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Effects of ball milling time and dispersant concentration on properties of a lead zirconate titanate aqueous suspension for tape casting

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This contribution explored the effects of ball milling time on properties of a lead zirconate titanate (PZT) aqueous suspension. The particle size distribution, stability and rheological behavior of the suspension were studied by means of laser diffraction particle size analysis, sedimentation height and viscosity measurement, respectively. It was found that ball milling the suspension for 30 and 40 h provided an average particle size of less than 1 μm with a unimodal distribution. The sedimentation height measurement showed that the suspension stability was also improved. Further increasing the ball milling time to 50 h, however, resulted in a significant increase of average particle size. In addition, the size distribution exhibited a bimodal characteristic. A shear thinning behavior was observed for all suspensions. The effects of dispersant concentration were studied using a commercial aqueous solution of ammonium polyacrylate, Dispex A40. The optimum concentration was determined to be 0.6 wt% Dispex A40 based on a PZT powder dried weight basis.

Key words: Milling, Tape casting, Titanates, Aqueous processing.

Introduction

Due to their ferroelectric and piezoelectric properties, lead zirconate titanate (PZT) family ceramics are widely used in commercial electronic applications, such as in sensors, actuators and transducers. Multilayered piezoelectric devices based on PZT involve fabricating the material into thin sheet by tape casting, which is the most effective and reliable method. The process requires preparation of high solid loadings, well-dispersed and highly stable suspensions with shear thinning behavior and optimized low viscosity to ensure uniform, dense and defect-free green tapes.

Traditionally, non-aqueous organic solvents such as alcohols, ketones and hydrocarbons are favored due to their low latent heat of evaporation and low surface tension. A well-dispersed suspension is easy to achieve with a non-aqueous system, leading to uniform and high density green tapes with smooth surfaces. However, organic solvents are toxic and inflammable. Therefore, recent developments tend to replace organic solvents with an aqueous media due to safety, environmental and economic considerations. Aqueous processing of systems such as alumina [1-3], $CaCO_3$ [4] and $BaTiO_3$ [5, 6] have been studied extensively for many years. Since the aqueous-based systems are highly sensitive to process perturbations, uniform green tapes can only be produced under extremely well-controlled conditions. Disadvantages of aqueous systems have been reported including low evaporation rate, the high binder concentration required and flocculation of particles due to hydrogen-bonding linkages [7, 8].

A dispersant is also required in aqueous system to stabilize particles in order to produce a well-dispersed aqueous suspension. Common dispersants for aqueous tape casting suspensions are polyelectrolytes such as sodium carboxymethyl cellulose, ammonium polyacrylate and ammonium poly(methacrylate). Polyelectrolytes coat the ceramic surfaces and stabilize the particles by means of electrosteric repulsion, a combination of electrostatic and steric mechanisms. The optimum level of dispersant is the minimum concentration necessary to stabilize a system and can be determined from the minimum in the suspension viscosity [9] or in the sedimentation volume [10].

In this study, effects of ball milling time on the particle size distribution and suspension behaviors were investigated in order to obtain the optimum conditions for a PZT aqueous suspension. Ammonium polyacrylate was used as a dispersant. The deflocculation curves, viscosity vs. %dispersant, were constructed to find the optimum dispersant concentration for the system. The dispersion and stability of the suspensions were studied through sedimentation heights.

Experimental Procedure

Commercial PZT powder (APC International, Ltd.) used in this experiment is a soft composition with a tetragonal structure. The as-received powder is highly agglomerated with a specific surface area of 1.248 m^2/g

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(BET specific surface area). PZT aqueous suspensions of 60 wt% solids loading were prepared by ball milling in a 125 ml high density polyethylene (HDPE) bottle using zirconia grinding media at a speed of 190 rpm. The ball milling times studied were 20, 30, 40 and 50 h. Particle size distributions after ball milling were measured by a laser diffraction particle size analyzer (Malvern Instrument Ltd.). The rheological behavior of the suspensions were investigated using a viscometer (Brookfield RVDV-E, E2841) with a small sample adapter (7 ml) and spindle number SC 4-21. The suspensions were left undisturbed in graduated test tubes for 2 weeks to allow precipitation of PZT particles. Then, sedimentation heights were measured to study the dispersion and stability of the suspensions.

