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Structural and Property Evolution of Aqueous-Based Lead Zirconate Titanate Tape-Cast Layers

James E. Smay[*] and Jennifer A. Lewis[*]

Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801

We have developed aqueous suspensions of lead zirconate titanate (PZT) and an acrylic latex emulsion binder for tape casting. Rheological measurements were conducted to optimize their flow behavior at high solids volume fraction (ϕ_{solids}). Concentrated suspensions ($\phi_{\text{solids}} > 0.45$) were tape cast onto a silicone-coated mylar carrier film, and the effect of cellulose (a viscosifier) and surfactant additions on wetting behavior was studied. Drying stress measurements were performed on tape-cast layers using a substrate deflection technique. The initial period of stress rise was analogous to that observed for binder-free ceramic films, whereas the stress decay was influenced by latex coalescence. Tape-cast layers exhibited a constant PZT volume fraction of 0.49 and uniform binder distribution independent of the PZT/latex volume ratio. The dielectric and piezoelectric properties of sintered multilayer samples were comparable to those obtained for bulk, isopressed samples. Our work provides guidelines for developing aqueous formulations for tape casting complex electroceramic oxide layers.

I. Introduction

Tape-cast layers serve as basic building blocks in many electroceramic components, including multilayer ceramic packages (MLCs) and capacitors (MLCCs). Multilayer ceramics may also find application as structural composites, solid oxide fuel cells, and piezoelectric sensor/actuator devices, e.g., those based on lead zirconate titanate (PZT). Tape casting produces a thin layer (or coating) on a carrier surface via the doctor blade technique.[1–3] The applied coating dries to form a flexible film that consists of a particle-filled, polymeric matrix with appreciable porosity. In previous studies, PZT laminates[4,5] and PZT/polymer composites[6–8] were fabricated using traditional nonaqueous formulations. The development of aqueous PZT formulations has been limited to one recent effort using water soluble binders.[9] Unfortunately, water soluble binders such as poly(vinyl alcohol) and cellulosics must be added in large quantities to ensure mechanical integrity of the green sheet.[10] This can severely limit the total solids loading achievable in suspension.[11,12] In related work, Nahass *et al.*[13] and Ushifusa and Cima[14] have developed aqueous alumina and mullite systems, respectively, that relied on the use of an insoluble acrylic latex binder. By tailoring interparticle forces in these binary colloidal systems, ϕ_{solids} approaching 0.50 have been achieved.[15,16] Building on this approach, we have developed a robust, aqueous-based PZT/latex system for tape casting of functional electroceramics.

In this paper, the rheological, wetting, and drying behavior of aqueous PZT/latex suspensions have been investigated. The influence of suspension composition on colloidal stability was assessed through stress viscometry measurements. Next, the wetting behavior of these suspensions on a mylar carrier was examined in the absence and presence of wetting aids. Drying stress histories were evaluated and found to be analogous to binder-free, particulate layers during the initial stage of drying.[17,18] However, as drying proceeded, latex coalescence[19] led to behavior characteristic of binder-filled, ceramic films.[20] Laminated PZT multilayers were sintered to high density and displayed piezoelectric and dielectric properties comparable to bulk PZT[21] produced by cold isostatic pressing.

II. Experimental Procedure

(1) Materials System

PZT (5H Navy Type VI, Morgan Matroc, Electro Ceramics Division, Bedford, OH) powder with a specific surface area of 1.86 m^2/g, an average particle size of 0.62 μm, and a density of 7.59 g/mL served as the ceramic phase. An aqueous solution of the ammonium salt of poly(acrylic acid) (APMA, Darvan 821A, R. T. Vanderbilt Co., Inc., Norwalk, CT) was used as an electrosteric dispersant.[22] The binder phase was an acrylic latex emulsion (Duramax B1001, Rohm and Haas Co., Philadelphia, PA) with solids loading (ϕ_{latex}) of 0.55, an average particle size of 0.32 μm, and a glass transition temperature of −6°C. Hydroxypropyl methylcellulose (Methocel F4M, DOW Chemical Co., Midland, MI) with a molecular weight of 3500 and an acetylenic diol surfactant (Surfynol 504, Air Products, Allentown, PA) were incorporated in the slurry to enhance its deposition onto a silicone-coated poly(ethylene terephthalate) carrier film (Mylar, PET blend EI-8526, Douglas-Hanson, Hammond, WI). The surface energy of the carrier film was ∼23 mJ/m^2.[23]

