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Nonaqueous Suspension Properties of High Purity Submicron Barium Titanate Powders

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비 수용매에서의 고순도, 극미립자 $BaTiO_3$ 분말의 Suspension 특성

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초 록

공침법에 의하여 얻어진 고순도, 극미립자인 $BaTiO_3$ 분말의 분산거동을 조사하였다. 분산매로는 수용매와 비수용매인 methyl ethyl ketone (MEK)과 ethanol (ETOH)을 이용하였다. Suspension에서의 입자의 분산상태는 pH변화와 MEK, ETOH의 몰 비를 조절하여 각각의 suspensions에 polymer (polyvinyl butyral)를 첨가시켜 변화하였으며, 그 거동은 유동학적 성질, 침강 거동, electrokinetic 성질을 측정함으로써 파악되었다.

비 수용매의 몰 비가 3 : 1, MEK / ETOH - $BaTiO_3$ 에서 polymer를 0.5 ~ 1 % 첨가시켰을때, 입자의 분산이 가장 잘 이루어졌다.

I. Introduction

Colloidal suspensions prepared with nonaqueous liquids are important in ceramic processing operations such as tape casting, slip casting, spray drying and extrusion (1, 2). However, investigations of the properties of such suspensions are limited.

In this present work, the suspension behavior of $BaTiO_3$ powder was investigated using two nonaqueous liquids-ethanol (ETOH) and methyl ethyl ketone (MEK).

Rheological, sedimentary and electrokinetic properties were modified for various mixed liquid ratios. The effect of polyvinyl butyral resin (PVB), a polymeric binder, on submicron $BaTiO_3$ suspension properties was also determined.

II. Experimental procedures

Experiments were carried out with high purity and submicron $BaTiO_3$ powders prepared by coprecipitation method (3) in $C_2H_2O_4$ solution (Fig. 1).

The $BaTiO_3$ had a medium equivalent Stokes diameter of 0.1 μm and specific surface area of ~ 2.47 m^2/g. Suspensions liquids were ethanol (ETOH, Merck, Co.) and methyl ethyl ketone (MEK, Rots Chem., Co.). The polymer used in this study was polyvinyl butyral (Monsanto, Co.).

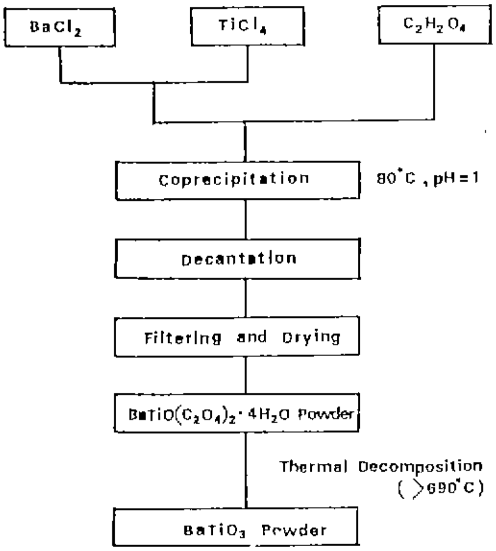

Fig. 1. Flow chart of $BaTiO_3$ preparation by coprecipitation method in $C_2H_2O_4$ solutions.

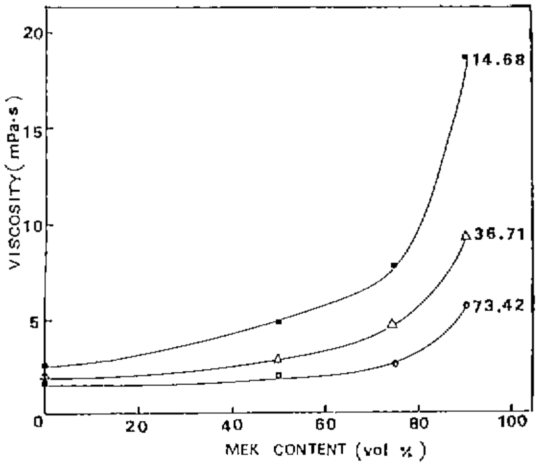

Fig. 2. Plots of suspension viscosity (at three shear rates) vs. vol.% MEK in suspension liquid phase.

