J Electroceram (2006) 17:345–349
DOI 10.1007/s10832-006-7725-y

Microstructural evolution of $BaTiO_3$/ultrahigh-molecular-weight poly(ethylene) (UHMWPE) cast body: influence of free organic additive in a nonaqueous medium

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Received: 30 June 2005 / Revised: 4 November 2005 / Accepted: 10 February 2006

Abstract The consolidation behavior of ultrahigh-molecular-weight polyethylene (UHMWPE) in $BaTiO_3$/UHMWPE suspension was investigated by the control of the non-adsorbed organic additives. The suspensions were characterized by adsorption isotherm, rheology, sedimentation behavior, and microstructural observation. The co-dispersion stability of the $BaTiO_3$/UHMWPE particulates was correlated with the uniformity of the green microstructure. These studies can be helpful for the successful fabrication of ultra thin dielectric layer of MLCC using newly improved extrusion method.

Keywords $BaTiO_3$ · Ultra high molecular weight polyethylene (UHMWPE) · Free organic additives · Microstructure · Multilayered ceramic capacitors (MLCCs)

1 Introduction

Currently, the miniaturization trend in the fabrication of electronic devices demands the multilayer ceramic capacitors (MLCCs) with increasingly smaller size and higher dielectric permittivity [1]. To meet this requirement, many attempts have been made to reduce the thickness of the active layer (i.e. the ceramic dielectric layer) using tape casting or lip coating [1–4]. However, there are many technical problems in those conventional techniques, e.g. difficulty in handling of the green sheets, peeling off the green sheet from PET film, and laminating the green blocks due to the poor mechanical properties such as weak tensile strength and low elongation [5]. Therefore, a new method, which can fabricate the green sheet with more desirable mechanical properties for the successive steps such as lamination, burnout, and sintering, is needed.

Currently, attention is being paid to a new technique modified from a polymeric extrusion method using ultrahigh-molecular-weight polyethylene (UHMWPE), which has been extensively used to fabricate homogeneous polymer thin film or fiber with good mechanical properties [6–9]. This technique can be adapted and expanded to the field of ceramic processing in order to provide proper thickness and excellent mechanical properties to green sheet of MLCCs. The flow chart of the proposed extrusion process is shown in Fig. 1.The co-dispersed multi component suspension of $BaTiO_3$ and UHMWPE is prepared and then it is thrown in the twin screw system of the extrusion machine at the condition of temperature of 120°C and high shear stress for the fabrication of the green tape. UHMWPE is melted and dissolves at a temperature higher than 120°C during extrusion, while the solvent, decalin, simultaneously evaporates in this process. As a result, the green tape with porous microstructure was produced in which UHMWPE acts as the matrix, providing high mechanical properties such as tensile strength and elongation. The thickness of the green tape can be easily reduced from 5 μm to 3 μm during the lamination and the cold isostatic pressing process to make denser structure by rearrangement of the ceramic particles in the sheet because of the porous microstructure. Finally, one can achieve ultra-thin sheet of 1 μm after burnout and sintering process. This modified technique was described in more detail in our previous work [10].

However, the instant phase segregation of a $BaTiO_3$/UHMWPE suspension inevitably occurs due to the difference in the particle sizes between 150 μm sized UHMWPE and 0.3 μm sized $BaTiO_3$ particulates and it leads to serious

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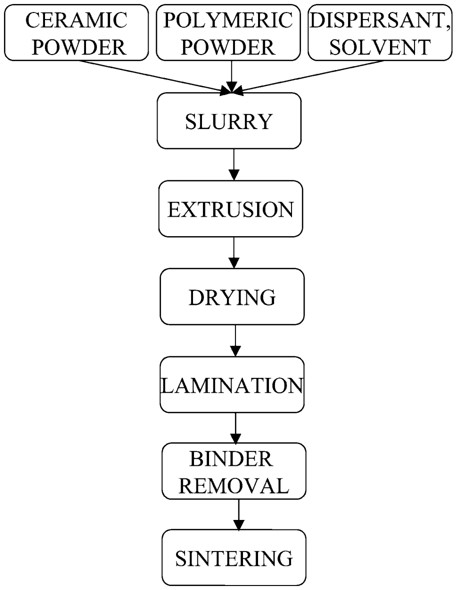

