The Effect of pH on the Suspension Properties and Homogeneity of Cast Green Bodies of Fine $BaTiO_3$ in Suspending Aqueous Medium

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ABSTRACT

Factors affecting the inter-particle forces between the colloidal $BaTiO_3$ particles were investigated in order to stabilise the suspension system for casting homogenous green bodies. Rheological measurements taken to assess the stability of $BaTiO_3$ particles against flocculation in aqueous medium were correlated with the Electro-kinetic Sonic Amplitude (ESA) to study the Electro-kinetic behaviour of the suspension. The aging kinetics of $BaTiO_3$ particles in aqueous systems was also monitored by ESA and rheological measurements. The analysis of the supernatant solutions from suspensions showed that the concentration of Ba^{2+} ions in solution increased with decrease of the initial pH of the suspension.

Keywords: Inter-particle forces, colloidal suspension, Electro-kinetic sonic amplitude (ESA), flocculation.

INTRODUCTION

Barium titanate ($BaTiO_3$), a high dielectric constant material, is widely used in the manufacture of Multi-Layer Capacitors (MLC). With increased miniaturisation and the tendency to increase the volumetric efficiency of MLCs the thickness of the ceramic capacitor film decreases. This coupled with the necessity to reduce sintering temperature and hence cost makes the use of $BaTiO_3$ powders in the colloidal-size range attractive. In order to utilise the advantages of a colloidal-size powder it is mandatory to control and minimise the inhomogeneities in particle packing and pore-size distribution of the green body. Previous studies (1, 2, 3) have shown that inhomogeneities can be minimised by controlling and manipulating the inter-particle forces in the suspension during processing and forming. Generally, colloidally stable suspensions are preferred since they usually produce higher average packing densities and a more narrow-size distribution than flocculated suspensions (4).

The dispersion of $BaTiO_3$ in non-aqueous solvents has been studied extensively (5-9) and many manufacturers still prefer non-aqueous processing. However, toxicity of the solvents and their environmental hazards coupled with the economic viability of water makes aqueous processing a more attractive option. Processing of $BaTiO_3$ in aqueous medium involves some difficulties because additive formulations are organic solvents, which are not readily soluble in water. Also it has been reported (10, 11, 12) that $BaTi0_3$ is thermodynamically unstable and reactions such as:

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$$BaTiO_3 + H_2O \rightarrow Ba^{2+} + TiO_2 + 2OH^- \quad (1)$$
$$BaTiO_3 + CO_2 \rightarrow BaCO_3 + TiO_2 \quad (2)$$

are theoretically possible.

This makes the aging kinetics and the dissolution of $BaTiO_3$ in aqueous systems, which directly affect the dispersion properties of the suspension, complicated. In this study, attempts have been made to investigate and hence clarify the factors that affect dispersion properties of $BaTiO_3$ particles in aqueous medium.

Ultrasonic waves applied to an electrolyte solution cause a periodic displacement of ion pairs when the ions differ in mass. The fluctuating dipoles generate an alternating electric field, known as the Ion Vibration Potential (IVP), at the frequency of the sound waves. This potential, if measured, could be used to determine the effective hydrated mass.

This effect occurs also in colloids. In colloids the charged particle and surrounding liquid (with counter-ion cloud) are periodically displaced in an acoustic field. The resulting potential termed the Colloid Vibration Potential (CVP) is proportional to the diffuse-layer charge. If a high frequency electric field is applied to a suspension of charged particles, the resulting coherent periodic Electro-kinetic motion generates an acoustic wave at the electrode surface. The amplitude of this wave is proportional to both the particle dynamic mobility and the density difference between the solid and liquid phase. This effect discovered by Oja *et al* (13) has been termed the Electro-kinetic Sonic Amplitude (ESA) which is described by the Equation 3 (14, 15) below:

$$ESA = \frac{P}{E} = c\Delta\rho\varphi f u_d(w) \quad (3)$$

where : P= ESA Pressure in Mpa
E= Electric field in V/m
C= speed of sound in m/s
$\Delta\rho$= Density difference between solid and liquid phase
φ= Particle volume fraction in %
f_g= Geometric factor
$U_d(w)$ = Dynamic mobility in $m^2V^{-1}s^{-1}$

