Ba^{2+} leaching among all the organic chemicals used. However, this low value might represent the formation of Ba-oxalate precipitate whose Ba^{2+} leached was not accounted for in the analytical method.[2]

All the commercial $BaTiO_3$ powders are contaminated with $BaCO_3$ in amounts of 0.6–2.8 wt.% according to the literatures.[16,17] BT-8, the powder used in this experiment, also contained approximately 1.2 wt.% of $BaCO_3$ based on TGA[17] and FT-IR[2] data. Surface $BaCO_3$ enhances the
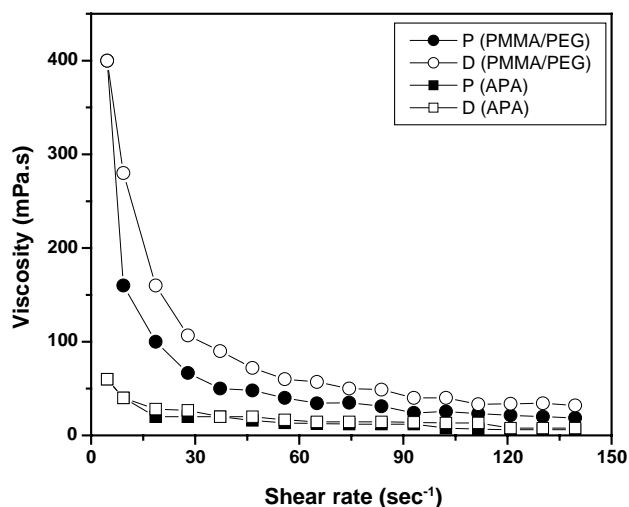
amount of Ba^{2+} leaching since $BaCO_3$ is soluble in water at room temperature.[2,16] However, the effect of surface $BaCO_3$ on the difference of Ba^{2+} leaching between two different modes must be negligible because the overall Ba/Ti ratio was kept constant during the PAL-coated powder preparation in this experiment. Although the surface $BaCO_3$ was dissolved during the PAL preparation, the leached Ba^{2+} remained in the system due to the inclusive drying process. Moreover, recarbonation process is known to be very fast in ambient atmosphere.[18,19] Therefore, the difference in the amount of Ba^{2+} leaching between two different modes did not come from the surface $BaCO_3$ effect but from the mode of polymer addition.

Fig. 3 compares the viscosity of slurries between two different modes of PAL and dispersant, where P stands for PAL or primer and D for dispersant. APA shows little difference in viscosity between PAL and dispersant, but PAL mode of PMMA/PEG shows lower viscosity than that of dispersant mode. This means that the effectiveness of dispersion is preserved or enhanced even with the drying process after adding polymeric species of PAL mode. Therefore, it is possible to use this PAL method in powder synthesis to make an easily dispersible ceramic powder in water. The slurry with APA shows lower viscosity than that with PMMA/PEG, which means more efficient dispersion with APA. However, when the slip is prepared by adding the binder and other processing additives, the slip shows quite different rheological behavior as shown in Fig. 4. Although there is still no difference between PAL and dispersant modes with the same dispersant, PMMA/PEG shows much lower slip viscosity than APA or PApA-Na, which is the opposite trend of slurry in Fig. 3. This result comes from the interaction among dispersant and other slip additives, which is a compatibility matter. Therefore, it is very important to check the rheological properties not with slurry but with final slip formulation, because MLCC process begins from slip preparation.
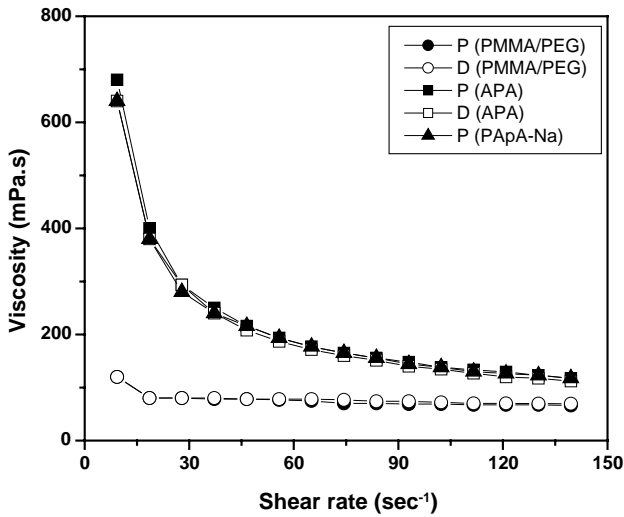
Fig. 4. Comparison of slip viscosity with different polymeric species and adding methods.

