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Ceramics International 33 (2007) 207–212

CERAMICS
INTERNATIONAL

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Dispersion of barium titanate in aqueous media

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Received 12 January 2005; received in revised form 26 June 2005; accepted 5 September 2005

Abstract

Four kinds of dispersants including poly(acrylic acid-co-maleic acid), poly-DL-aspartic acid, polyacrylic acid and ammonium citrate were chosen from more than seventy kinds of dispersants by screening experiments concerning their dispersing abilities for barium titanate (BT) suspension in aqueous media. Sediment experiments, rheology characterization and particle distribution measurements were conducted through orthogonal experiments. The optimum concentrations of dispersants, pH value and ball-milling time have been obtained. Judging from the results of both rheological behavior and particle distribution curves, we can conclude that the best effective dispersant for BT particles in aqueous media is poly(acrylic acid-co-maleic acid), while the least effective one is ammonium citrated among these four kinds of dispersants.

Keywords: Barium titanate; Dispersant; Rheological behavior; Orthogonal experiment

1. Introduction

Barium titanate ($BaTiO_3$ or BT) is the most useful ferroelectric material with good electrical properties including high dielectric constant. BT-based dielectrics have dominated the multilayer ceramic capacitor (MLCC) industry since 1950s, representing 80–90% of the business [1]. Tape-casting is a well-established technique used for large-scale fabrication of ceramic substrates and multi-layered structures which involves wet processing of micrometer-sized ceramic particle suspensions to produce green sheets with high packing densities and uniform microstructure. Well-dispersed slurry is the key issue in tape-casting.

Dispersing BT powders into organic media, such as toluene, n-hexane, acetone and benzaldehyde has been widely studied in detail to get well-stabilized suspensions [2–6]. At present, most of manufacturers are producing BT tapes in this way. Using aqueous media instead of organic solvent is desirable nowadays due to obvious reasons such as economic and environmental considerations [7–19]. There are many kinds of dispersants which could be used for dispersing BT into aqueous media. It was the purpose of this work to test as many dispersants as possible to compare their dispersing effect and find the optimum parameters to achieve perfectly dispersed BT suspensions. In this article, some kinds of organic dispersants and polyelectrolyte dispersants were chosen to test their dispersing abilities in BT suspension. More than 70 kinds of possible dispersants were tested and 25 kinds of effective ones were selected to conduct further study. Then we compared the three most effective kinds of polyelectrolyte dispersants, namely poly(acrylic acid-co-maleic acid), poly-DL-aspartic acid and polyacrylic acid with ammonium citrate. Polyacrylic acid and ammonium citrate dispersants are commonly used in aqueous media. Poly-DL-aspartic acid has ever been reported to be effective for dispersing BT [20]. It has been found in our study that poly(acrylic acid-co-maleic acid) is the most potential dispersant [21]. But no work has been reported on the differences of their dispersing effect. A method of orthogonal design has been adopted to compare different dispersants and determine the main factors which affect their dispersing behaviors.

2. Experimental procedures

2.1. Raw materials

$BaTiO_3$ powder (Guoteng Limited Corporation of Functional Ceramics, Shandong, China) with an average particle size of 100 nm, a specific surface area of 8.19 $m^2 g^{-1}$ and a Ba/Ti ratio of 1.000 ± 0.002 was used as-received form. Deionized water was used as a solvent to prepare BT suspensions and the pH was adjusted via addition of HCl and $NH_3 \cdot H_2O$.

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doi:10.1016/j.ceramint.2005.09.006

Some dispersants were supplied by Aldrich Chemical Company (USA), Arcos Organics (Belgium) and Beijing Chemical Reagent Corporation (China). Others were synthesized in our laboratory. These dispersants are listed in Table 1.

2.2. Experimental methods

Aqueous suspensions of 10 wt% BT powders in deionized water of different conditions were prepared in 10 ml graduated cylinders to conduct sedimentation experiments. The suspensions were left untouched to allow the particles to settle down and the volume of supernatants was measured during a certain period of time. The rheological behaviors of BT suspensions with different BT concentrations, different concentrations of dispersants, different kinds of dispersants etc were studied using Modular Compact Rheometer (PHYSICA MCR300, Physica, Germany), a shear rate of $130\ s^{-1}$ was chosen to compare the viscosity values of different BT suspensions. Particle size distributions of BT suspension with different dispersants were determined using BI-XDC sizing analyzer (Brookhaven Instrument Corporation, USA) in order to test and verify the effects of dispersants directly.