Fig. 1 The process flow chart of novel extrusion method

quality problem in MLCCs. There have been numerous studies about the suspension stability of the complex mixture systems. In these systems, the interaction between two species through charge mechanism has been carefully considered. However, these are limited to explore the ceramic-ceramic particulates mixture and there has been little investigation about the co-dispersion of the ceramic-polymeric particulates. In addition, because of the non-colloidal characteristics of UHMWPE (150 μm), the conventional techniques such as the electrostatic and steric stabilization used in the colloidal science and technology can not be properly adapted and a new approach for the achievement of the stability of this complex system should be introduced. Thus, the stability control of the multi-component system of ceramic $BaTiO_3$ and non-colloidal polymeric UHMWPE can be a key factor for the successful fabrication of the green sheet having both well-packed $BaTiO_3$ and the uniform UHMWPE gel network using the modified extrusion method.

In this study, an attempt was made to achieve homogeneous $BaTiO_3$/UHMWPE cast body by controlling the suspending lifetime of UHMWPE in the $BaTiO_3$ suspension with the presence of a non-adsorbed organic additive. The adsorption behavior of dispersant on $BaTiO_3$ and the suspension stability were correlated with the green microstructure of $BaTiO_3$/UHMWPE.

2 Experiment procedure

2.1 Materials system

Commercial 0.3 μm sized $BaTiO_3$ powders (BT03, Sakai Chemical Industry Co. Ltd., Japan) were used. UHMWPE (PE4012, Ticona, Germany) with diameter of 150 μm and molecular weight of 3,000,000 g/mol was chosen as the polymeric powder. Decalin (decahydronaphtalene) was used as the dispersion medium because it is known to be a good solvent for UHMWPE [6]. Hypermer KD-3 (ICI Chemicals, London, U.K) was used as a dispersant [16, 17].

2.2 Suspension preparation and characterization

For the preparation of the 25 vol% $BaTiO_3$ suspension except for the adsorption study of the dispersant on $BaTiO_3$, the dispersant stock solutions in the range of 0–5% based on the solids contents were mixed with $BaTiO_3$ particulate and then ball-milled for 3 hrs. The resulting slurry was then agitated for 24 hrs using a mechanical shaker. And then UHMWPE was subsequently added to the ceramic suspension and stirred for 3 hrs for the achievement of the co-dispersion of multi component system of $BaTiO_3$ and UHMWPE. Finally, a green sheet was extruded at 120°C.

Adsorption isotherms were measured to analyze the adsorption behavior of KD-3 on the $BaTiO_3$. Suspensions containing 2% $BaTiO_3$ solid were prepared with an adequate amount of KD-3. The suspensions were ball-milled for 3 hr. After milling, those were centrifuged at 12,000 rpm and the supernatant was decanted. The remaining sediment was washed with fresh solvent and again centrifuged; this process was repeated twice. The final sediment was dried in an oven for 24 hr at 150°C, and its organic content was determined by thermo-gravimetric analysis (TGA, SDT2960, TA instruments, U.S.A.).

To investigate the sedimentation behavior of UHMWPE as a function of the suspension viscosity, the supernatants with different concentrations of free polymer were made. A determined amount of UHMWPE was added to those supernatant solutions and their settling time was measured by a light scattering method (Turbiscan MA 2000, Formulaction, U.S.A).

The rheological behavior of the ceramic suspension as a function of an amount of dispersant was measured using controlled-stress rheometer (MCR 300, Paar Physica, Stuttgart, Germany). Viscosity was measured as a function of shear rate in ascending order from 0 to 700 s^{-1}. Apparent viscosities of the suspensions with different dispersant concentration were compared at a shear rate of 104 s^{-1}.