(2) Suspension Preparation

Ceramic suspensions were prepared by a multi-step process. First, an appropriate amount of PZT powder was added to a stock solution of deionized water and dispersant (0.5 mg dispersant/m^2 PZT) that was preadjusted to pH 9.0 with 1*M* NH$_4$OH and continuously stirred. The pH and dispersant concentration were optimized in a separate study to achieve a maximum ϕ_{PZT} of 0.56. Next, the suspension was ultrasonicated (Model 550 Sonic Dismembrator, Fisher Scientific, Itasca, IL) for 150 s using a 1 s pulse interval followed by stirring for 12 h to allow for dispersant adsorption. The latex emulsion was stirred into the suspension followed by a modest addition of either a 2 wt% stock solution of cellulose or surfactant for casting formulations. Finally, the suspension pH was readjusted to 9.0 ± 0.1 using 1*M* NH$_4$OH.

Samples for rheological measurements were prepared with a varying PZT volume fraction at a constant latex solution composition of 0.00, 0.10, or 0.20. Moreover, casting formulations were prepared with a total solids loading ($\phi_{\text{PZT}} + \phi_{\text{latex}}$) of 0.45 or 0.53 at a volumetric ratio $\phi_{\text{PZT}}:\phi_{\text{latex}} = 2:1$, and cellulose or surfactant concentrations of 3.5 to 5.0 mg/mL.

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[*] Member, American Ceramic Society.

(3) Rheological Measurements

The rheological behavior of latex solutions and PZT suspensions was characterized using a controlled stress rheometer (Model Rheolgi CS-10 and CVO, Bohlin, Cranbury, NJ). The measurements utilized either a concentric cylinder (C-25, 0.025–240 Pa) or a double concentric cylinder (double gap, 0.0035–34 Pa) sample geometry at a constant temperature of 22°C. A solvent trap minimized evaporation during each measurement. The rheometer was operated in stress viscometry mode and the apparent viscosity (η_{app}) was measured as a function of shear rate in ascending order.

(4) Wetting Experiments

Surface tension measurements were conducted on cellulose and surfactant solutions using the Wilhelmy plate method.[24] The measurement apparatus consisted of a glass slide that was vertically suspended from an analytical balance. The edge of the slide (25.17 mm × 0.97 mm) was brought into contact with the surface of the liquid and the surface tension was calculated from the change in force. The effect of cellulose and surfactant additives on the wetting behavior of PZT/latex suspensions on mylar carrier film was inspected visually.

(5) Drying Behavior

The stress evolution and solvent loss of PZT tape-cast layers were simultaneously monitored as a function of drying time in a temperature and humidity controlled environment. The stress was measured by a cantilever deflection technique in which a clamped stainless steel beam (6.35 mm × 50.8 mm × 0.203 mm, $E = 1.9 \times 10^{11}$ Pa) was coated with a 300 μm thick layer of suspension. The cantilever deflection was determined as a function of drying time using an optical lever consisting of a 3 mW HeNe laser, position sensitive photodiode, and appropriate intermediary optics. The deflection data were recorded by a computer and subsequently related to the average in plane stress (σ) of the coating via the expression:[25]

$$\sigma = \frac{dEs^3}{3cl^2(s+c)(1-\nu)} \tag{1}$$

where c is the final coating thickness, d is the cantilever deflection, and E, ν, s, and l are the elastic modulus, Poisson's ratio, thickness, and length of the cantilever, respectively. The accuracy of stress values was ±10 kPa based on propagation of uncertainty analysis.[26]

Solvent loss was measured by coating a similar stainless steel shim and monitoring the weight change as a function of drying time with an analytical balance housed in the same chamber. The temperature and relative humidity of the chamber were held constant at 25°C and 30%, respectively.

(6) Green Tape Characterization

PZT slurries of varying composition (i.e., ϕ_{solids} from 0.40 to 0.53, ϕ_{PZT}:ϕ_{latex} from 1.5:1 to 3:1) were cast onto a stationary carrier film with a dual doctor blade casting head set at a height of 300 μm and a width of ~100 mm. The casting rate was 10 mm/s over a length of 1 m. The tapes were allowed to dry in air at 25°C and a relative humidity of ~30%. An array of 30 samples (25 mm × 25 mm) were cut along the length of the as-dried tape from both the center and near the edges. Their green density was determined by a geometric method. The volume fractions of PZT, binder, and porosity were calculated based on the known weight fractions and densities of each phase.

