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Effect of the hydroxyl content and molecular weight of polyvinyl butyral on tape properties

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Abstract

Despite the desire to replace organics with water in tape casting systems, thick films often use solvent in order to speed up drying rates. Polyvinyl butyral having hydroxyl contents ranging between 11 and 20% and molecular weights between 40,000 and 120,000 g/mol was plasticized with butyl benzyl phthalate at solids contents between 62 and 75 vol.% $La_{0.5}Sr_{0.5}CoO_3$ once the toluene/ethanol solvent was evaporated. High-hydroxyl content was more important than high molecular weight in increasing the Young's modulus, yield strength, and tensile strength of the tapes at room temperature. Annealing tapes at low temperatures (65 °C) for short times (10 min) relaxed stresses and tended to equalize modulus, strength, and ductility. Low hydroxyl content and low molecular weight enhanced particle packing, which resulted in cracking as tape thickness increased from 0.2 mm to 0.7 mm at higher solids contents. Crack-free tapes were made at all solids contents when the hydroxyl content was greater than 18%. Lower molecular weight at high-hydroxyl content, along with high solids content, was important for minimizing the amount of solvent used.

Keywords: Tape casting; Binder chemistry; Tensile strength; Viscosity; Young's modulus

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1. Introduction

Tape casting was introduced over 60 years ago as a means of making flat dielectrics.[1,2] Alumina packages for integrated circuits allowed tape casting to mass produce high-valued added ceramic components.[3,4] The process relies on dispersion principles well known in the paint industry[5] and an excellent review has been given by Hellebrand,[6] with practical details outlined by Mistler and Twiname.[7] Aqueous processing is quickly replacing organic solvents in thin-film technology.[8,9] While it would be desirable to use aqueous processing for all systems, solvent systems are still used for making thicker films or for systems where materials are incompatible with water. One such application is the tape casting of complex perovskite structures for ion transport membranes used in gas separation.[10] $La_xSr_{1-x}CoO_{3-\delta}$, a simple perovskite, has been used for decades as an electrode material due to its excellent ionic conductivity[11] and is used as a model system in this study.

Toluene–alcohol (methanol or ethanol) is a popular carrier for organic tape systems, using polyvinyl butyral (PVB) both as a dispersant[12] and a binder,[13] with a phthalate as a plasticizer.[14] Even when a different dispersant is used in conjunction with PVB, a significant portion of the particle surface is covered by the butyral due to its excellent adsorption.[15] PVB is a vinyl polymer where one of the CH_2 groups in the mer structure has been replaced by an acetal group ($C_6O_2H_{12}$) to give the general mer formula $C_8O_2H_{14}$. PVB resins, however, have controlled amounts of alcohol (OH groups) or acetate ($C_3O_2H_4$ groups) in the polymer chain as shown in Fig. 1. It is well known that the molecular weight and hydroxyl content of the PVB affect the properties of the slurry.[12–14,16,17] While it is understood that rheological properties of the slurry affect the pore volume and anisotropy of the material, little attention has been paid to mechanical properties of green tapes made with different types of PVB.

This paper presents mechanical property data on $La_{0.5}Sr_{0.5}CoO_3$[11] tape cast in toluene–ethanol using polyvinyl butyral (PVB) having hydroxyl contents ranging between 11 and 20% and molecular weights between 40,000 and 120,000 g/mol when plasticized with butyl benzyl phthalate (BBP) at solids contents between 62 and 75 vol.% (once the

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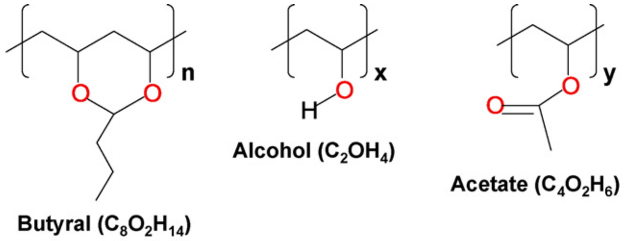

Fig. 1. Mer structures for polyvinyl butyral, polyvinyl alcohol, and polyvinyl acetate, where *n*, *x*, and *y* are the number of repeat units for each mer. PVB resins contained controlled numbers of alcohol and acetate mers randomly located in the polymer chain.

toluene/ethanol solvent was evaporated). The purpose of the work is to understand how hydroxyl content and molecular weight affect the ability to make thick perovskite tapes while minimizing the amount of solvent used in the process. The authors have applied this same binder system to a wide variety of oxide and non-oxide powders and this perovskite is simply one example of a wide variety of powders that can be used.

