Journal of the European Ceramic Society, Volume 24, Issue 6, 2004, Pages 1073-1076.

Aqueous Colloidal Processing and green sheet properties of Lead Zirconate Titanate (PZT) ceramics made by Tape Casting.

A. Navarro, J.R.Alcock and R.W.Whatmore

Nanotechnology Dept, SIMS, Cranfield University, Cranfield, Bedford, MK 43 0AL.

Abstract

An aqueous system for tape casting PZT ceramics was developed using poly (vinyl alcohol) binder, poly (propylene glycol) plasticizer, D3021 dispersant and Surfynol SE-F wetting agent. Screening experiments were performed to assess the stability of the suspension in the presence of the dispersant by performing pH, conductivity and Zeta potential measurements. Viscosity measurements were used to find the optimum level of dispersant needed to produce a stable slip at pH 10.2. Subsequently, the rheological and mechanical characteristics were also investigated.

Keywords: Tape casting, Lead Zirconate Titanate (PZT), Suspensions, colloidal processing.

1 Introduction

Tape casting (1) is mainly used for manufacturing thin, flat ceramic sheets, which can be cut, punched or stacked to produce multilayered structures. Some applications include transducers, solid oxide fuel cells and pyroelectric infrared detectors. Traditionally, tape casting has been done using organic solvents however water-based

tape casting is becoming more commonplace because of environmental, health, safety and economic reasons. Increased problems of the aqueous route include slower drying, increased stress sensitivity of tapes, increased flocculation and poor wetting of slips due to the high surface tension of water and, in the case of barium titanate (2) reactions with water can occur.

The present work aims to study the colloidal behaviour of aqueous PZT suspensions dispersed by an anionic polyelectrolyte. It is important to achieve a well-dispersed slurry before the addition of the binder and plasticizer in the slip, which helps to eliminate defects in the green tape and improve its mechanical performance. In this paper the stability of the slurry is studied by rheological measurements and mechanical properties of the green tapes made by tape casting is also investigated.

2 Experimental Procedures

2.1 Materials

PZT powders (Pb $[\{(Mg_{1/3}Nb_{2/3})_{0.075}\ (Zr_{0.925}Ti_{0.075})_{0.925}\}_{0.99}\ U_{0.01}]O_3$) with an average particle size of 1 μm and a specific surface area of 1.209 m^2g^{-1} (BET specific surface area) were produced by the mixed oxide route. A polycarboxylate ammonium salt (Duramax 3021, M_W = 2500, Rohm and Haas, France) was used as the dispersant. D3021 dissociates in water to produce negatively charged polyions and ammonium counter ions. The polymers utilised for tape casting slurries was poly (vinyl alcohol) (PVA, 87-89 % partial hydrolysis, M_W = 110, 000 g $mole^{-1}$) (Sigma-Aldrich U.K.) binder and a Poly (propylene glycol) (PPG 400, Sigma-Aldrich, U.K.) plasticizer. To

improve the wetting behaviour of the slip during tape casting a Surfynol SE-F (Air products and Chemicals, Holland) wetting agent was also added to the PZT slip.

2.2 Zeta Potential measurements

Dilute 1 vol.% PZT suspensions containing D3021 and deionised water were prepared for the analysis. The suspension was placed in 100 ml silicate milling jar with 200 g of cylindrical yttrium-stabilised zirconia milling media and ball-milled for 18 hours prior to the analysis. Acetic acid (1M) and ammonium hydroxide (1M) were used as the titrants to adjust the suspension pH accordingly. Zeta potential measurements were performed using a Malvern Zetasizer 3000.

2.3 Rheological characterisation of slip

Viscosity measurements were at room temperature conducted using a rheometer (Bohlin Instruments, Ltd. Cirencester, U.K.). PZT suspensions were prepared at solids loadings of 20 and 30 vol.% with different amounts of D3021 for a dispersant optimisation study. The samples were allowed to reach thermal equilibrium before the measurements. The viscosity was then measured at a single shear rate of 100 s^{-1}.

