Improved Ceramics through New Measurements, Processing, and Standards

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PARTICLE SIZE CHARACTERIZATION OF HIGHLY CONCENTRATED BARIUM TITANATE SLURRIES BY ULTRASONIC ATTENUATION SPECTROSCOPY

Shin-ichi Takeda, Hidehiko Suenaga, Isao Tari

Faculty of Engng. Okayama University, 3-1-1 Tsushimanaka, Okayama 700-8530, Japan

ABSTRACT

The present paper investigated the feasibility of acoustic and electroacoustic spectroscopy to characterize the microscopic properties of $BaTiO_3$ aqueous slurries for developing an actual producing process for electronic ceramics. It is demonstrated that the acoustic and electroacoustic spectroscopy can have the capability to obtain information on the microscopic properties of the slurry, such as PSD, size distribution width and zeta potential. But, the delicate control of the macroscopic properties of slurry, such as viscosity and microstructure of the casted green tape, requires other information on the structural attenuation and micro-viscous attenuation.

INTRODUCTION

Organic solvents such as ethanol, trichloroethylene or toluene have been used for many years as dispersing media for the preparation of $BaTiO_3$ tape-casting slurries [1]. For safety, environmental and economic reasons, there is a need to move away from the use of organic solutions toward aqueous solutions. The first step in the study of aqueous $BaTiO_3$ dispersion is the evaluation of the microscopic properties of slurries, which has to meet critical requirements for controlled viscosity and resulting in green tapes with well-controlled properties. In this sense, the evaluation of the microscopic properties of slurries could be a key technique to control the macroscopic properties of slurries, such as viscosity and microstructure of the cast green tape. Many techniques have been used to characterize slurries. Techniques that measure macroscopic properties of slurry include rheological measurements, settling test, and measurement of packing density of cast bodies [2]. But insight into the microscopic slurry properties such as particle size distribution and surface charge has not been obtained, because most of the techniques for particle sizing and determination of surface charge were restricted to very diluted suspensions.

Recently, acoustic and electroacoustic spectroscopy are developing rapidly as an alternative to light scattering methods [3-5]. The capability of spectroscopy to characterize concentrated disperse systems probably provides much of the useful information for developing an actual production process for electronic ceramics through aqueous slurry routes. Therefore, this study investigated the feasibility to characterize the microscopic properties of $BaTiO_3$ aqueous slurries.

EXPERIMENTAL PROCEDURE

Commercially available $BaTiO_3$ powder was used in this study; BT-02 (Sakai-Kagaku Co., Japan) with a BET specific surface area of 7.1 m^2/g. The average particle size reported by the manufacture was 0.20 μm, which is the size measured by SEM. The chemical analysis results give: Ba/Ti=0.999, SrO 0.02%, CaO 0.003%, Na_2O 0.002%, SiO_2 0.002%, Al_2O_3 0.001%, Fe_2O_3 0.001%. The polymer dispersant used in this study was polyacrylic acid (PAA) and polymaleic acid (PMA) (Aldrich.,USA) with an average molecule weight of 2,000 and 13,000, respectively.

$BaTiO_3$ powder was mixed into aqueous solutions with different amounts of added dispersant (0.10~0.75mass% on the basis of $BaTiO_3$ weight), then ultrasonicated for 30sec. The solid loading in the slurry was fixed at 10vol%. The viscosity of prepared slurry was determined by a cone-and-plate viscometer at a shear rate of $192s^{-1}$. Particle size distribution in highly concentrated slurry and the zeta potential of $BaTiO_3$ particle with various amounts of polymer dispersant were measured by ultrasonic attenuation spectroscopy and colloid vibration current, respectively (DT-1200; Dispersion Technology, Inc., NY, USA). The adsorbed fraction of polymer on $BaTiO_3$ particles was determined by measuring the amount of free polymer in supernatant solution, which was obtained from $BaTiO_3$ slurry using by centrifugal sedimentation at 10,000 rpm for 15 min. The amount of free polymer was measured using a total carbon analyzer (TOC-5000, Shimazdzu Co., Ltd., Japan).

RESULTS AND DISCUSSION

The rheological behavior of $BaTiO_3$ slurries is shown in Figure 1, which was represented by apparent viscosity as a function of the added amount of dispersants. Prepared mixtures of powder and solutions were so viscous that measurement was not made when no dispersant was added to the slurry for both PAA and PMA. It is observed that apparent viscosity abruptly decreases when the added amount of dispersant was at around 0.1mass% and remains constant in the range of 0.2mass% to 0.75mass%. The pH of slurry was also shown in Figure 1, and found to increased slightly (from pH 8.3 to 10.5) with increasing the added amount of each dispersant. The adsorption densities of polymer dispersants onto the $BaTiO_3$ surface as a function of the added amount of dispersants are shown in Figure 2. The result is that adsorption densities of each dispersant increased with increasing the added amount of dispersant and that the adsorption density curves as a function of the added amount of dispersants largely deviate from the straight line at 0.3mass% for PAA and 0.4mass% for PMA. It is evident that the adsorption density of dispersants does not explain the viscosity behavior of $BaTiO_3$ slurries.