Table 1
Dispersants chosen by screening tests

No.	Chemical composition
J1	Cetanyl butyl diacid[a]
J2	Cetanyl propyl diacid[a]
J3	Poly[(isobutylene-alt-maleic acid), ammonium salt-co-(isobutylene-alt-maleic anhydride)], Mw ~6000[b]
J4	Polyacrylamide, Mw ~1500[b]
J5	Poly(acrylic acid-co-maleic acid), Mw ~3000[b]
J6	Poly-DL-aspartic acid, Mw ~3000[b]
J7	Lignosulfonic acid, Mw ~12000[b]
J8	Polyacrylic acid, Mw ~2000[b]
J9	Polyacrylic acid, Mw ~5000[b]
J10	Polyacrylic acid, Mw ~3000[b]
J11	Polyacrylic acid, Mw ~4000[b]
J12	Poly(acrylic acid-co-maleic acid), sodium salt, Mw ~3000[b]
J13	Polyacrylic acid, Mw ~8000[b]
J14	Polyacrylic acid, Mw ~10000[b]
J15	Polyacrylic acid, Mw ~12000[c]
J16	Polyacrylic acid, Mw ~15000[c]
J17	Polyacrylamide, Mw ~3000[b]
J18	Polyacrylamide, Mw ~2000[b]
J19	Polyacrylamide, Mw ~5000[b]
J20	Octyl propyl diacid[a]
J21	Octyl butyl diacid[a]
J22	Hexadaca alkyl ethyldiamine triacetic acid[a]
J23	Sodium salt of hexadaca alkyl ethyldiamine triacetic acid[a]
J24	Ammonium citrate[d]
J25	Hexadecyl trimethyl ammonium chloride[d]

[a] Synthesized in laboratory.
[b] Supplied by Aldrich Chemical Company, Inc., USA.
[c] Supplied by Acros Organics, Belgium.
[d] Supplied by Beijing Chemical Reagent Corporation, China.

3. Results and discussion

3.1. Screening tests

Screening tests for different dispersants were conducted to evaluate their effect for dispersing BT in aqueous suspension. More than 70 kinds of possible dispersants including amines, imidazoles, organic acids and their salts, polymeric substances and some kinds of cationic surfactants have been investigated through initial sediment experiments.

From the initial sediment tests, 25 kinds of dispersants were selected for further evaluation. Both their experimental code number and their chemical composition are listed in Table 1.

Further sediment experiments were designed to evaluate the dispersing effects of these 25 kinds of dispersants. 10 wt% BT suspensions with 0.5 wt% various dispersants were prepared in 10 ml graduated cylinders. Dispersant concentration was calculated by dividing dispersant weight by the weight of $BaTiO_3$ particles. Diluted $NH_3{\cdot}H_2O$ was used to adjust pH value of 10. The volume of supernatants in every cylinder was measured at regular intervals to compare their dispersing effects. Fig. 1 shows some results of these dispersants.

Dispersants that were not shown in Fig. 1 such as J1, J2, and J4 were eliminated because of their strong foam-forming