The flow behaviour of the slip listed in Table 1 was assessed by measuring the viscosity over the shear rate range of 0.06 s^{-1} to 150 s^{-1} in an up and down sweep taking approximately 15 minutes.

To detect thixotropic behaviour of the slip in Table 1 the shear stress was measured as a function of increasing shear rate in a loop test with up sweep of $0.06s^{-1}$ to 150 s^{-1} and a down sweep of 150 s^{-1} to 0.06 s^{-1} in 15 minutes.

2.4 Tape casting

PZT slips were prepared for tape casting by ball milling PZT powder, deionised water and ammonium polycarboxylate dispersant in 100 ml silicate milling jars with 200 g of cylindrical zirconia milling media for approximately 8 hours. Surfynol SE-F wetting agent was then added to the slip and ball milled for a further 1hr. Poly (vinyl alcohol) was pre-dissolved in a sufficient amount of water by heating the PVA solution in water to 95^0C for at least 2hrs (3). The dissolved binder solution and poly (ethylene glycol) plasticizer were then added to the slip and ball milled, for a further 18 hrs to aid the dissolution of the organics into the slurry. The composition of the slip used for tape casting is listed in Table 1. Tape casting was achieved using a laboratory-scale, table top tape caster (TTC-1000, Richard E. Mistler Inc. Morrisville, PA) with a stationary casting head using a casting rate of 0.75 cm s^{-1} and gap height of 550 μm and polypropylene carrier film (Western Wallis, CA). After tape casting, the tapes were left to dry at room temperature and relative humidity.

2.5 Tensile testing of green tapes

The tensile testing of green tapes was accomplished using an Instron universal testing machine (Model 6025, Instron, England). Tensile measurements were done at room temperature (20 ± 1^0C) and humidity of 35 ± 5%. Dog bone shape tensile specimens with 7mm width and 90 mm gauge length were used and tensile measurements were

performed at a crosshead speed of 5mm min^{-1}. At least 10 specimens were tested to obtain an average value.

3 Results and discussion

3.1 Colloidal processing of PZT suspensions

Figure 1 shows the variation of the Zeta potential of a 1 vol.% PZT suspension as a function of pH. Stabilisation of PZT particles in water was achieved by electrostatic means using acetic acid and ammonium hydroxide. Figure 1 shows that the IEP of PZT is approximately pH 6.5, ie the pH at which the Zeta Potential is zero.

Electrosteric stabilisation of PZT particles in water was achieved by using D3021. The Zeta potential of a 1 vol.% PZT aqueous suspension containing 1 wt % D3021 (PZT dried weight basis) measured as a function of pH is shown in Figure 1. At pH 10.2 the charge on the ceramic particles has increased significantly from -30 mV to – 60 mV on the addition of D3021 to the PZT suspension.

pH is known to affect the extent of dissociation of the polyelectrolyte in water. The dissociation of the polyelectrolyte increases as the pH increases. This effect can be seen in Figure 1, where at low pH values (< pH 6.0) the polyelectrolyte is almost undissociated and so possess a low charge (< -20 mV). Subsequently at high pH values (> pH 10.0) the polyelectrolyte is fully dissociated which leads to a large charge (> -60mV).

Figure 2 shows the measure of conductivity of the suspension as D3021 is added to a 1 vol.% aqueous PZT suspension. The conductivity of the suspension increased on the addition of D3021. This increasing trend could be due to an increase in concentration of ions in solution. Since D3021 dissociates in water to produce negatively charged polyions, such as $RCOO^-$ and positively charged counter ions, in this case NH_4^+ ions the increase in conductivity of the suspension could due to increasing release of free NH_4^+ and any free or excess negatively charged polyions in solution.