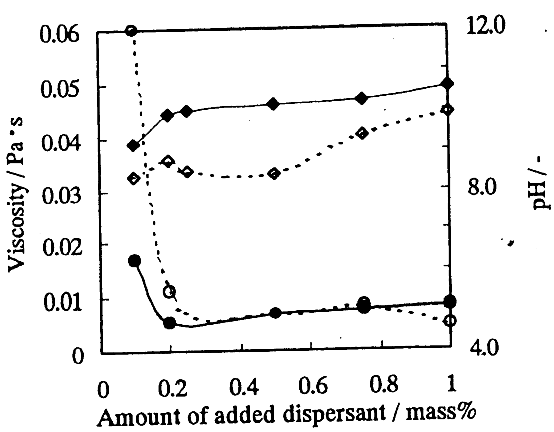

Fig.1 Viscosity ((●)PAA(○)PMA) and pH of the slurries ((◆)PAA(◇)PMA) as a function of the added amount of dispersant.

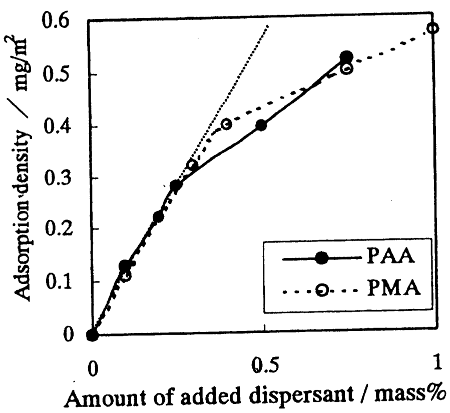

Fig.2 Adsorption density as a function of the added amount of dispersant.

Then, zeta potential of $BaTiO_3$ particles and the PSD (median size and distribution width depicted as log $[d_{84}/d_{50}]$) of $BaTiO_3$ slurries with various amounts of dispersant were measured in order to clarify a correlation between macroscopic properties and microscopic properties.

The zeta potential of the $BaTiO_3$ particles as a function of the added amount of dispersant, measured by colloid vibration current, is shown in Figure 3. It is found that the measured zeta potential of $BaTiO_3$ particles shows a negative charge and increases its magnitude abruptly up to 0.3mass% in the case of PAA. The same tendency of zeta-potential was observed for PAA with an average molecular weight of 10,000. On the other hand, for the case of PMA, $BaTiO_3$ particles are slightly charged, but the magnitude of the measured zeta potential was small and does not change so much with an increase in the added amount of dispersant. These results suggests that difference in zeta potential could be arised not

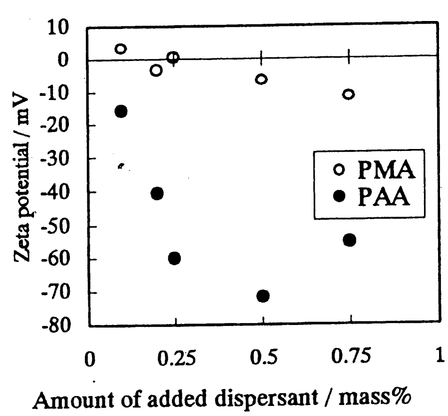

Fig.3 Zeta potential as a function of the added amount of dispersant.

from molecular weight, but from conformational difference of dispersant molecule.

Figures 4 and 5 show the attenuation spectra of the $BaTiO_3$ slurries when the added amount of PAA and PMA were changed, respectively. It is evident that the shape of the curves was changed, which reflects the change in dispersed/flocculated state of the slurry. The slurry having a log normal distribution of the particles shows a bell shaped curve. On the other hand, the slurry having a bi-modal distribution or broad distribution of particle size shows a broad or flat curve. The attenuation curves indicate that PSD greatly changes depending on the added amount of dispersant.

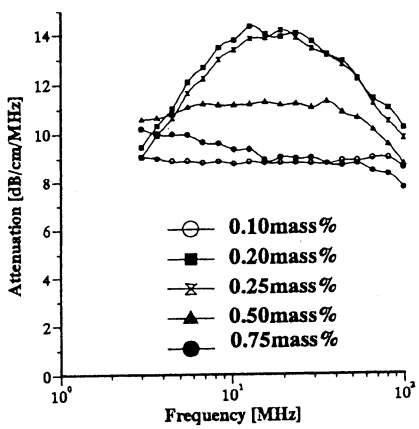

Fig.4 Attenuation spectra of barium titanate slurry as a function of the added amount of dispersant, PAA.

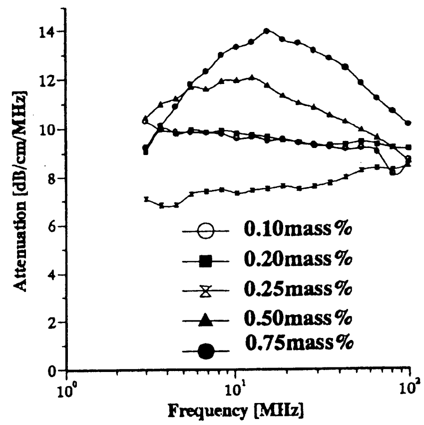

Fig.5 Attenuation spectra of barium titanate slurry as a function of the added amount of dispersant, PMA.