The dispersant used in this study was Dispex A40 (Allied Colloids, Inc.), a commercial dispersant consisting of 40 wt% ammonium polyacrylate. PZT aqueous suspensions were prepared with 0.2-1.2 wt% Dispex A40 based on a PZT powder dried weight basis. Viscosity measurements were conducted at shear rate of 46.5 and 93 s^{-1} (50 and 100 rpm) as a function of Dispex A40 concentration to verify the optimum dispersant level for the system. Sedimentation of the suspensions with various dispersant concentrations was investigated. The sedimentation heights were measured and compared among suspensions that precipitated completely.

Results and Discussion

Effects of ball milling time

To obtain a well-dispersed and highly stable suspension, particles smaller than 1 μm are preferred because the sedimentation occurs slowly. Ball milling is a widely-used comminuting process in wet processing to reduce the average particle size and break agglomerates. For each material and solids loading, an effective ball milling time can be acquired from the particle size distribution of the milled product. Mass median diameters of PZT particles in 60 wt% solids loading aqueous suspensions prepared with various ball milling times are plotted in Fig. 1(a) and corresponding particle size distributions are illustrated in Fig. 1(b). For ball milling times of 20, 30 and 40 h, the particle size distributions were unimodal. The median diameter decreased from 1.12 μm to 0.90 and 0.84 μm with increasing ball milling time. This is due to an increase of the total numbers of media collision and particle impact with time, which increases probability of particle fracture [11]. For 30 and 40 h ball milling times, although 10 h