3.2 Optimisation of the dispersant concentration

The optimum dispersant level is the concentration of dispersant (in wt.% based on ceramic powder dried weight basis, dwb) required to provide the maximum level of stabilisation of particles in a slip. This helps to produce a uniformly dispersed slurry, in which flocculation and sedimentation of particles can be reduced during casting and drying. As a result, homogenous, crack-free green tapes can be produced. Figure 3 shows the variation in viscosity, at 100 s^{-1} of a 20 and 30 vol. % PZT suspension as a function of D3021 concentration. On D3021 addition the viscosity decreased indicating an increasing adsorption of the dispersant onto the PZT powder particles. From Figure 3 a viscosity minima was observed for both 20 and 30 vol.% PZT at approximately 1.0 wt % D3021 (PZT dwb). Slurries with 30 vol.% PZT solids loading exhibited a higher viscosity as compared to the 20 vol.% PZT suspension. This is expected as more particles in the suspension decrease the interparticle separation distances in the suspension.

3.3 Rheology of tape casting slurries

The rheological behaviour of the PZT slip listed in Table 1 exhibited a shear thinning type flow behaviour (Figure 4). Shear thinning flow behaviours of suspensions usually indicate a weakly flocculated system (4). However, this type of flow behaviour is desirable in tape casting as low shear rates render a high viscosity of the slip at rest, which helps to prevent flocculation and sedimentation of particles during drying and at high shear rates the slip possess a low enough viscosity for tape casting. At a shear rate of 100 s^{-1} the viscosity remains approximately at 0.2 Pa.s.

Figure 4 shows the shear stress versus shear rate curves for the full PZT slip (Table 1). The shear stress of slips shows an almost identical increase and decrease with shear rate with little or no hysteresis. This indicates that the flow behaviour of the slips may not be time dependent or thixotropic.

3.4 Mechanical properties of green tapes

The mechanical behaviour of the green PZT tape which was made by tape casting using the slip composition listed in Table 1 was measured using tensile testing. The ultimate tensile strength of the tape was 0.014 MPa with a standard deviation of 0.002 MPa and the strain to failure of PZT green tapes was 0.013 mm/mm with a standard deviation of 0.004 mm/mm. These mechanical properties produced sufficient handling of the green tapes for further processing ie subsequent binder burnout and sintering stages. Green tapes produced a maximum green density of 4.40 g cm^{-3}.

4 Conclusions

PZT suspensions were stabilised both electrostatically using acetic acid and electrosterically by adsorption of dissociated dispersant molecules on ceramic particles. However electrosteric mechanisms proved to be more effective at stabilising PZT particles in water. The isoelectric point of PZT was found to be around pH 6.5. Viscosity measurements were used to find the optimum dispersant concentration, which corresponded to 1.0 wt.% D3021 (PZT dwb). The rheological behaviour of the slip proved to be shear thinning corresponding to a weakly flocculated system with very little time dependent viscosity effects. However robust, defect-free PZT green tapes were produced for subsequent processing such as binder burnout and sintering.

Acknowledgements: This work would not have been possible without financial support from IRISYS Ltd. and EPSRC. R.W.Whatmore gratefully acknowledges the financial support of the Royal Academy of Engineering.

5 References

1. Mistler, R.E, Runk R.B & Shanefield D.J., Ceramic Processing before firing, Ed. John Wiley and sons, New York, 1978, pp. 411-448.
2. Lopez, M. C. B., Fourlaris G & Riley F. L., Interaction of Barium Titanate powders with an aqueous suspending medium. *Journal of European Ceramic Society.*, 1998, **18**, 2183.
3. Bassner, S. L. & Klingenberg E. H., Using Poly (Vinyl Alcohol) as a binder., *American Ceramic Society Bulletin*, 1998, **77**, 71.
4. Ogden, A. L. & Lewis, J. A., Effect of nonadsorbed polymer on the stability of weakly flocculated suspensions., *Langmuir*, **12**, 1996, 3413.