The distribution of acrylic binder through the thickness of representative layers was investigated to determine compositional homogeneity. A PZT/latex suspension ($\phi_{solids} = 0.40$, ϕ_{PZT}:ϕ_{latex} = 2:1) with 3.5 mg/mL cellulose in solution was cast at a height of 300 μm. Slices of the dried tape were cut parallel to the top and bottom surfaces in 5 μm increments by first freezing a 10 mm diameter disk in liquid nitrogen, and then sectioning it with a microtome (820 Microtome, American Optical Corp., Buffalo, NY). The distribution of organic species through the thickness of the as-cast tape was determined by thermogravimetric analysis (TGA) (Model 2950, TA Instruments, Inc., New Castle, DE), in air, of select slices.

(7) Sintered Layer Characterization

Sintered samples were formed by laminating layers of green tape between parallel plates for 60 s at an applied pressure of 35 MPa. The binder was burned out by heating the samples at 10°C/min to 250°C, 1°C/min to 300°C, 1 h dwell at 300°C, 1°C/min to 600°C, and finally, a 1 h dwell at 600°C. The laminates were then placed on a dense PZT setter plate inside a covered alumina crucible with a $PbZrO_3$ powder bed to retard lead loss. As

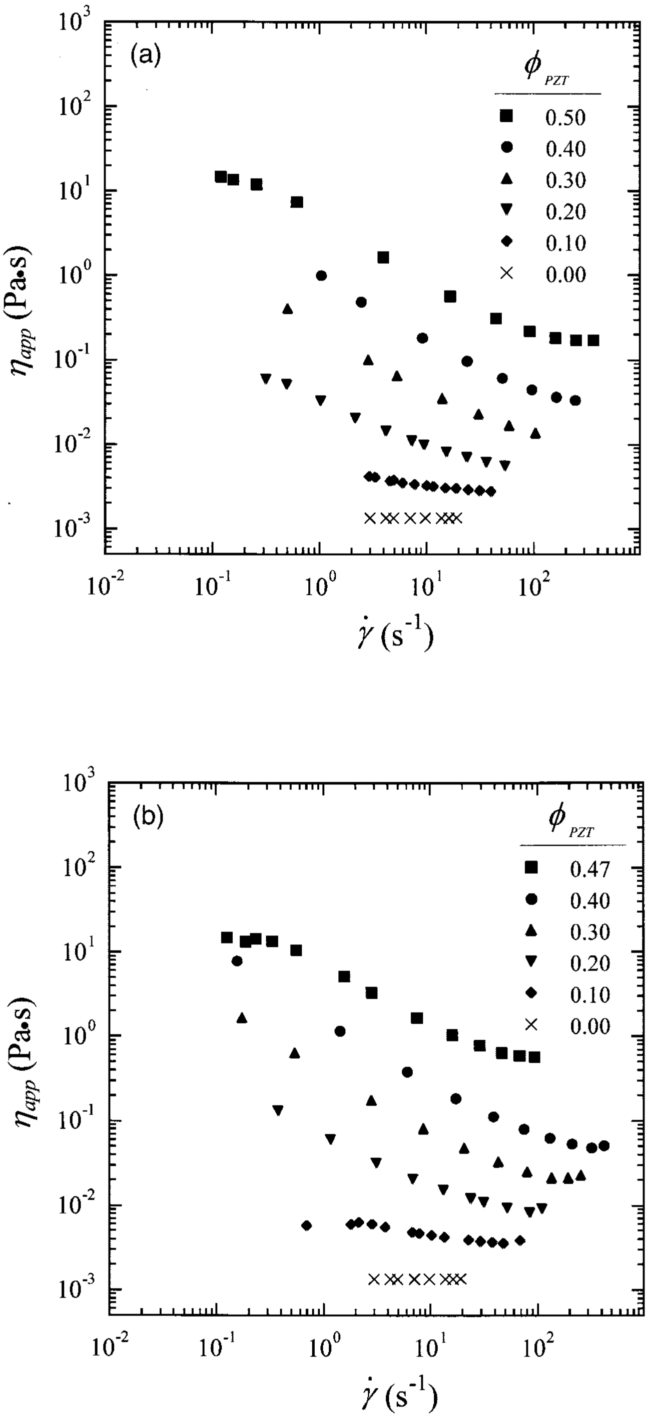

Fig. 1. Apparent viscosity as a function of shear rate for PZT/latex suspensions of varying ϕ_{PZT} with (a) $\phi_{latex}^{soln} = 0.10$ and (b) $\phi_{latex}^{soln} = 0.20$.