Suspension rheological flow curves were determined using a rotational viscometer (Bookfield Inc.).

Sedimentation density was determined by pouring suspension (of known weight) into a 25 ml graduated cylinder. The measured bulk density was divided by the powder true density in order to obtain the relative density. Electrical conductivity measurements (Metrohm, Inc.) were made on the "pure" liquids (various MEK ratios) and on the supernatant liquids of extremely well centrifuged suspensions. A microelectrophoresis apparatus (Zeta-Meter Inc.) was use to measure the electrokinetic mobility of particles. Zeta potentials were determined from the electrophoretic mobilities using the Helmholtz-Smoluchowski equation (4). Polymer adsorption isotherms were gravimetically determined. The dielectric constant (k) and $\tan\delta$ were measured by the digital LCR meter (HP 4262 A) at 1 KHz.

III. Results and Discussion

1) Effect of MEK/ETOH ratio on suspension properties

The effect of liquid ratio (MEK/ETOH) on suspension properties was investigated for $BaTiO_3$/liquid suspension. Plots of viscosity (at shear rates of 14.68, 36.71 and $73.42S^{-1}$) vs. vol.% MEK (in the liquid phase) are shown in Fig. 2. Several observations are noted:

(1) All suspensions show shear thinning behavior, i.e. the viscosity decreases as the shear rate increases. This behavior is characteristic of flocculated suspensions. Under low shear rate conditions, liquid is immobilized in the interparticulate phase channels of flocs and floc networks. The viscosity is increased (relative to dispersed suspensions) due to the increased "effective" solid loading. Shear thinning flow results from the breakdown of the flocculated structure (and the release of entrapped liquid) as the shear rate is increased.

(2) In $BaTiO_3$ suspensions, the viscosity increases continuously with increasing MEK content. This result indicates that more extensive flocculation occurs at high MEK/ETOH ratios.

Sedimentation behavior (Fig. 3.) for $BaTiO_3$/

liquid suspension also indicates that increased flocculation occurs at higher MEK contents.

Highly flocculated suspensions tend to form sediments with low relative density due to the large amounts of interparticulated porosity associated with flocs and floc networks. For $BaTiO_3$ suspensions, the sedimentation density increases slowly over the range 0 ~ 75 vol.% MEK, but decreases significantly at higher MEK contents.

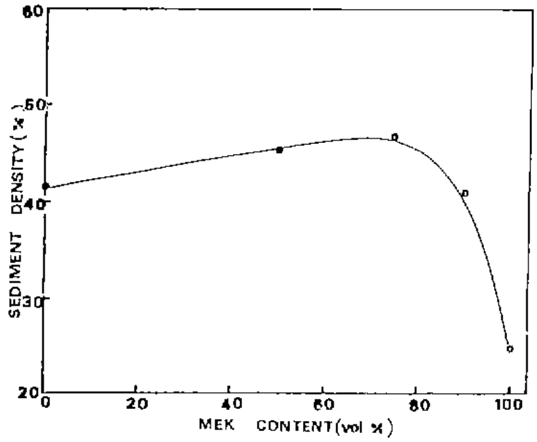

Fig. 3. Plots of sediment density vs. vol. % MEK in suspensions liquid phase.

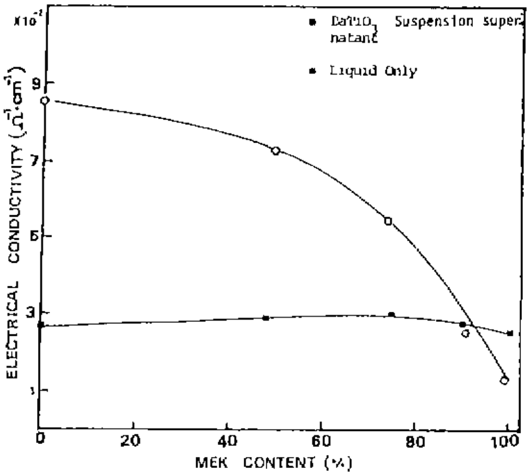

Fig. 4. Plots of electrical conductivity vs. vol. % MEK in (a) various MEK/ETOH liquid compositions and (b) supernatant liquids obtained from centrifugation of $BaTiO_3$ / liquid suspensions.