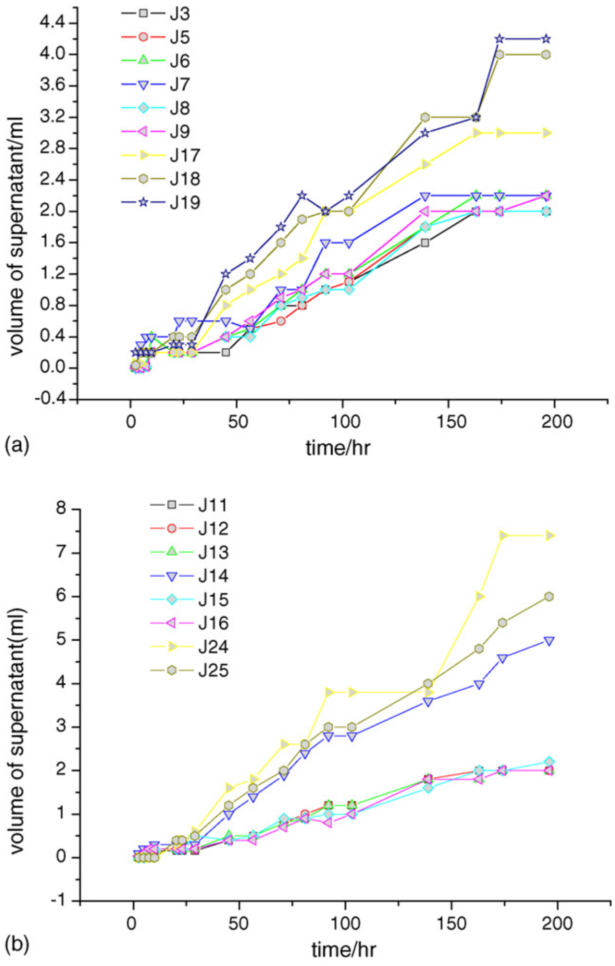

Fig. 1. Results of the sediment experiments.

properties. From Fig. 1, it is obviously found that three kinds of polyelectrolyte including polyacrylic acid, poly(acrylic acid-co-maleic acid) and poly-DL-aspartic acid have good dispersing effects. Further studies were focused on these three kinds of polyelectrolytes and ammonium citrate which is a common used dispersant with low molecular weight. In order to minimize the influence of the molecular weight, the polyelectrolytes with same molecular weight were used for the following study.

3.2. Sediment experiments

In order to compare the effects of these dispersants, orthogonal experiments have been carried out. Dispersant kind, dispersant concentration, suspension temperature, ultrasonic dispersing time and pH value serve as five factors, each factor containing four levels (see Table 2). Therefore, a L16 (4^5) table of orthogonal design was used for the experiment. Random sampling method was used to minimize the influence of changing order. The least volume of supernatants at the same period was the optimum goal. The experimental results are presented by a set of diagrams as shown in Fig. 2.

Table 2
Factors and levels for orthogonal sediment experiment

Factors	Levels			
	1	2	3	4
Dispersant kind	A	B	C	D
Dispersant concentration (wt%)	0.1	0.5	1.0	2.0
Dispersing temperature (°C)	20	30	40	50
Dispersing time (min)	0	2	5	10
pH value	4	7	10	12

A: Poly(acrylic acid-co-maleic acid), Mw ~3000; B: poly-DL-aspartic acid, sodium salt, Mw ~3000; C: polyacrylic acid, Mw ~3000; D: ammonium citrate. A, B, C and D means similarly hereafter.

From the orthogonal sediment experiments, it can be concluded that pH value plays the most important role in suspension stabilization. When pH value is below 7, all of the dispersants could not make favorable contribution to the stability of the suspension. When pH is above 7, suspensions with dispersants are more stable than those without dispersants. The higher the pH, the more stable the suspension is. Because dispersants used in this experiment are anionic surfactant, dissociation becomes more complete when pH increases. This means dispersants adsorbed on the ceramic particles stretch and