a benchmark, PZT pellets were isopressed at 206 MPa and heat-treated under analogous conditions. The samples were densified for 1 h at 1275°C. Sintered density was measured by the Archimedes method[27] in kerosene (ρ = 0.814 g/mL). Gold electrodes were sputtered onto the sample surfaces and their hysteresis behavior was recorded (RT 6000 HV Test System, Radiant Technologies, Albuquerque, NM) using field strengths of 10kV/cm and 20kV/cm. The dielectric constant (K) and loss tangent (tan δ) were measured at 1 kHz and 10 V/cm with an impedance meter (HP 4284A precision LCR meter, Yakogama-Hewlett-Packard, Tokyo, Japan). The constant stress piezoelectric constant (d_{33}) was determined with a Berlincourt meter (Model CPDT3300, Channel Industries, Inc., Santa Barbara, CA).

III. Results and Discussion

(1) *Rheological Properties*

The apparent viscosity (η_{app}) as a function of shear rate for aqueous suspensions of varying ϕ_{PZT} and fixed solution composition (ϕ_{latex}^{soln}) are shown in Fig. 1. Pure latex solutions ($\phi_{PZT} = 0$) displayed Newtonian behavior, with an η_{app} of 1.34 mPa•s and 2.27 mPa•s for ϕ_{latex}^{soln} of 0.10 and 0.20, respectively. On the addition of PZT, both η_{app} and the degree of shear thinning increased, with a power law exponent of n =1.0 and 0.3 for $\phi_{PZT} = 0$ and 0.5, respectively. The relative viscosity ($\eta_{rel} = \eta_{susp}/\eta_{soln}$) of various ϕ_{PZT} suspensions was found to be independent of the latex content, as shown in Fig. 2, suggesting that there are no deleterious interactions between these colloidal species in suspension.

The effect of cellulose additions on suspension rheology ($\phi_{solids} = 0.45$, ϕ_{PZT}:ϕ_{latex} = 2:1) is illustrated in Fig. 3. Over the shear rate range studied, η_{app} increased by an order of magnitude as the cellulose concentration in solution increased to 5.0 mg/mL. Note, their shear thinning ($n \approx 0.55$) behavior did not vary significantly with added cellulose. Therefore, the observed rise in η_{app} is attributed primarily to the increased solution viscosity accompanying such additions (see inset in Fig. 3). In contrast, surfactant additions had little effect on suspension rheology over the concentration range (0–5 mg/mL) probed.

(2) *Wetting Behavior*

Although the use of a silicone-coated mylar carrier facilitated easy release of the dried tape, the as-deposited suspensions experienced strong dewetting forces during casting. Dewetting phenemona are influenced by both thermodynamic (i.e., surface energy) and kinetic (i.e., viscosity) considerations. The velocity of a receding solid–liquid interface is proportional to $\gamma_{lv}(1 - \cos\theta)/(\eta)$, where θ is the contact angle between the solid and liquid, γ_{lv} is the liquid–vapor interfacial energy, and η is the liquid viscosity.[28] Therefore, to improve shape retention of as-cast layers, the effects of reducing the surface tension and enhancing the low shear viscosity of this system were explored. The addition of 5 mg/mL cellulose or surfactant yielded a surface tension of ~50 mN/m and ~30 mN/m, respectively, for these suspensions, as shown in Fig. 4. In comparison, the measured surface tension of deionized water was 71.7 mN/m. Although the surface tension reduction achieved with these wetting aids lessened the driving force for dewetting, these values still exceeded the surface energy of the carrier film (~23 mN/m).[23] Low viscosity suspensions (e.g., $\phi_{solids} < 0.40$ with cellulose-only additions and $\phi_{solids} < 0.53$ with surfactant-only additions) therefore receded too rapidly for the cast layers to maintain their as-deposited shape during drying. By increasing the solids loading, higher viscosity aqueous suspensions were prepared that could be successfully cast, as shown in Table I.