Suspensions with different concentrations of the dispersant were heated up to above 150°C to induce sol-gel transition of UHMWPE particulates and the green body was formed after 6 hrs. The bodies were dried in stagnant air for 24 hrs and cut into rectangular samples ($2.5 \times 2.5\ cm^2$). The cross-sections of as-dried films was examined by a scanning electron microscope (SEM, JSM 5900 LV, JEOL, Tokyo, Japan). The samples were then gold-coated and examined at an accelerating voltage of 15 kV.

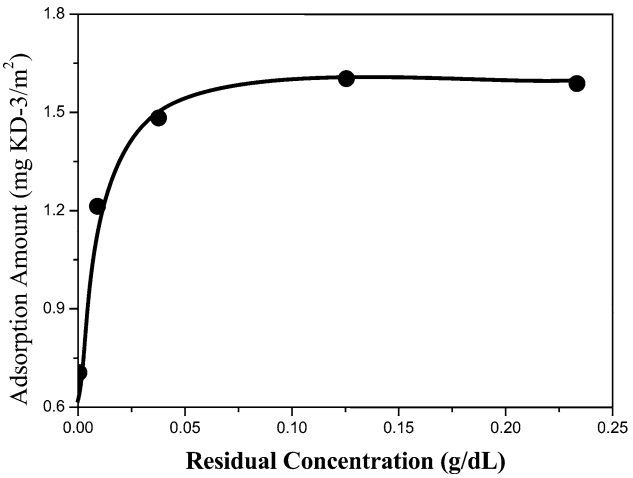

Fig. 2 Adsorption isotherm of KD-3 on $BaTiO_3$ as a function of dispersant concentration

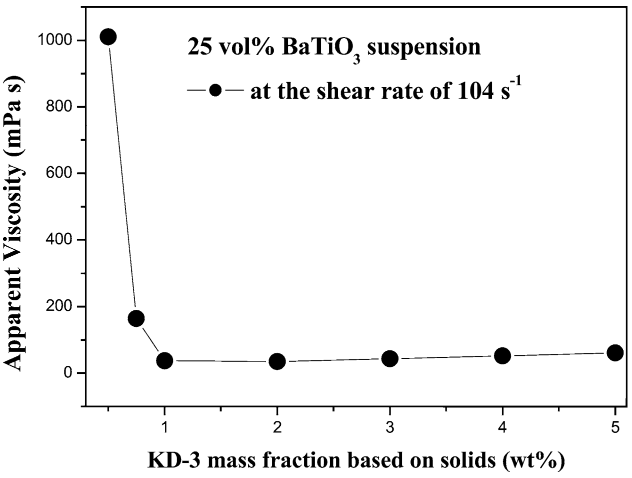

Fig. 3 Apparent viscosity of 25 vol% $BaTiO_3$ suspension as a function of dispersant mass fraction at shear rate of $104\,s^{-1}$

3 Results and discussion

For the control of green microstructure of $BaTiO_3$/UHMWPE cast body in the presence of the non-adsorbed organic additives, it is necessary to predetermine the adsorption isotherm of the dispersant on $BaTiO_3$ and to obtain the dispersion stability of the $BaTiO_3$ suspension. Figure 2 shows the adsorption behavior of KD-3 on $BaTiO_3$ in decalin. It was found that the adsorption amount sharply increases up to the saturation point, without the residual KD-3, which means the non-adsorbed on $BaTiO_3$ surface and freely exists in the bulk solution. This means that KD-3 can be linearly adsorbed on $BaTiO_3$ up to 1 wt% of the solid. Its plateau coverage occurred at 1.55 mg/m^2 KD-3 at 0.04 g/dl residual concentration which corresponds to dispersant mass fraction of 1% based on solid. Beyond this concentration, the dispersant is no longer adsorbed onto $BaTiO_3$ and remains free in the bulk solution.