Fig. 4. shows the electrical conductivity of (a) MEK/ETOH liquids of various liquid ratios. In each case, the conductivity decreases as the MEK content in the liquid phase increases. Higher electrical conductivities are observed in the suspension supernatants (i.e. compared to the "pure" liquids) due to the presence of ions leached into the liquid phase from the ceramic particles.

The results indicate that MEK supports less electrolytic dissociation compared to ETOH.

2) Effect of polymer additions on suspension properties

Plots of suspension viscosity vs. shear rate are shown in Fig. 5 for $BaTiO_3$ - 3:1, MEK/ETOH suspensions containing various amounts (0 ~ 2 vol.%) of polyvinyl butyral resin.

The suspension with no polymer addition shows extensive low shear rate flocculation, as indicated by the high suspension viscosities and highly shear thinning behavior. In contrast, sus-

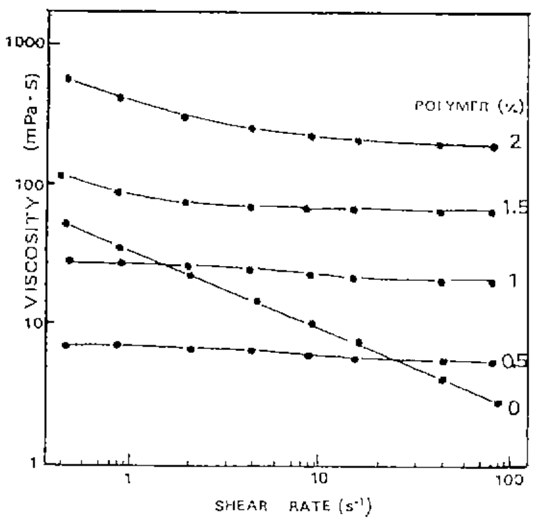

Fig. 5. Plots of suspension viscosity vs. shear rate for $BaTiO_3$ - 3:1 MEK/ETOH suspension.

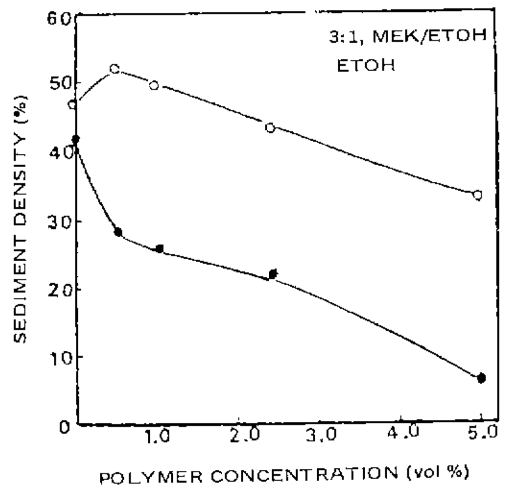

Fig. 6. Plots of sediment density vs. polymer concentration for $BaTiO_3$-ETOH and 3:1 MEK/ETOH suspensions.

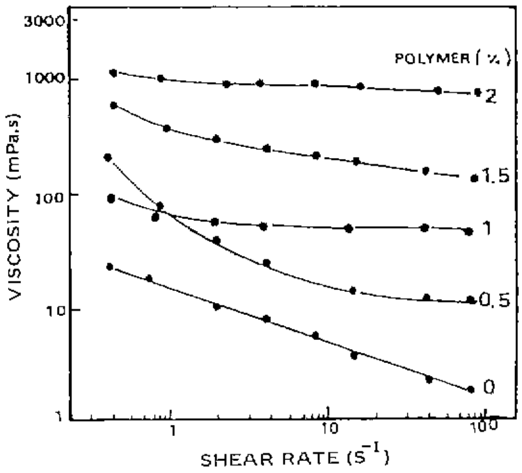

Fig. 7. Plots of suspension viscosity vs. shear rate for $BaTiO_3$-ETOH suspensions containing indicated amount of polymer.

pensions with small polymer additives (0.5 ~ 1.0 vol.%) have low viscosities and approximately Newtonian behavior.

Thease observations indicate that suspensions with small polymer additions are well-dispersed. The effect of polymer additions on the state of dispersion in $BaTiO_3$ — 3:1 MEK/ETOH suspensions was also monitored by sedimentation density measurements (Fig 6).