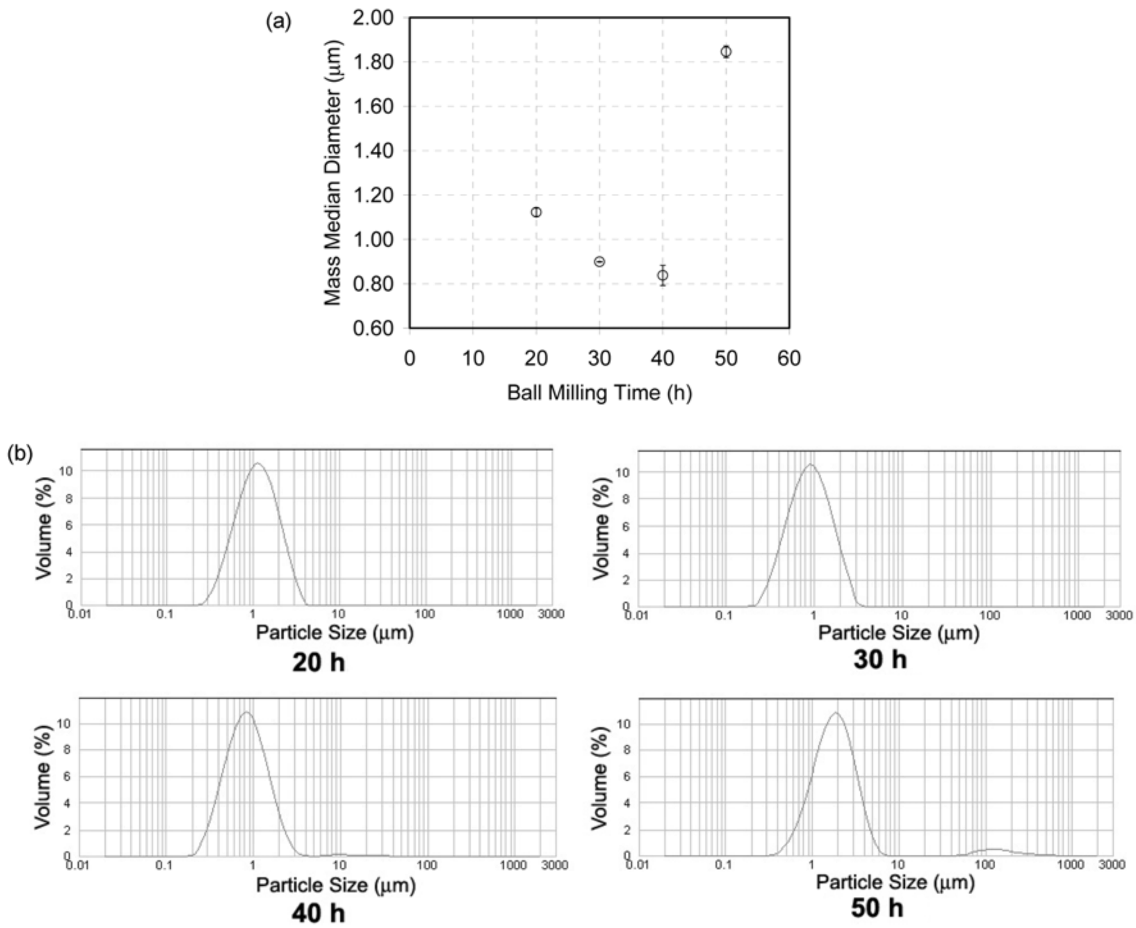

Fig. 1. (a) Average particle size for various ball milling times. (b) Particle size distribution of PZT for various ball milling times shown under the plots.

difference, the mean particle sizes were similar since the grinding limit for the material and mill was reached. The particle sizes produced by ball milling for 30 and 40 h were in the same range of sizes reported in the literature for aqueous tape casting suspensions of the PZT family [12, 13]. At a ball milling time of 50 h, the mass median diameters of PZT particles was found to significantly increase to 1.85 μm. The particle size distribution exhibited a bimodal characteristic, showing a large fraction of particles with diameter ~2 μm and some agglomerates with a diameter of ~150 μm. The increase in median particle size and the existence of large agglomerates resulted from particle repacking caused by prolonged impact of the grinding media to the wall of the milling bottle. Thus, in terms of particle size reduction efficiency, ball milling times of 30 or 40 h should be employed. With energy saving and cost considerations, however, 30 h was considered the most effective ball milling time.

In addition to particle size reduction, ball milling also provides dispersion and mixing of a suspension. The effects of ball milling time on the dispersion and stability of a suspension can be studied from its sedimentation behavior. A well-dispersed and highly stable suspension precipitates slowly, presenting a low sedimentation height, dense sediment and a cloudy supernatant. By contrast, a poorly dispersed suspension precipitates relatively quickly, showing a relatively high sedimentation height and a clear supernatant. In this study, the ratios of sedimentation height (h) to initial suspension height (h_0) were investigated for suspensions prepared with various ball milling times as illustrated in Fig. 2. The h/h_0 ratios decreased from 0.75 for 20-h ball milled suspensions to 0.73 and 0.72 for 30- and 40-h ball milled suspensions, respectively. Then, the h/h_0 ratio increased to 0.77 for 50-h ball milled suspensions due to disorderly packing of the rapidly-precipitated large agglomerates. The similarly low h/h_0 ratios of 0.73 and 0.72 suggested that 30- and 40-h ball milling times promoted the dispersion and stability of the suspensions. Repeated measurements performed on independently prepared suspensions showed the same trend.