Fig. 5 presents the surface morphology of green tapes. Tapes with PMMA/PEG show a dense and smooth surface with regardless of the adding mode, while tapes with APA and PApA-Na show much porous and rough morphology. It means that the surface morphology does not depend on the adding mode but on the type of dispersant significantly. These agree with the viscosity data in Fig. 4, i.e., lower slip viscosity represents better dispersion and generates denser surface morphology resultantly.

Fig. 6 shows the green density of the K-squares. High green density is important to get a high reliability of final MLCC products, especially those with very thin dielectric layers. The green density with PMMA/PEG is much higher than others with approximately 10% difference in percent theoretical $BaTiO_3$ density (6.05 g/cm^3). This difference can be explained in conjunction with the green surface microstructure as shown in Fig. 5. Therefore, we can conclude that the lower slip viscosity with PMMA/PEG results
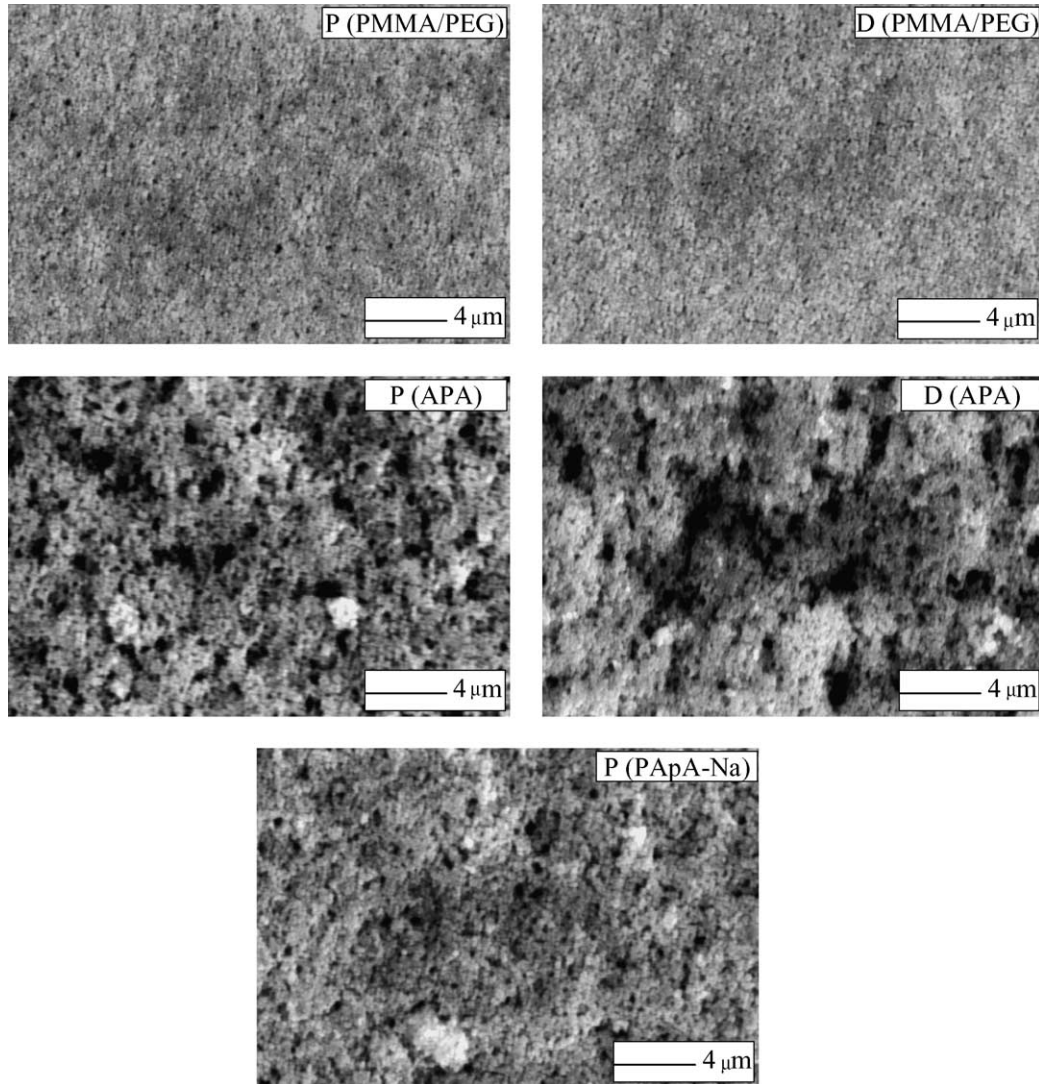