The suspension with no polymer addition has a low sedimentation density which is consisted with rheological data (Fig. 5) indicating that suspension is highly flocculated at low shear rates. Small additions of polymer (0.5 ~ 1.0 vol.%) increase the sedimentation density. This is consistent with rheological data which (Fig. 5) indicates that these suspensions are well-dispersed Since polyvinyl butyral is a nonionic polymer, suspension dispersion is attributed to a steric stabilization mechanism (5) (i.e. as opposed to electrostatic stabilization).

The effect of polymer additions on the suspension properties of $BaTiO_3$ - ETOH suspensions was also determined. Plots of suspension viscosity vs. shear rate (Fig. 7) show that shear thinning behavior is observed for all suspensions. In the suspension without polymer, electrostatic repulsion forces are too weak to prevent flocculation at low shear rates. Polymer additions in $BaTiO_3$ - ETOH suspensions apparently do not promote dispersion via steric stabilization (such as observed with $BaTiO_3$ — 3:1 MEK/ETOH suspensions, Fig. 5 and Fig. 6).

In fact, the decrease in sedimentation density with polymer additions (Fig. 6) indicates that some bridging flocculation occurs in the $BaTiO_3$-ETOH suspensions.

Experimentally determined polymer adsorption isotherms support that amount of polymer adsorption in 3:1 MEK/ETOH suspensions is much greater than in ETOH suspensions (Fig. 8).

3) Effect of pH on suspension properties

The state of particulate dispersion in suspension is governed by the electrostatic repulsion and London-van der waals attraction forces that operate between particles (1). The decrease in stability (against flocculation) at lower pH is attributed to decreased electrostatic repulsive forces between particles. This is supported by electrophoresis measurements. Plots of zeta potential vs. pH are shown in Fig. 9.

Electrokinetic measurements (Fig. 9) revealed that zeta potential (absolute values) vary by ≈ 45 mV over the pH range 2 ~ 12 (with other factors constant, better dispersion is obtained when particles have zeta potentials, since electrostatic repulsion forces between particles are increased).

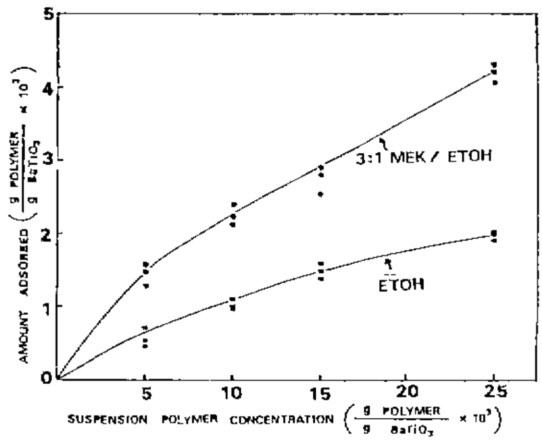

Fig. 8. Polymer adsorption isotherms for $BaTiO_3$-ETOH and $BaTiO_3$-3 : 1 MEK/ETOH suspensions.

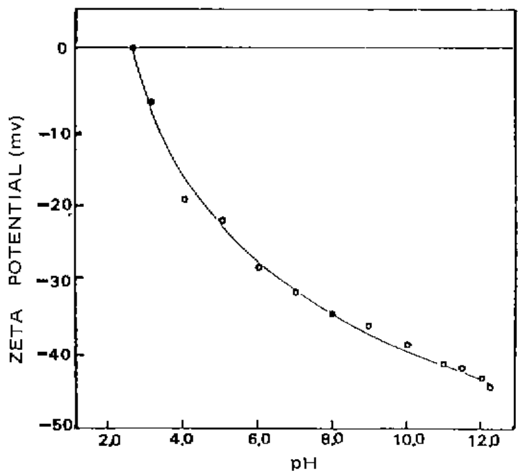

Fig. 9. Plots of zeta potential vs. vol. % MEK in suspension liquid phase.