To clarify the relationship between the adsorption behavior of KD-3 and the stability of the 25 vol% $BaTiO_3$ suspension, the rheological behavior of suspension was studied and the results are shown in Fig. 3. As the amount of dispersant was increased, viscosity decreased up to a dispersant mass fraction of 1%. Beyond this concentration, the suspension viscosity became nearly constant, indicating that the non-adsorbed KD-3 does not deteriorate the suspension stability. This is in good agreement with work of V. Moloney et al. [18]. They demonstrated that the residual dispersant, SP3000, with low molecular weight (approximately 1400 g/mol) leads to the increase in solution viscosity of the dispersion medium, but it does not result in the depletion flocculation. KD-3 used in the present study has the same order of molecular weight as that of SP3000, and thus it is expected that the depletion phenomena are not observed in this work.

However, when UHMWPE is added in $BaTiO_3$ suspension, the instant phase segregation of a $BaTiO_3$ and UHMWPE particulates inevitably occurs due to the huge difference in the particle size between 0.3 μm sized $BaTiO_3$ particulates and 150 μm sized UHMWPE. This unstable suspension gives rise to a serious stabilization problem in the fabrication of MLCCs [19]. Thus, we attempted to minimize the settling velocity difference between $BaTiO_3$ and UHMWPE particulates and to obtain the co-dispersion stability of the multi-component system of $BaTiO_3$ and UHMWPE by changing the suspension viscosity via the control of non-adsorbed dispersant concentration. As mentioned above, the fully-covered monolayer is formed at the concentration of 1 wt% KD-3 based on solid contents and thus the excess of KD-3 remains freely in the suspension beyond this concentration; the non-adsorbed KD-3. Figure 4(A) shows the supernatant solution viscosity as a function of KD-3 fraction. It was found that the supernatant viscosities proportionally increase with the amount of the non-adsorbed polymer, beyond the concentration of 1 wt% KD-3 based on solid contents. This results in increase in the sedimentation time of UHMWPE (Fig. 4(B)). The settling velocity of UHMWPE particulates in the suspension with 5 wt% KD-3 is slower reduced than twice compared to that in the suspension with 1 wt% KD-3. Thus, the instant phase segregation of a $BaTiO_3$/UHMWPE suspension containing the non-adsorbed dispersant is expected to be avoided by the control of the suspension viscosity.

In order to examine the relationship between the consolidation behavior of UHMWPE and the microstructural evolution of $BaTiO_3$/UHMWPE, SEM images of the sheets prepared from three suspensions containing different concentrations of the dispersant were examined. The green body prepared from the suspension with 0.5 wt% (Fig. 5(A)) clearly shows many large pores and agglomerated particulates, indicating the flocculated system. The green body with 1 wt%