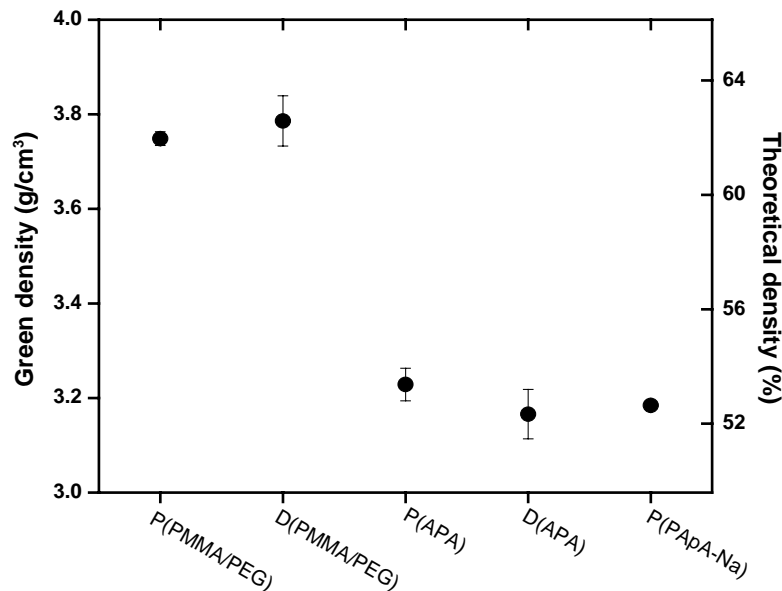Fig. 5. SEM microstructure of top surface of green tapes.

Fig. 6. Green density of the K-squares with different polymeric species and adding methods.

in the denser surface morphology and higher green density than the slips with APA or PApA-Na.

Based on our other report,[3] the excess free Ba^{2+} resulted in the increase of slip viscosity, green tape porosity, agglomeration along with a decrease in mechanical properties and green/sintered density. Although PAL mode is more effective than dispersant mode in passivation of Ba^{2+} leaching, there is no difference in other output responses such as the viscosity of slurry and slip, tape surface morphology, and green density in this experiment. This can be explained with that the amount of Ba^{2+} leaching in the actual condition of this experiment is too small to see any significant differences in output responses.

4. Conclusions

Introducing a PAL by drying the slurry after adding a dispersant was effective in reducing the amount of Ba^{2+} leaching in water, while a conventional dispersant adding mode was less effective in passivating of Ba^{2+} leaching. This PAL mode did not deteriorate any properties in terms of the viscosity of slurry and slip, green tape morphology and density, and sintered properties including a sintered density and dielectric permittivity. However, it was impossible to see any significant advantages by using the PAL because the actual amount of Ba^{2+} leaching is relatively small. The green properties of tapes such as morphology and density depended significantly on the type of dispersant used. The PMMA/PEG was a more effective dispersant than APA or PApA-Na. In addition, using a slip instead of slurry for an investigation was suggested due to the difference in viscosity between them.

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