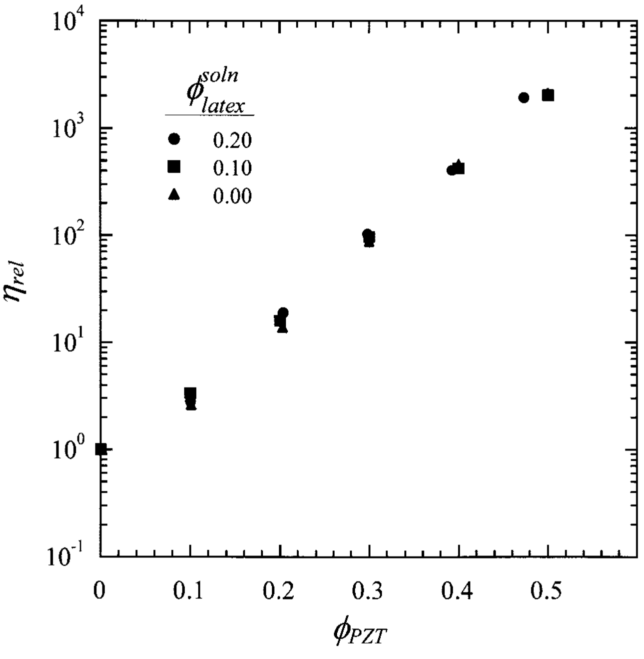

Fig. 2. Relative viscosity as a function of ϕ_{PZT} at a shear rate of 2 s^{-1}.

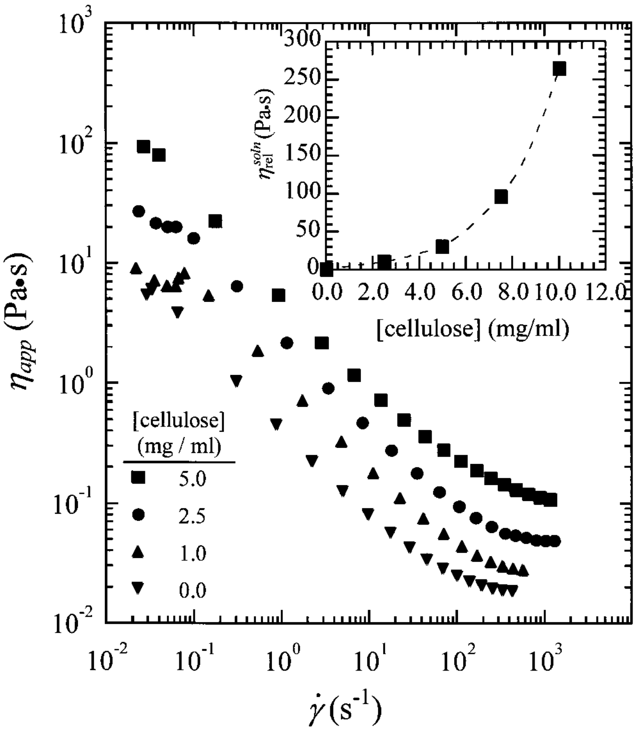

Fig. 3. Apparent viscosity as a function of shear rate for PZT/latex suspensions with $\phi_{solids} = 0.45$ and ϕ_{PZT}:ϕ_{latex} = 2:1. Inset plot depicts relative solution viscosity as a function of cellulose concentration.

(3) *Drying Behavior*

Drying stress and solvent loss were measured for tape cast layers prepared from three suspensions of ϕ_{PZT}:ϕ_{latex} = 2:1, as follows: (1) $\phi_{solids} = 0.45$ containing no cellulose or surfactant, (2) $\phi_{solids} = 0.45$ with [cellulose] = 3.5 mg/mL in solution, and (3) $\phi_{solids} = 0.53$ with [surfactant] = 5.0 mg/mL in solution (see Table II). A sample drying history plot is shown in Fig. 5, illustrating the common features observed for each suspension. The measured solvent loss is reported on the secondary **y**-axis. The drying stress evolution displayed three distinct regions: (1) stress rise (σ_{rise}), (2) stress maximum (σ_{max}) followed by relaxation, and (3) secondary stress rise ($\sigma_{secondary}$) followed by the presence of a residual stress ($\sigma_{residual}$).