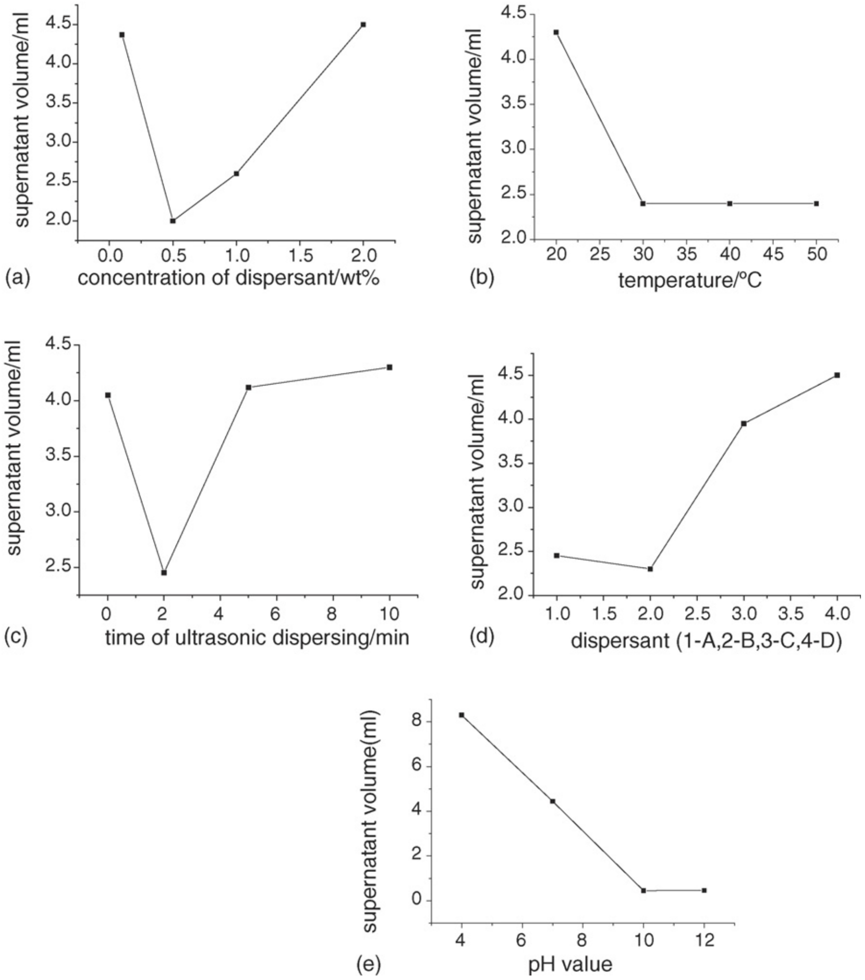

Fig. 2. Results of orthogonal sediment experiments.

repel to form stable suspension by both the electrostatic and steric mechanism. Thus in thereafter experiments pH value over 7 should be adopted. Obviously concentration of dispersant, suspension temperature, dispersants kind and ultrasonic-dispersing time also affect the suspension stabilization. To get a quantitative knowledge of these dispersants, rheological experiments were conducted according to above sediment experiments.

3.3. Rheological behavior

Orthogonal design was again adopted to study their rheological behavior. In experiments, the dispersant concentration, dispersant kind, pH value, concentration of BT and ball-milling time serve as five factors, each factor containing four levels (see Table 3). Suspension temperature is not included in the experiments since the less possibility of its application in industrial manufacture, while ball-milling time is added as an experimental factor. A L16 (4^5) table of orthogonal design was used for the experiment. The experiment results are presented by a set of diagrams (see Fig. 3).

Table 3
Factors and levels for orthogonal rheological experiment

Factors	Levels			
	1	2	3	4
Dispersant kind	A	B	C	D
Dispersant concentration (wt%)	0.1	0.3	0.5	1
Concentration of BT (vol%)	7	15	17	25
pH value	7	9	11	13
Ball-milling time (h)	0	6	16	26

Viscosity of the $BaTiO_3$ suspension decreases sharply at first and reach a minimum at pH 9, followed by a slight increase. This may be explained through a combination mechanism of electrostatic repulsion and steric hindrance to stabilize the BT suspensions. All the dispersants under investigation are anion surfactants, they have higher dissociation rate at higher pH. As a result there are more anions as COO^- group to adsorb onto BT surface at higher pH. Meanwhile, pH will also affect the conformation of polyelectrolytes in water. At higher pH, the polymer molecules tend to be more stretched due to