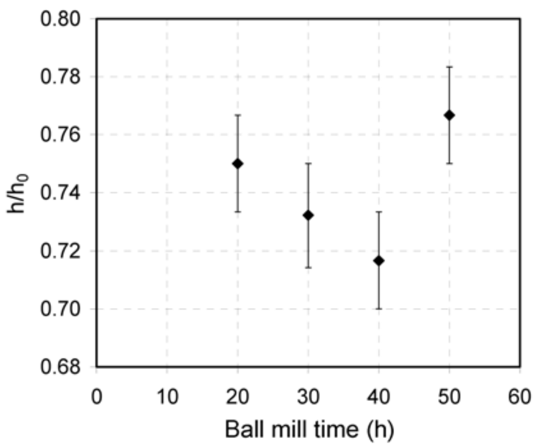

Fig. 2. Effects of ball milling time on sedimentation height (h/h_0) of PZT aqueous suspensions.

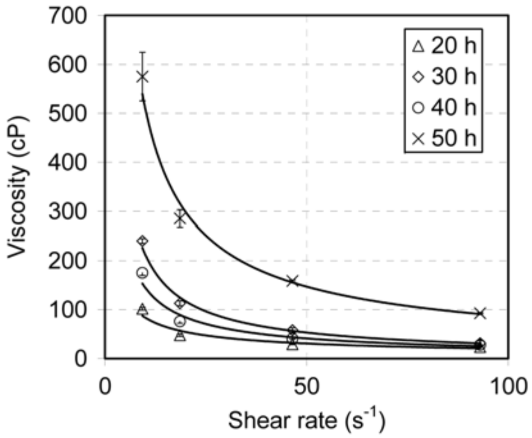

Fig. 3. Viscosity versus shear rate of various suspensions prepared using different ball milling times. Solid lines are fitted to power law equations (see text) indicating the shear thinning behavior of PZT aqueous suspensions.

The effects of ball milling time on the rheological behavior of PZT aqueous suspension were studied and illustrated in Fig. 3. At a high shear rate the 20-, 30- and 40-h ball milled suspensions exhibited a similar viscosity. Decreasing the shear rate allowed a difference of viscosity to be detected. Due to the larger particle size, the viscosity of a 20-h ball milled suspension was lower than those of 30- and 40-hr ball milled suspensions. However, the viscosity of a 50-h ball milled suspension was significantly higher than the others. The existence of large agglomerates in this suspension as shown in Fig. 1 is attributed to this behavior.

Shear thinning (pseudoplastic) behavior was observed for all suspensions. This behavior is important for tape casting in order to provide a homogeneous suspension that is fluid enough to be cast and does not run after being deposited. During storing under a very low shear rate, high viscosity prevents settling of particles providing a well-dispersed and homogeneous suspension. At a high shear force through tape casting, a low viscosity allows flowing of the suspension. Once deposited, a high viscosity under a low shear rate sets the tape on the supported surface.

The degree of pseudoplastic behavior can be evaluated from the relationship between the apparent viscosity (η) and shear rate ($\dot{\gamma}$) expressed by a power law model [11]:

$$\eta = K(\dot{\gamma})^{n-1} \qquad (1)$$

where K is the shear rate factor (consistency index) and n is the shear thinning constant (shear rate exponent) which indicates the divergence from Newtonian behavior. For a shear thinning system, n is less than 1. A lower value of n specifies the stronger shear thinning behavior. Based on the power law model, K and n of suspensions

Table 1. Calculated K and n of suspensions prepared with different ball milling times.

Ball milling time (h)	K (mPa)	n
20	350	0.38
30	1541	0.14
40	878	0.22
50	3022	0.23

prepared with different ball milling times were determined and are listed in Table 1.

The 30-h ball milled suspension exhibited the lowest n value of 0.14 corresponding to the strongest shear thinning behavior, which is preferred for tape casting. The 40-h and 50-h ball milled suspensions displayed higher n values of 0.22 and 0.23, respectively. The highest n value of 0.38 was determined for the 20-h ball milled suspensions, which displayed the weakest shear thinning behavior. Thus, from the results of the rheological behavior in conjunction with particle size reduction, mixing and dispersing efficiency, 30 h was the optimum ball milling time for preparing a PZT aqueous suspension in this research.