List of Tables

Table 1 Composition of PZT tape casting slip (vol.%)

Slip additive	Amount (vol.%)
PZT	18.34
PVA binder	4.98
PPG 400 plasticiser	4.96
Surfynol SE-F wetting agent	0.82
D3021 dispersant	1.23
Deionised water	69.67

List of Figures

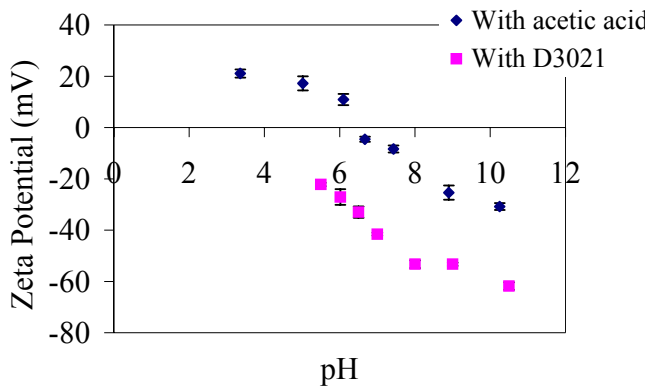

Figure 1 Zeta potential of 1 vol.% PZT suspension as a function of pH

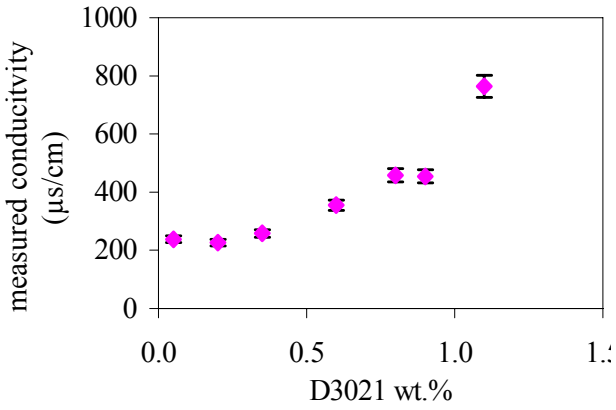

Figure 2 Conductivity of a 1 vol.% PZT suspension on increasing D3021 amount.

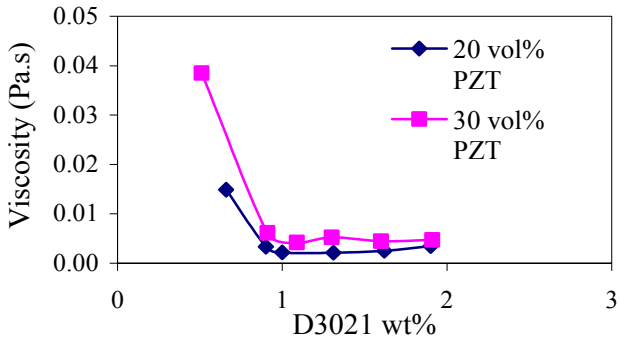

Figure 3 Viscosity of 20 & 30 vol.% PZT suspension as a function of increasing D3021 amount.

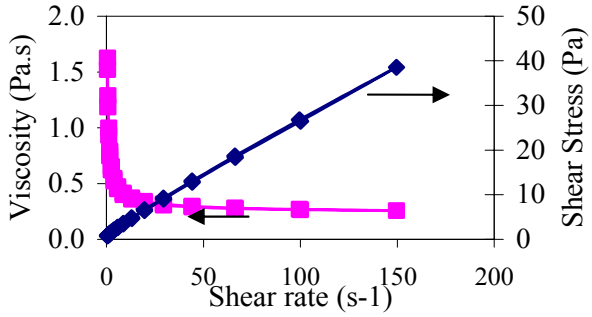

Figure 4 Flow curve of PZT slip for tape casting

https://dspace.org/

Aqueous colloidal processing and green sheet properties of lead zirconate titanate (PZT) ceramics made by tape casting

Navarro, A.; Alcock, Jeffrey R.; Whatmore, Roger W.

2004-01-01T00:00:00Z
Elsevier Science B.V., Amsterdam.
http://dx.doi.org/10.1016/S0955-2219(03)00460-6
A. Navarro, J. R. Alcock and R. W. Whatmore, Aqueous colloidal processing and green sheet properties of lead zirconate titanate (PZT) ceramics made by tape casting, Journal of the European Ceramic Society, Volume 24, Issue 6, 2004, Pages 1073-1076.

Downloaded from a DSpace repository. https://dspace.org/