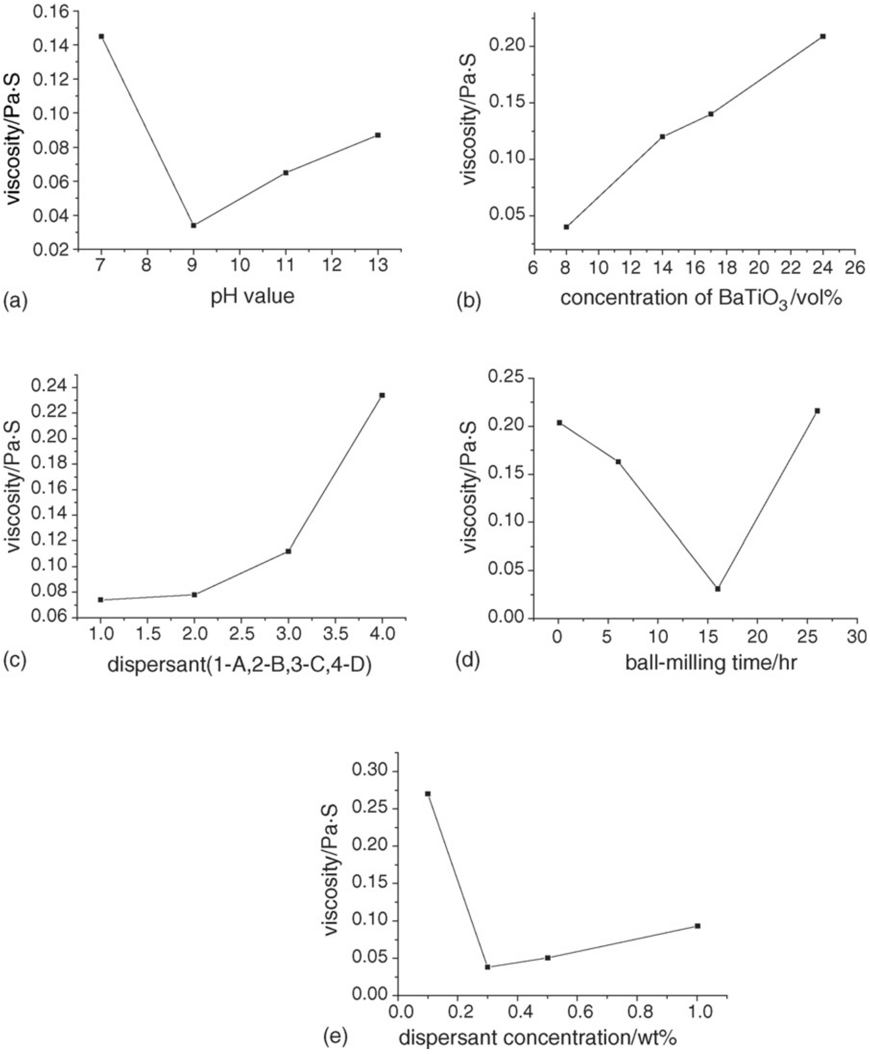

Fig. 3. Results of rheological experiments.

electrostatic repulsion between negatively charged side groups. While at a lower pH, a coiled and compact structure is more preferred, which negatively affects the stabilization of suspensions. However after a complete dissociation, a higher pH means a higher ion strength which will cause the colloidal particle to agglomerate. This can explain the slight increase of viscosity at pH value higher than 9.

With the extension of ball-milling time viscosity of $BaTiO_3$ suspension decrease at first and reach a minimum at 16 h, followed by an obvious increase. At the beginning of ball-milling, agglomeration is destructed which results in a lower viscosity. But after a critical ball-milling time, prolonged time will raise the opportunity for a secondary agglomeration. At the same time, some of the BT particles may be destroyed and leads to a higher viscosity.

Viscosity of $BaTiO_3$ suspension decreases at low dispersant concentration and reaches a minimum at 0.3 wt%. More dispersant adsorb onto the BT surface along with the increase of dispersant concentration at the beginning which results in the decrease of viscosity. It reaches a saturated adsorption at 0.3 wt%. After that too much dispersants may cause a slight increase of viscosity due to tangled chain of the polyelectrolytes.

The three polyelectrolytic dispersants have more effective dispersing ability than ammonium citrate. Dispersing capacities increase in the order of ammonium citrate, poly(acrylic acid), poly-DL-aspartic acid and poly(acrylic acid-co-maleic acid). As it is well known poly(acrylic acid) is a commonly used polyelectrolytic dispersant in aqueous media. Conclusions can be drawn from Fig. 3 that both poly(acrylic acid-co-maleic acid) and poly-DL-aspartic acid are more effective than poly(acrylic acid) with the same molecular weight. This indicates the potential use of poly(acrylic acid-co-maleic acid) and poly-DL-aspartic acid in dispersing BT suspension. From Fig. 3 the optimum conditions can be obtained for dispersing BT suspension. Under such conditions as dispersant concentration of 0.3 wt%, ball-milling time of 16 h and pH value of 9, the best dispersing effect will be achieved.