2. Experimental procedure

2.1. Slip preparation and tape casting

$La_{0.5}Sr_{0.5}CoO_3$ (LSCo) was prepared by direct calcination of appropriate amounts of La_2O_3 (grade 99.999%, PIDC, Ann Arbor, MI, USA), $SrCO_3$ (grade SL 300, Solvay, Italy), and Co_3O_4 (grade OMG, Apex/OMG, Finland). The powder (1.5 kg/pot) was vibratory milled (model M-18, Sweco, Inc., Florence, KY, USA) in neoprene-lined pots for 24 h using 700 g isopropanol and 7 kg of high-purity zirconia milling media. The powder was dried, screened −60 mesh, and calcined in zirconia-lined alumina saggers at 1150 °C for 10 h. The calcined powder was vibratory milled, as described above, to a surface area of $1.9 \pm 0.1\ m^2/g$. Multiple batches of powder were mixed together to make a large homogeneous lot of powder for this study.

Reagent grade toluene and denatured ethanol (grade PM-509, Ashland Chemical, Columbus, OH, USA) were added to 1 L high-density polyethylene (HDPE) bottles filled with 1 kg spherical zirconia media. The ratio of toluene to ethanol was generally 4:1 on a mass basis, with 0.5 wt.% PVB (grade B-79, Solutia, St. Louis, MO, USA) added as a dispersant. The appropriate amount of LSCo powder was then added and the bottle was put on a paint shaker for 30 min to break up agglomerates. The selected PVB binder (see Table 1) and butyl benzyl phthalate (BBP) plasticizer (grade S-160, Solutia, St. Louis, MO, USA) were then added in the ratio 2:1 on a mass basis and put back on the paint shaker for 1 h. The slips were subsequently mixed overnight by rolling the bottles. The viscosities were measured (model DV-II+, Brookfield Engineering, Middleford, MA, USA) using a spindle (LV-03) at ambient temperature before degassing and casting the slips on uncoated polyester. The volume percent liquid (i.e., toluene plus ethanol) in the slip was calculated and the doctor blade height was set assuming that shrinkage was only due to liquid evaporation and occurred only in the z-direction. Casting was performed in air on a tabletop caster (model TTC-1000, EPH Engineering, Orem, UT, USA) using a doctor blade that traveled along a polyester-coated glass plate at a speed of 0.5 m/min. Evaporation rates were determined for 62 vol.% solids (solids content calculated after evaporation of all solvent) using gravimetric analysis for the first hour of drying. Tapes were allowed to dry for 24 h before removing the polyester.

Table 1
Characteristics[18] of polyvinyl butyral used in this study.

Grade	Molecular weight (g/mol)	Density (g/cc)	Chemistry (% of PVB)		
			Butyral	Hydroxyl	Acetate
B-79	50,000–80,000	1.083	88	10.5–13.0	0–1.5
B-76	90,000–120,000	1.083	88	11.0–13.0	0–1.5
B-98	40,000–70,000	1.100	80	18.0–20.0	0–2.5
B-90	70,000–100,000	1.100	80	18.0–20.0	0–1.5