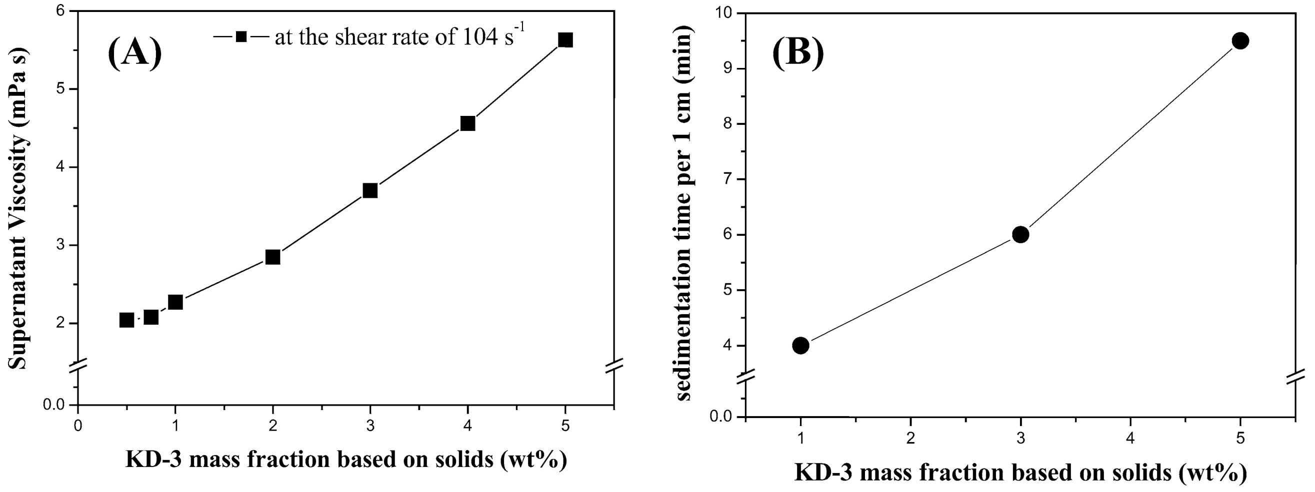

Fig. 4 The supernatant viscosity of the suspensions (A) and the sedimentation time of UHMWPE (B) as a function of dispersant concentration

KD-3 (Fig. 5(B)) has a more homogeneous and denser microstructure than that with 0.5 wt% KD-3, but non-uniform UHMWPE gel networks are still present. This is attributed to the inevitable phase segregation between both particulates, as mentioned above. On the other hand, it was confirmed that the uniformity of the green microstructure from the suspension with 5 wt% KD-3 (Fig. 5(C)) was significantly improved. This reflects that the control of the consolidation behavior of UHMWPE by the residual dispersant in the suspension enhances the uniformity of the green microstructure of the sheet. Consequently, these findings can be helpful for the preparation of a homogenous green sheet for the fabrication of the ultra-thin layers less than 1 μm through a modified polymeric extrusion method.

4 Conclusion

We have shown that the consolidation behavior of UHMWPE particulate in $BaTiO_3$ suspension strongly influences the uniformity of the green microstructure. From the adsorption isotherm data, the optimum amount of the dispersant to obtain a complete coverage was determined to be 1% mass fraction based on solids. The suspension viscosity significantly decreased up to this point and it became nearly constant with a further addition of the dispersant. It was found that the sedimentation behavior of 150 μm sized UHMWPE is improved by the control of the non-adsorbed dispersant in the bulk solution. This led to the homogeneous microstructure of $BaTiO_3$/UHWMPE cast body.

Acknowledgments This work was supported by the Korea Institute of Science and Technology Evaluation and Planning (KISTEP) program through the National Research Laboratory (NRL) program in 2005.

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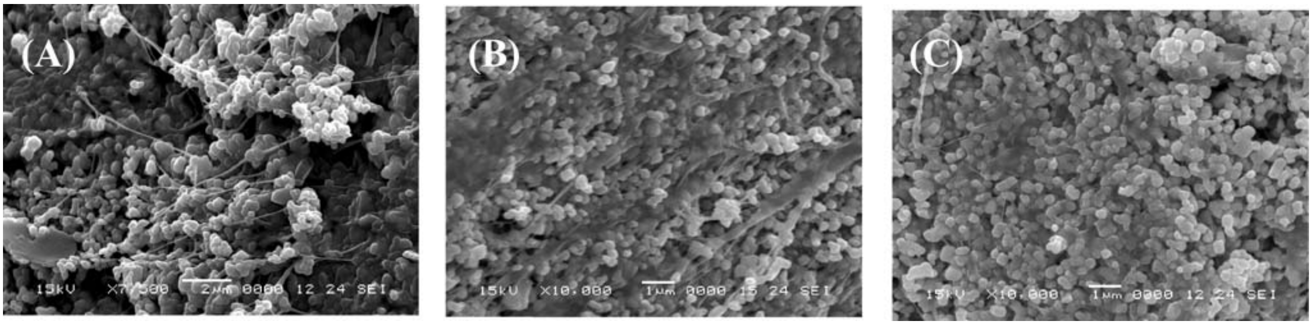

Fig. 5 Scanning electron micrographs of the green bodies prepared from the suspensions with dispersant mass fraction of 0.5% (A), 1.0 (B), and 5.0 wt% (C) based on solids, respectively

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