Fig. 10 shows that the viscosity is independent of shear rate (i.e. Newtonian behavior) in a pH = 11 suspension (5 vol.% solids content). In contrast, the viscosity in a pH = 2 suspension decreases rapidly with increasing shear rate (Fig. 10), i.e., highly shear thinning behavior. The Newtonian behavior and low viscosity observed at pH = 11 are characteristic of well-dispersed suspension. The shear thinning flow and high viscosities observed at pH = 2 indicate that the suspension is highly flocculated.

Green bodies are prepared by particle sedimentation. Plots of intrusion volume vs. pore

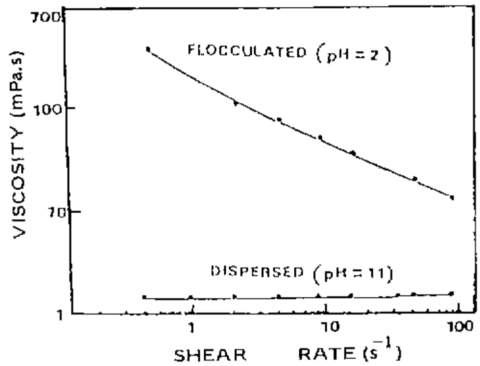

Fig. 10. Plots of suspension viscosity vs. shear rate for $BaTiO_3$ in pH=2 and pH=11 solutions.

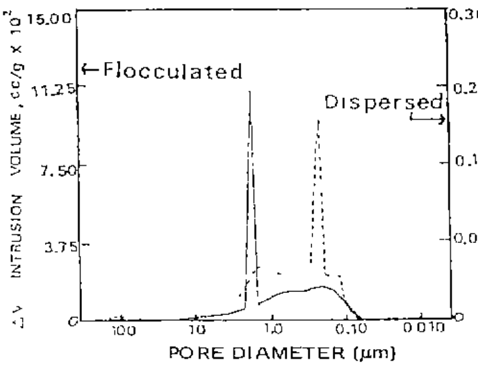

Fig. 11. Mercury Intrusion pore size distribution for compacts with the same green density, prepared from flocculated $BaTiO_3$ powder and the same powder after dispersion.

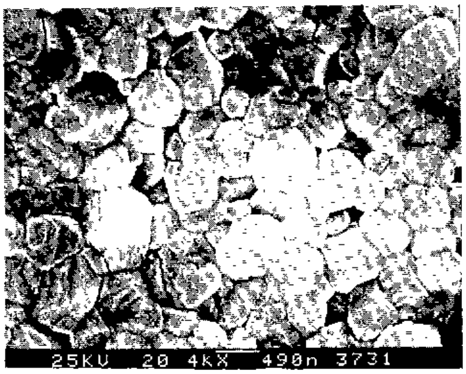

Fig. 12. Scanning electron micrographs of sintered $BaTiO_3$ compacts prepared from dispersed suspension, (pH= 11).

diameter are shown in Fig. 11 for compacts prepared from dispersed (pH=11) and flocculated (pH=2) suspensions. The median pore radius for the flocculated sample is approximately three times as large as for the dispersed sample. Fig. 12 shows an SEM microstructure of the polished surface of sintered $BaTiO_3$ compact, which was prepared from a suspension of well-dispersed and was sintered for 2hrs. at 1320°C.

By using submicron power from a suspension of well-dispersed (pH=11), the dielectric properties of $BaTiO_3$ ceramics were improved. In this materials, grain size was 0.5 μm the dielectric constant (k) was 5200 and tan δ was 0.4%.

IV. Conclusion

The suspension behavior of $BaTiO_3$ powder was investigated using two nonaqueous liquid-ethanol (ETOH) and methyl ethyl ketone (MEK). The effects of liquid ratio (MEK/ETOH) and polyvinyl butyral resin additions on suspension properties were determined.

Rheological and sedimentation measurements showed that all suspensions without polymer were at least partially flocculated. However, increased flocculation was observed at high MEK contents.

Electrokinetic measurements revealed that this was due to decreased electrostatic repulsion between particles. Rheological and sedimentation measurements indicated that small polymer additions promote good dispersion (via steric stabilization) in $BaTiO_3$ − 3.1 MEK/ETOH suspension. In contrast, bridging flocculation apparently occurs in $BaTiO_3$ − ETOH suspensions containing polymer. These differences in suspension behavior are associated with differences in the adsorption behavior of the polymer onto the $BaTiO_3$ particles.

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