In region (1), the latex and ceramic particles remain suspended, and the system behaves analogously to a binder-free particulate suspension. The observed σ_{rise} reflects the increased capillary

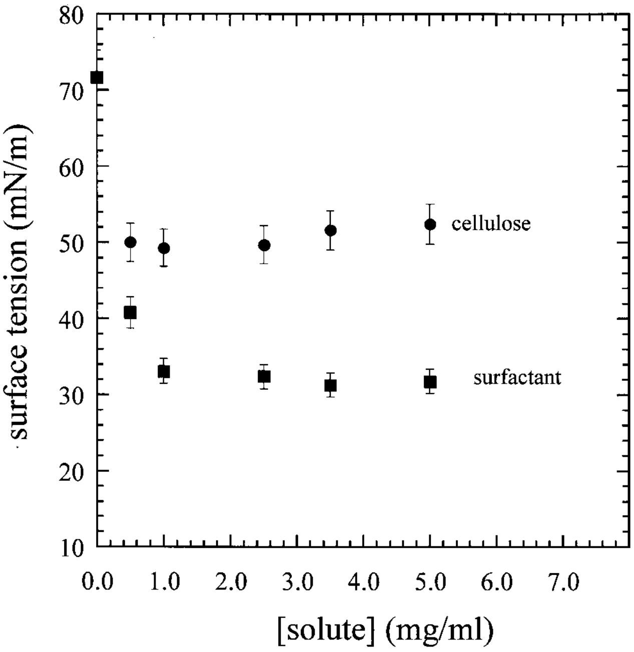

Fig. 4. Surface tension of solutions of varying surfactant and cellulose concentration, as measured by the Wilhelmy plate method.[24]

tension in the liquid phase, which drives consolidation. Alternately, one can correlate these data to the resistance of the particle network to consolidation (i.e., the osmotic pressure for dispersed systems), as shown by Guo and Lewis.[18] Consolidation ceases when the solid network can support the drying stress. For each suspension studied, σ_{max} occurred at $\phi_{PZT} \approx 0.49 \pm 0.005$.

In region (2), σ_{max} is dictated by the capillary pressure (ΔP):

$$\Delta P = \frac{2\phi\gamma}{d} \tag{2}$$

which depends on the particle packing factor ϕ, the surface tension of the liquid phase γ, and the particle diameter d. σ_{max} varied from 0.25 MPa for suspensions with pure water ($\gamma_{soln} \approx 72$ mN/m) to 0.19 MPa for those with added cellulose ($\gamma_{soln} \approx 52$ mN/m) and 0.07 MPa for those with added surfactant ($\gamma_{soln} \approx 32$ mN/m). The observed reduction in σ_{max} scaled roughly with the corresponding reduction in the liquid surface tension because of the presence of cellulose or surfactant addition.

In region (3), the drying behavior of PZT/latex films deviated significantly from the behavior observed previously for binder-free particulate films.[17,18] For charged–stabilized SiO_2 and Al_2O_3 films,[17,18,29] the drying stress fully relaxes in the absence of salt species or organic aids. In contrast, a secondary stress rise was observed for the PZT/latex films, which was attributed to latex coalescence. The onset of latex coalescence is expected to occur when the volume fraction of latex particles in the pore solution, ϕ^{soln}_{latex}, approaches 0.6, i.e., its maximum solids loading. Note, this requires additional drying of the composite layer to a point well beyond σ_{max}, where $\phi^{soln}_{latex} \approx 0.32$ for the 2:1 ϕ_{PZT}:ϕ_{latex} films. Latex coalescence involves a complex sequence of particle consolidation caused by evaporation, deformation of the lattices and rupture of the emulsifying layer by capillary pressure, and, finally, permanent deformation driven by capillary pressure and polymer interfacial tension.[19,30] The transition from distinct lattices to a continuous, interpenetrating organic film results in contraction of the binder phase and increased compressive force on the PZT network, resulting in a secondary stress rise and retention of stress in the dry film. In related studies, Lewis and coworkers[20] showed that stress relaxation of binder-containing ceramic films is governed by polymer relaxation processes, and, hence, is markedly affected by polymer chain mobility (or T_g).