Figure 6 shows particle size distribution of slurries at various amounts of PAA. The PSD in $BaTiO_3$ slurry shows the bi-modal distribution with two peaks at 0.1mass% and the log normal distributions above 0.2mass% addition of PAA. Figure 7 also shows particle size distribution of slurries at various amounts of PMA. The PSD in $BaTiO_3$ slurry shows a bi-modal distribution at 0.1mass% as well as the case of PAA and exhibits truncated log normal distributions above 0.2mass% addition of PMA. The smaller peak at 0.1mass% addition of PAA and PMA corresponds to the primary particle size (0.20 μm) as reported by the manufacture, and the larger peak should _correspond to the flocculated size (1.4 μm and 1.7 μm). Figures 8 and 9 show median size and distribution width of PSD as a function of the added amount of dispersant, except 0.1mass% (only the size of the two peaks is plotted in the figure).

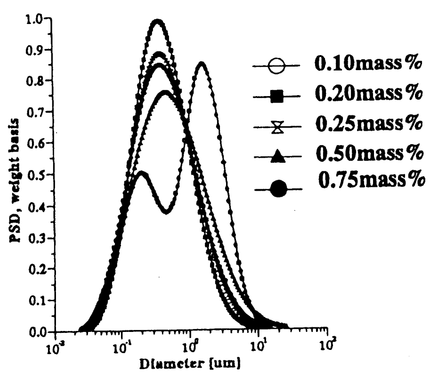

Fig.6 Particle size distribution of barium titanate slurry as a function of the added amount of dispersant, PAA.

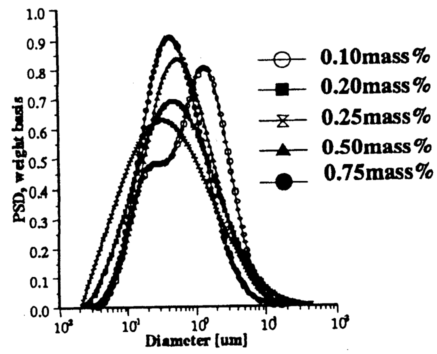

Fig.7 Particle size distribution of barium titanate slurry as a function of the added amount of dispersant, PMA.

In the case of the PAA shown in Fig.8, it is found that the median size slightly increases and distribution width increases as a function of the added amount of PAA. In the case of PMA shown in Fig.9, the median size has the minimum and distribution width has a maximum at 0.25mass%.

Comparison between viscosity and changing median size and distribution width with the added amount of dispersant indicated that flocculation existed below 0.1mass% and this resulted in the high value of the viscosity. But, this comparison cannot give a rational explanation for the

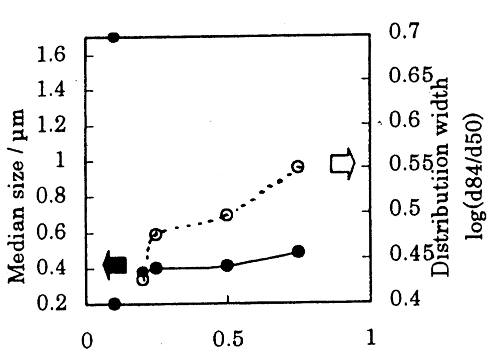

Fig.8 Median size as a function of the added amount of dispersant, PAA.

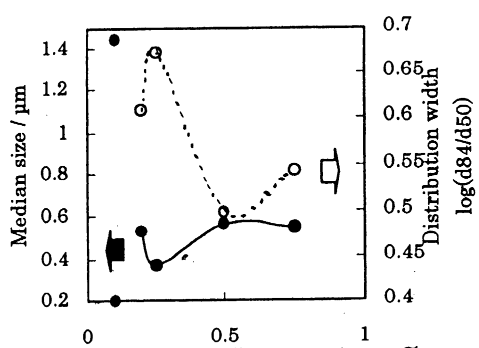

Fig.9 Median size as a function of the added amount of dispersant, PMA.

viscosity-PSD relation above the range of 0.2mass%, which implies that precise control of the macroscopic properties of the slurry requires information on microscopic properties of the slurry.

SUMMARY

This study investigated the feasibility to characterize the microscopic properties of $BaTiO_3$ aqueous slurries for developing an actual production process for aqueous systems. The obtained results demonstrated that the microscopic properties of a slurry, such as PSD, size distribution width and zeta potential, can provide information on the reason for decrease in viscosity in the range of the added amount of dispersant below 0.1mass%. But, the comparison cannot give a rational explanation for the viscosity-PSD relation above 0.2mass%, which implies that precise control of the macroscopic properties of the slurry requires information on the microscopic properties of the slurry other than PSD. The acoustic spectroscopy has the capability to obtain information on structural attenuation and micro-viscous attenuation, which could help the delicate control of macroscopic properties such as viscosity.

ACKOWLEDGEMENT

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