3.4. Particle size distribution

Optimum conditions obtained from the above experiments were applied to prepare BT suspensions for particle size distribution study in order to get a direct view of dispersing effects of these dispersants (Fig. 4). BT suspension without dispersant and BT suspension with ammonium citrate are badly dispersed, their differential distribution curves are presented in Fig. 4 separately for clearer view. Ammonium citrate is a kind of organic dispersant with low molecular weight. It stabilizes the ceramic suspension only by electrostatic mechanism. Polyelectrolyte dispersants can stabilize the ceramic suspension both by electrostatic and steric mechanism. Consequently, polyelectrolytic dispersants have a relatively ideal dispersing results compared with ammonium citrate (Fig. 4). Poly(acrylic acid-co-maleic acid) and poly-DL-aspartic acid are more effective than polyacrylic acid. But poly-DL-aspartic acid was more difficult to decompose during binder removal period. As a result poly(acrylic acid-co-maleic acid) is a potential effective dispersant that can be used in BT aqueous suspension.

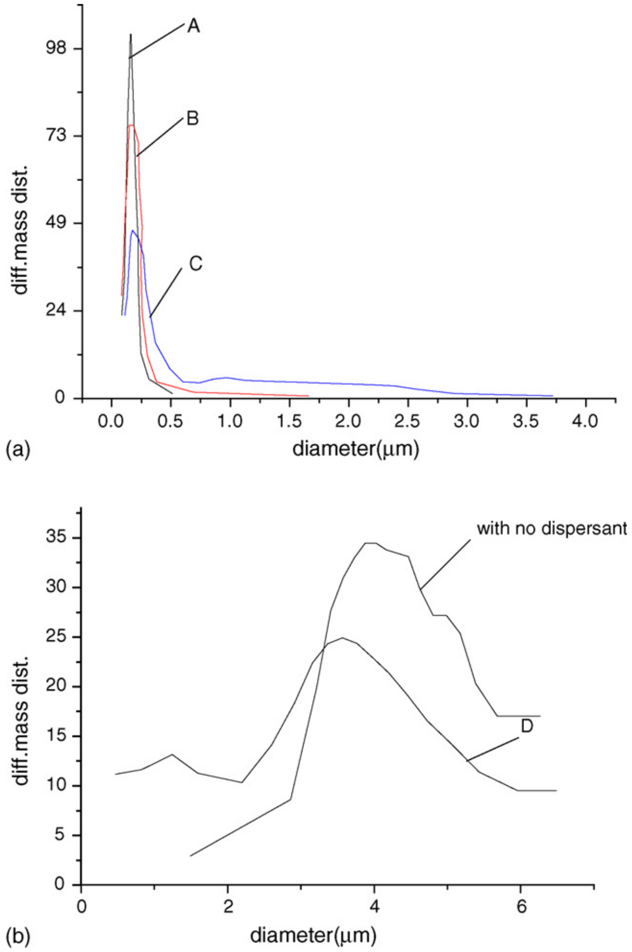

Fig. 4. Differential distribution curves.

4. Conclusions

Four kinds of dispersants, namely, poly(acrylic acid-co-maleic acid), poly-DL-aspartic acid, polyacrylic acid and ammonium citrate were chosen by screening experiment concerning their dispersing effects for BT suspension in aqueous media. Sediment experiment, rheology characterization and particle distribution measurements were conducted through orthogonal experiment. Under an optimum condition with dispersant concentration of 0.3 wt%, ball-milling time of 16 h and pH value of 9, the best dispersing effect has been obtained. From rheological behavior and particle distribution curves, ammonium citrate is the least effective in dispersing BT suspension in aqueous media, while poly(acrylic acid-co-maleic acid) is better than poly-DL-aspartic acid and polyacrylic acid.

Acknowledgements

This work was supported by the High Technology Research and Development Project, China under Grant No. 863-

2001AA325010 and the Ministry of Sciences and Technology of China through 973-Project under Grant No. 2002CB613301.

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