The dynamic mobility differs from the static mobility by an inertial factor:

$$U_d = U_e G\left(\frac{wa^2}{v}\right)$$

Where:
v= *Kinematic vis cosity in Pa.s*
U_e= *static (electrophoretic) mobility in* $m^2s^{-1}V^{-1}$
w= *speed of rotation*
a = *Particle radius in* μm
G= *Inertial parameter*

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In this experiment suspension properties were monitored by the ESA technique and correlated with rheological measurements to assess their effects on suspension characteristics and stability.

II. EXPERIMENTAL

High purity $BaTiO_3$ was used in this study. The mean diameter and particle size distribution of $BaTiO_3$ powder were determined by the laser scattering technique. The BET specific surface area was measured using N_2 sorption on Autosorb-1, Quantachrome. Pore size distribution of cast samples was determined by mercury porosimetry on an Autoscan Porosimeter to give an indication of the green microstructure. Highly purified de-ionised water was used to prepare the $BaTiO_3$ suspensions. Titrants, 1.0 mol/L HNO_3 or 1.0 mol/L NH_4OH were used to adjust the suspension pH.

The $BaTiO_3$ suspensions were prepared in volume fractions ranging from 2-20% depending on the particular experiment. Suspensions were subjected to ultrasonic treatment in order to break down the agglomerates and promote mixing. An ice bath was used to control the temperature of suspensions during the ultrasonic treatment. The suspensions were aged for 12 h at 298°K, using a wrist-action shaker, to establish an equilibrium dispersion system. $BaTiO_3$ suspensions were then adjusted to various pHs and aged further for a week. After the one-week aging period, the suspensions were centrifuged at 1800 rpm and the clear supernatant was withdrawn. Further clarification of supernatant was attained by using a 0.1 µm Acrodisc™ filter cartridge (Gelman Sciences, Ann Arbor, MI, USA). The clear supernatant solutions were analysed to determine the amount of Ba^{2+} in solution.

The Electro-kinetic behaviour of the barium titanate suspension was characterised by the Electro-acoustic technique using ESA-8000 from Matec Applied Sciences. The rheological characteristics of $BaTiO_3$ suspensions were measured at 298°K using a rheometer with a double gap cylinder geometry (RS 75, Haake, Karlsruhe, Germany), in order to assess the stability behaviour of the suspensions. The rheological characterisation was carried out on suspensions containing 20 v/v% solids.

III. RESULTS AND DISCUSSION

The particle size distribution of $BaTiO_3$ powder was as shown in Fig. 1. The median particle size was 0.5 ± 0.01 µm and the surface area was $2.85 \pm 0.10 m^2$.

Concentrated $BaTiO_3$ suspensions prepared under acidic conditions were characterised by an increase in the initial pH (Fig.2). The rate of increase slowed with time and the pH eventually attained an equilibrium value after approximately 5 days. Suspensions with pHs in the alkaline range reached equilibrium at a relatively fast rate and exhibited virtually no subsequent changes in pH. The observed increase in pH associated with acidic suspensions was consistent with the hydrolysis of $BaTiO_3$ (Equation 1). Increase in initial pH reversed the hydrolysis reaction leading to less Ba^{2+} in solution as shown in Table 1. It was necessary to monitor the concentration of Ba^{2+} in solution since dielectric properties of $BaTiO_3$ are affected by the Ba/Ti ratio.