2.2. Characterization

Dried tapes were examined using a stereomicroscope (model SMZ-U, Nikon Corp., Japan) for cracks and other defects before removal from the polyester. Selected tapes were imaged with a scanning electron microscope (model JSM 5900/LV, JEOL, Peabody, MA, USA). Density was measured by the Archimedes method after vacuum infiltration in water. A universal testing machine (model 5566, Instron Corporation, Canton, MA, USA) was used to assess tape properties at room temperature (nominally 25 °C and 20–40% relative humidity) using tapes (nominal cross-section was 0.25 mm × 20 mm) with a 55 mm gage section at a strain rate of $0.1\ min^{-1}$.[19] Engineering strain (ε) was converted to true strain (ε_T), assuming uniform deformation, as

$$\varepsilon_T = \ln(1+\varepsilon) \tag{1}$$

and engineering stress (σ) to true stress (σ_T), again assuming uniform deformation, as

$$\sigma_T = \sigma(1+\varepsilon) \tag{2}$$

Young's modulus was calculated based on the steepest portion of the initial linear loading and yield stress, as the stress at 10% deviation in slope of true stress/true strain. The energy at break was taken as the total area under the true stress–true strain curve. Tapes were annealed at 65 °C for 10 min to assess changes in room temperature tape properties.

The ability to bond tapes was assessed by heat laminating two layers (polyester side to air side) together at 65 °C or 85 °C with 60 MPa pressure for 2 min, punching out 25 mm diameter tape disks, and then gluing the tape disks to individual sandblasted 25.4 mm diameter steel cylinders with cyanoacrylate (drying time for the glue was at least 1 h). The cylinders were threaded to rod-ends with sockets, which allowed triaxial rotation for alignment. These were attached to the universal testing machine and pulled with a crosshead extension of 1 mm/min in uniaxial tension. The fixture used for testing is shown in Fig. 2. The strength was assessed by dividing the load by the cross-sectional area of the tape. Five samples were measured

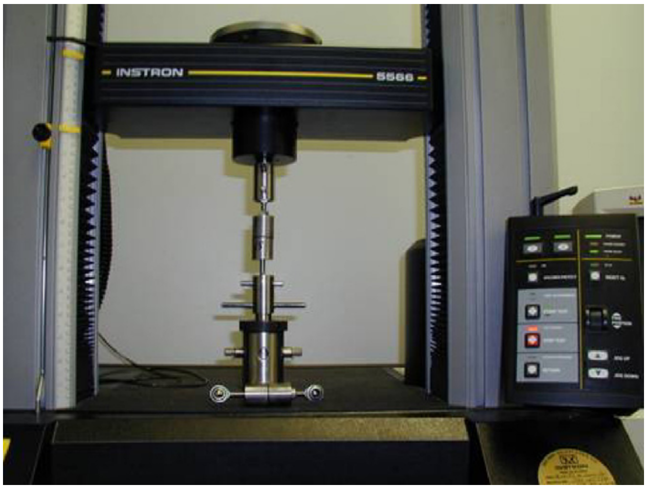

Fig. 2. Uniaxial pull test for assessing bond strength. Test fixture with rod-ends, allowing triaxial swiveling for alignment, is shown unattached from test machine at bottom of photograph, as well as attached for assessing strength (note that swivels fit inside metal collars and are hidden from view).

to obtain a mean and standard deviation for a given lamination condition.

3. Results and discussion

3.1. Toluene/ethanol ratio and evaporation rates

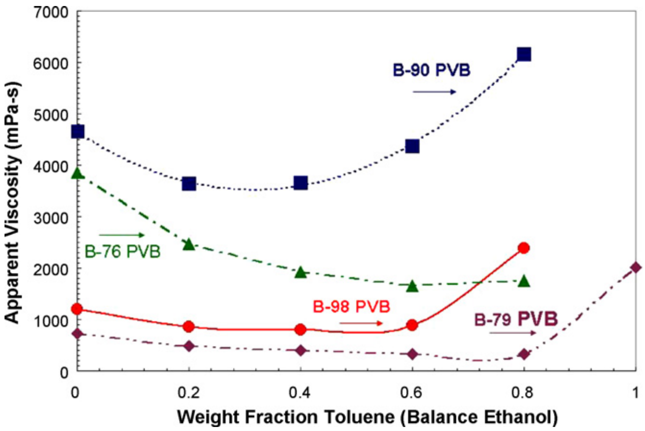

Fig. 3. Viscosity of constant volumes of binder (14.3 vol.%) plus liquid as a function of liquid composition. B-90 and B-98 were not totally soluble in toluene and viscosity data were not measured. B-76 had a viscosity of 71,000 mPa s in toluene and this data point is not included in the graph. Symbols are triangles, diamonds, squares, and circles for PVB types B-76, B-79, B-90, and B-98, respectively. Note that fits are only used to connect data.