Effects of dispersant concentrations

The deflocculation curves displaying a relationship between viscosities and dispersant concentrations were constructed for a 60 wt% solids loading PZT aqueous suspension, ball milled for 30 h, as shown in Fig. 4. The optimum dispersant concentration to produce a well-dispersed suspension was determined from the curve where the viscosity reached a minimum. Measuring at the shear rates typical for tape casting, 46.5 and 93 s^{-1} (50 and 100 rpm), the optimum amount of Dispex A40 was found to be 0.6 wt% based on a PZT powder dried weight basis. In this study, the measured viscosities of 8 and 12 cPs at the optimum dispersant concentration of 0.6 wt% were too low for a tape casting process. To achieve the required viscosity of at least 100-200 cPs at the shear rates mentioned [14], increasing the solids loading in the suspension is a promising approach and is being investigated. In addition, a high solids loading offers an advantage in reducing shrinkage during drying and then avoiding cracks in the tape.

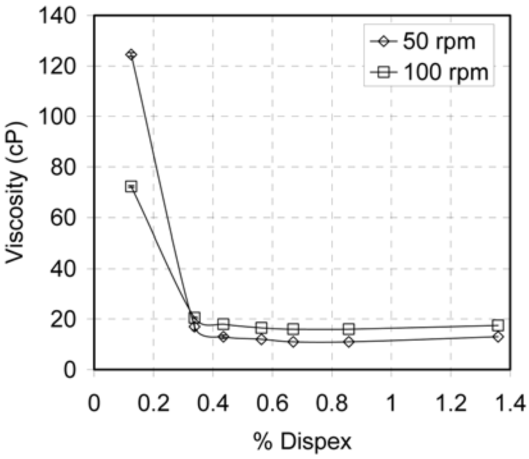

Fig. 4. Deflocculation curve of a 60 wt% solids loading PZT aqueous suspension ball milled for 30 h.

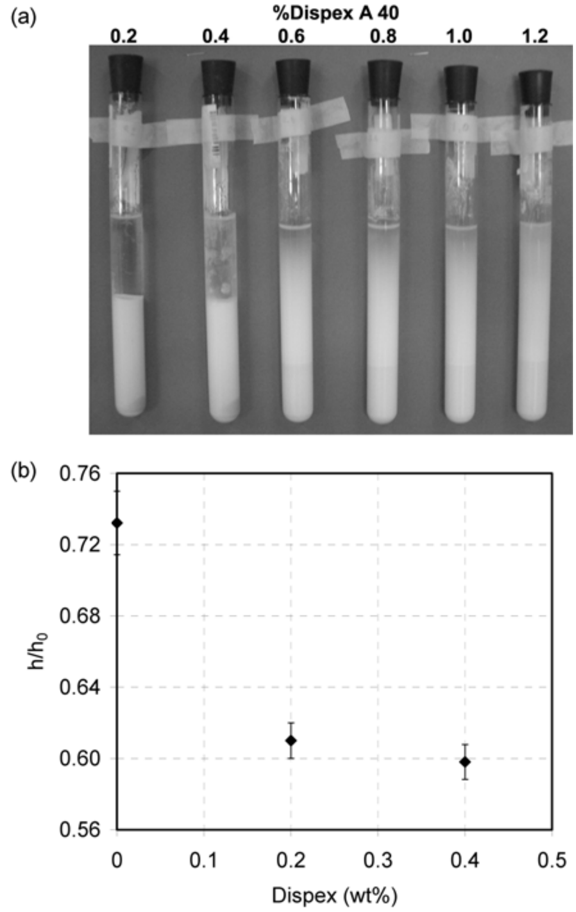

Fig. 5. (a) Precipitation behaviors of suspensions prepared with various Dispex A40 concentrations and (b) h/h_0 ratios of completely precipitated suspensions.