Table I. Summary of PZT/Latex Suspension Properties

Suspension composition ϕ_{PZT}:ϕ_{latex} = 2:1	η_{app} (Pa·s) at $\dot{\gamma} = 0.1\ s^{-1}$	Solution surface tension (mN/m)
[methylcellulose] = 2.5 mg/mL		
ϕ_{solids} = 0.45	16	49.7
0.50	29	49.7
[methylcellulose] = 3.5 mg/mL		
ϕ_{solids} = 0.40	13	51.6
0.45	20	51.6
0.50	46	51.6
[methylcellulose] = 5.0 mg/mL		
ϕ_{solids} = 0.40	36	52.4
0.45	39	52.4
0.50	82	52.4
[surfactant] = 5.0 mg/mL		
ϕ_{solids} = 0.53	7.7	31.8

Table II. Summary of Stress Measurements of PZT/Latex Layers

Initial solution composition	σ_{max} (MPa)	$\sigma_{residual}$ (MPa)
0 mg/mL surfactant or methylcellulose	0.25	0.06
3.5 mg/mL methylcellulose	0.19	0.12
5.0 mg/mL surfactant	0.07	0.06

(4) *Green Tape Characterization*

The as-cast tapes were allowed to dry for 24 h at 25°C and ~30% relative humidity before handling. Figure 6 shows that the void volume fraction (ϕ_{void}) increases with increasing ϕ_{PZT}:ϕ_{latex} ratio over the range of 1.5:1 to 3:1. The PZT volume fraction was determined to be 0.49 ± 0.005 independent of ϕ_{PZT}:ϕ_{latex} ratio for

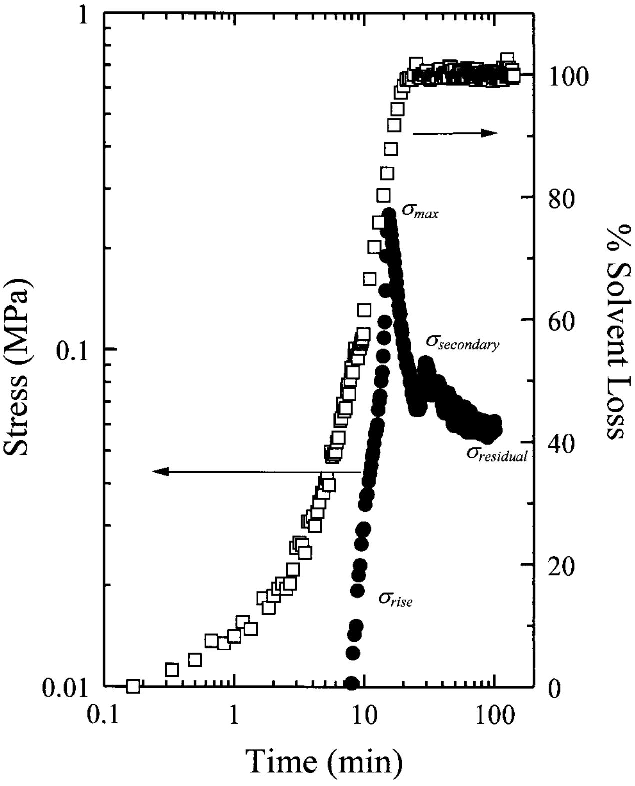

Fig. 5. Drying stress and solvent loss as a function of drying time for PZT/latex suspensions.

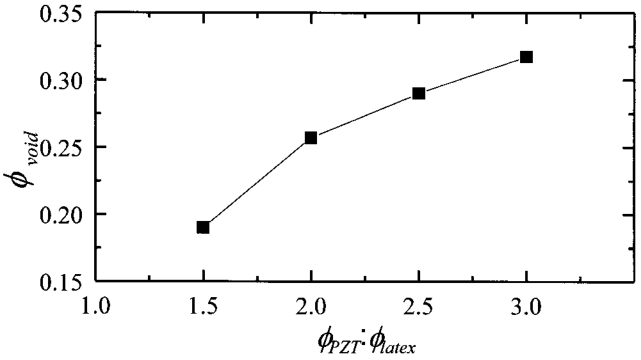

Fig. 6. ϕ_{void} for as-cast PZT tapes from suspensions with $\phi_{solids} = 0.45$, [cellulose] = 3.5 mg/mL, and varying $\phi_{PZT}:\phi_{latex}$.

tapes that contained an initial 3.5 mg/mL cellulose concentration. This result strongly suggests that the PZT particles form a structural network during the initial stage of drying (as σ approaches σ_{max}) followed by coalescence of latex particles suspended in the pore solution around this skeletal structure in the later stage of drying. Tapes containing surfactant additions were found to have similar values of ϕ_{void} and ϕ_{PZT} at 0.27 and 0.48, respectively, for $\phi_{PZT}:\phi_{latex} = 2:1$.