The concentration of Ba^{2+} increased with a decrease in the initial pH of the suspension in the entire range investigated. Thus, the high mobility of the low pH suspensions (Fig. 3) can be attributed to the adsorption of Ba^{2+} which causes the development of a high positive charge inside the Stern layer causing inter-particle repulsive forces strong enough to stabilise the system. The increasing strength of the electrolyte causes compression of the diffuse parts of the double layers around the particles and may, in addition, exert a specific effect through ion adsorption into the Stern layer. In

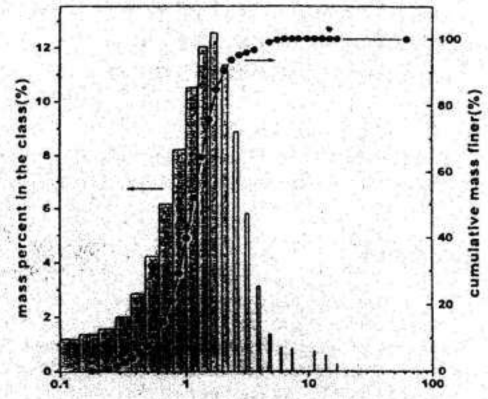

Fig 1. Particle Size Distribution of Raw $BaTiO_3$ Powder.

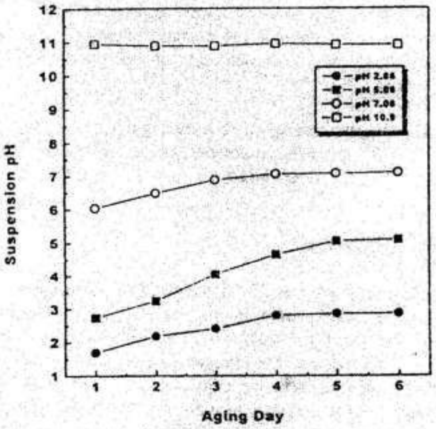

Fig 2: Behaviour of Suspensions with Respect to pH During Ageing.

Table 1: Variation of the Concentration of Ba^{2+} Ions with the Suspension pH

pH of Suspension	Concentration of Ba^{2+} Ions
2.60	8.26
3.04	8.24
4.00	8.16
6.93	4.80
9.64	0.26

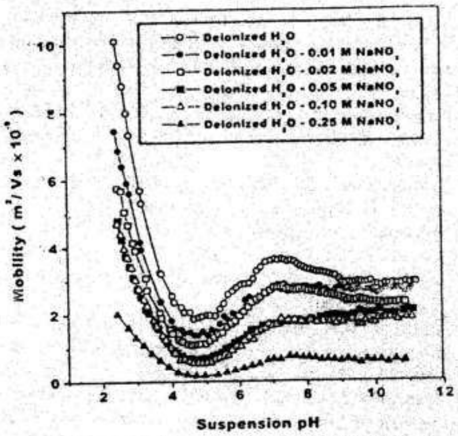

Fig 3. Dynamic Mobility of Particles at Different Ionic Strengths as a Function of Suspension pH.

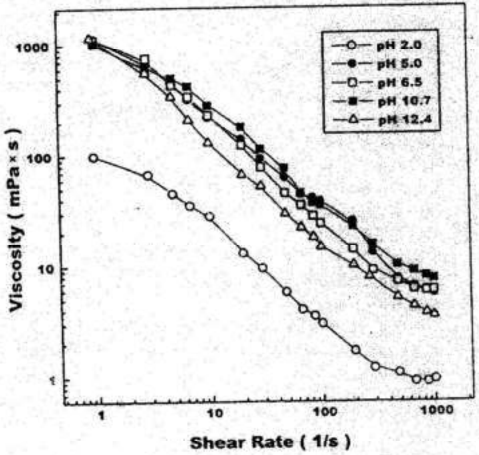

Fig 4. Variation of the Viscosity of Suspensions at various pHs with Shear Rate

this experiment, the range of double layer-layer repulsive interaction was sufficiently reduced to permit particles to approach close enough for van der Walls forces to predominate as evidenced by the reduced mobilities with increasing strength in Fig. 3.