The sedimentation results of PZT aqueous suspensions prepared with various dispersant concentrations are illustrated in Fig. 5(a) and (b). For a suspension prepared without Dispex A40 and with low concentrations of 0.2 and 0.4 wt%, the precipitation was complete within only a few days, displaying a clear supernatant solution. The h/h_0 ratio was 0.73 for the suspension without Dispex A40, and 0.61 and 0.60 for the suspensions with 0.2 and 0.4 wt% Dispex A40, respectively. The decrease in the h/h_0 ratio with increasing dispersant concentration showed the improvement in suspension stability. A similar effect of Dispex A40 has been reported for barium titanate aqueous suspensions [15]. At higher dispersant concentrations of 0.6, 0.8, 1.0 and 1.2 wt%, the suspensions were well-dispersed. The supernatant solutions were still cloudy after 2 weeks. Thus, the sedimentation heights of 0.6, 0.8, 1.0 and 1.2 wt% Dispex A40 suspensions can not be measured accurately (not included in Fig. 5(b)). It can be concluded from these sedimentation experiments that the minimum Dispex A40 concentration necessary for preparing a well-dispersed PZT aqueous is 0.6 wt%, which is in agreement with the result from the deflocculation curves.

Conclusions

A ball milling time of 30 h was found to be effective in particle size reduction, mixing and dispersing a PZT aqueous suspension. The median particle size of the PZT after being ball milled was 0.90 μm with a unimodal distribution. The suspension was well-dispersed and highly stable with the strong shear thinning behavior preferred for tape casting. This study confirmed the improvement of suspension stability by the addition of a dispersant. The optimum dispersant concentration was determined from deflocculation curves to be 0.6 wt% Dispex A40 based on a PZT powder dried weight basis. This result was in agreement with the sedimentation experiment to produce a well-dispersed and highly stable PZT aqueous suspension.

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References

1. C. Pagnoux, T. Chartier, M.F. Granja, F. Doreau, J.M. Ferreira, and J.F. Baumard, J. Eur. Ceram. Soc. 18 (1998) 241-247.
2. T. Chartier, and A. Bruneau, J. Eur. Ceram. Soc. 12 (1993) 243-247.
3. B. Ryu, M. Takahashi, and S. Suzuki, J. Ceram. Soc. Japan. 101 (1993) 626-631.
4. G. Tari, S. Touchal, and J.M. Ferreira, Key Eng. Mat. 132-136 (1997) 289-292.
5. D.H. Yoon, and B.I. Lee, J. Eur. Ceram. Soc. 24 (2004) 739-752.
6. C. Gomez-Yanez, H. Balmori-Ramirez, and F. Martinez, Ceram. Int. 26 (2000) 609-616.
7. D. Hotza, and P. Greil, Mat. Sci. Eng. A202 (1995) 206-217.
8. P. Nahass, W.E. Rhine, R.L. Pober, H.K. Bowen, and W.L. Robbins, in Materials and processes for microelectronic systems, Ceram. Trans., 1990 edited by K.M. Nair, T. Pohanka, and R.C. Buchanan (Am. Ceram. Soc., 1990) p.355.
9. K. Nagata, J. Ceram. Soc. Jpn. 101[10] (1992) 1271-1275.
10. N. Ushifusa, and M. Cima, J. Am. Ceram. Soc. 74[10] (1991) 2443-2447.
11. J.S. Reed, in “Introduction to the Principles of Ceramic Processing” (John Wiley & Sons, Inc., 1989).
12. H.S. Shin, D.K. Lee, C.Y. Kang, J.W. Choi, H.J. Kim, and S.J. Yoon, Kor. J. Ceram. 7[1] (2001) 16-19.
13. J.H. Feng, and F. Dogan, Mat. Sci. Eng. A283 (2000) 56-64.
14. A. Navarro, J.R. Alcock, and R.W. Whatmore, J. Eur. Ceram. Soc. 24 (2004) 1073-1076.
15. M.C. Blanco López, B. Rand, and F.L. Riley, J. Eur. Ceram. Soc. 20 (2000) 1579-1586.