The as-dried tapes showed no obvious signs of binder segregation to the top or bottom surface such as a lustrous or tacky film, despite the large density difference between the PZT and latex species. This qualitative observation was verified by measuring the weight fraction organic species as a function of position through the thickness of a tape cast from a representative PZT suspension. The average thickness of the dried tape was measured to be 167 ± 10 μm, and the first 55 μm from both surfaces was analyzed by TGA. The binder was observed to decompose beginning at ~200°C, with the majority of weight loss occurring between 300° and 350°C, and finishing by 450°C. The weight fraction organic of each slice was normalized by the weight fraction organic of the bulk sample and plotted in Fig. 7 as a function of position from both surfaces. There was minimal binder variation within 55 μm of either surface, as the reported values were within the experimental error of ~7% of the average value.

(5) Sintered Layer Characteristics

Laminates were formed from the $\phi_{PZT}:\phi_{latex} = 2:1$ green tape and showed no remnants of the individual layers on visual inspection, indicating the latex binder was appropriately acquiescent under the applied 35 MPa load. The samples remained flat after binder burnout in air without the aid of a cover plate. The sintered density was measured as ~98% of the powder density.

The measured dielectric and piezoelectric properties are summarized in Table III, along with the specified values of the Navy Type VI[21] piezoelectric material. The d_{33} coefficient of the tape-cast sample remained within specification, albeit slightly lower than the isopressed disk. The piezoelectric and dielectric data indicate that the aqueous slurry processing within the pH range and processing time studied did not adversely affect PZT performance.

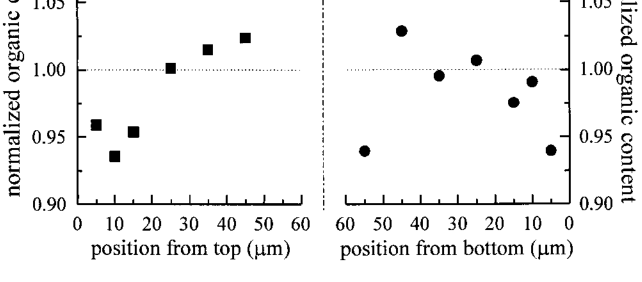

Fig. 7. Normalized organic content as a function of position in the as-cast PZT tape from a PZT/latex suspension of $\phi_{solids} = 0.40$, $\phi_{PZT}:\phi_{latex} = 2:1$, and [cellulose] = 3.5 mg/mL.

Table III. Dielectric and Piezoelectric Properties of Sintered PZT Layers

	$K^{\dagger}$	$\tan \delta^{\dagger}$	P_r (μC/m^2)	d_{33} (pC/N)
Navy Type VI (PZT5H)	3250 ± 12.5%	$\leq$0.025		575 ± 15%
Isopressed	2991	0.025	31.5	627
Tape-cast	3221	0.029	27.0	566

†Measured at 1 kHz.

IV. Summary

Aqueous PZT tape-casting suspensions were formulated using an acrylic latex emulsion binder. Rheological characterization of latex solutions as a function of increasing PZT volume fraction showed no deleterious interaction between the two colloidal species. Concentrated suspensions ($0.45 < \phi_{solids} < 0.53$) were successfully cast on a silicone-coated mylar carrier film. Dewetting problems were alleviated by the presence of a surfactant or viscosifying agent. The dried green tapes exhibited uniform binder distribution as well as good lamination properties. The drying stress evolution was evaluated for films with and without wetting agents. During initial drying, the stress history followed the behavior expected for binder-free ceramic films, indicating that the latex particles remained colloidal in nature. The maximum stress was strongly influenced by the surface tension of the liquid phase, whereas the residual stress was governed by the latex phase that underwent coalescence during the later stage of drying. Our work provides guidelines for developing aqueous tape-casting slurries for complex electroceramic oxides.

Acknowledgments

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