Fig. 4 shows the measured flow curves for 20v/v% $BaTiO_3$ suspensions at various pHs. The state of particulate dispersion in the suspension was varied by pH adjustment and monitored by rheological measurements. Suspension viscosity is a macroscopic property that measures the collective effects of many coincidental contributions to flow behaviour. Viscosity is not a direct measure of the state of dispersion, however, some inference can be made with regard to the suspension structure if the relative contributions of both solid and liquid phases are taken into account. Flow curves of suspensions are highly sensitive to variations in sample preparation and shear history, and are often subject to time-dependent effects, which make it difficult to achieve true equilibrium flow conditions. As the flow curves in Fig. 4 show, suspensions were shear thinning. The shear thinning behaviour can be explained by a perturbation of the suspension structure. At low shear rates suspensions maintain their structure, since thermal motion dominates over the viscous forces. However, at higher shear rates the viscous forces affect the suspension structure causing it to become distorted and leading to shear thinning. The flow curve of suspensions having a pH of 2.0 deviated from those of other pHs as in Fig. 4. This deviation may be attributed to the high mobility and relatively low viscosity of low pH suspensions. Fig. 5a and b show the pore-size distribution of a slip-cast sample carried out by mercury porosimetry. The slip casting was carried out under conditions uniform for all test pieces. The pore-size distribution was found to be influenced by pH; suspensions with relatively low pHs (Fig. 5a) had a comparatively narrow and uniform pore-size distribution, characteristic of a homogenous green body, whilst those at higher pHs (Fig. 5b) covered a wider range of particle sizes.

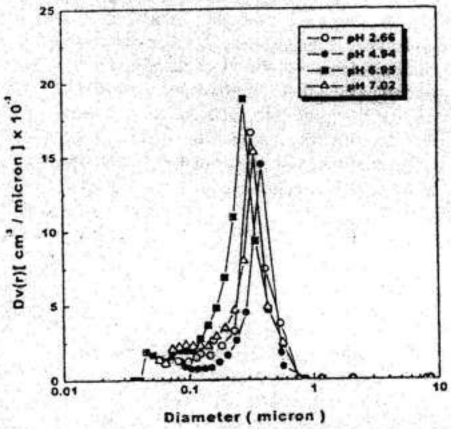

Fig 5a. Pore Size Distribution of Cast Samples from Slips with Relatively Low pH Levels.

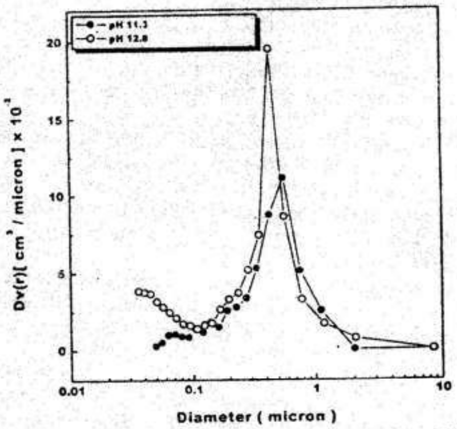

Fig 5b. Pore Size Distribution of Cast Samples from Slips with High pH Levels

Generally, samples cast from suspensions with pHs higher than 7 had the tendency to exhibit the pore-size distribution shown in Fig. 5b which does not enhance the homogeneity of the green samples and therefore leads to inhomogeneous microstructures and deteriorated material properties.

IV. SUMMARY AND CONCLUSION

The hydrolysis of $BaTiO_3$ and hence Ba^{2+} concentration in the suspension was found to be highly dependent on the pH of the suspension. The lower the pH the higher the concentration of Ba^{2+} ions found in the suspension. Suspensions with the lowest pH were found to have the highest mobility within the pH ranges investigated due to the high concentration of Ba^{2+} ions, which exert some deflocculating effect on the suspension. The high dissolution of Ba^{2+} ions need to be investigated further since it may cause a variation in the Ba/Ti molar ratio and hence affect dielectric properties of the sintered material. Suspension rheology at a solids loading of 20% was dependent on the mobility of $BaTiO^3$ and showed a shear thinning behaviour. The decrease in viscosity with increasing shear rate was observed due to the reversible breakdown of the flocculated particles and the release of entrapped water. Suspensions at relatively low pHs showed a narrow pore-size distribution and higher green density of cast bodies. Thus, for improved density and homogeneity relatively low pH-suspensions must be employed for the casting green bodies.

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