Table 2
Hansen parameters and the interaction radius of B-76 PVB.[20].

Compound	δ (MPa$^{0.5}$)[a]				Ra (MPa$^{0.5}$)[b]
	δ_d[c]	δ_p[d]	δ_h[e]	δ_t[f]	
Ethanol (C_2OH_5)	15.8	8.8	19.4	26.5	9.6
Toluene (C_7H_8)	18.0	1.4	2.0	18.2	11.5
PVB	18.6	4.4	13.0	23.1	10.6
C_2OH_5–20 wt.% C_7H_8	16.2	7.4	16.2	24.1	6.5
C_2OH_5–40 wt.% C_7H_8	16.6	6.0	12.8	21.8	4.7
C_2OH_5–60 wt.% C_7H_8	17.1	4.5	9.4	20.0	7.8
C_2OH_5–80 wt.% C_7H_8	17.5	3.0	5.7	18.6	10.6

[a] Solubility parameter.
[b] Hansen interaction "radius" (see Eq. (5)).
[c] Dispersive forces.
[d] Polar forces.
[e] Hydrogen bonding effects.
[f] Square root of Hansen parameter (see Eq. (4)).

Fig. 3 shows the viscosity of PVB as a function of toluene content in the liquid. It should be noted that these solutions contain no plasticizer or LSCo powder. These are similar to curves supplied by the PVB manufacturer[18] except that they compare equivalent volume, rather than equivalent weight, solutions. High-hydroxyl PVB does not completely dissolve in toluene, but does dissolve in the same volume of ethanol. The higher-molecular weight of B-90, as compared to B-98, results in the decreased solubility (i.e., increased viscosity as shown in Fig. 3) and requires more of the toluene/ethanol at an equivalent viscosity. Neither B-90 nor B-98 is soluble in toluene, whereas B-76 and B-79 were soluble. The viscosity of B-76 in toluene, however, was 71,000 mPa s and is therefore not plotted in Fig. 3. Literature data for solubility parameters[20] can give insight to the viscosity data. The solubility parameter for dispersive forces, δ_d, represents attraction due to fluctuating dipoles. The solubility parameter for orientation effects resulting from molecules with permanent dipoles is δ_o. Induced dipoles result in Debye interactions with a solubility parameter of δ_i. Lewis acid pairs lead to Lewis acid (δ_a) and Lewis base (δ_b) cohesion parameters. Hildebrand suggested a total cohesion parameter (δ_t) as[20]

$$\delta_t^2 = \delta_d^2 + \delta_o^2 + 2\delta_i\delta_d + 2\delta_a\delta_b \tag{3}$$

Hansen proposed a practical extension of the Hildebrand parameter for polar (δ_p) and hydrogen-bonding (δ_h) systems. The Hansen parameter is given as[21]

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{4}$$

The Hansen parameters are used to calculate the center of a solubility sphere. The "distance" of the liquid from the center of the solubility sphere is given by an interaction "radius" (Ra) which is[21]

$$\mathrm{Ra} = [4(\delta_{d'} - \delta_d)^2 + (\delta_{p'} - \delta_p)^2 + (\delta_{h'} - \delta_h)^2]^{0.5} \tag{5}$$

where the superscript (d′, p′ or h′) is used to denote the solubilities of the binder. Table 2 gives Hansen parameters and the interaction radius of the solutions used, as well as parameters for B-76 PVB from the literature.[20] The important point of these data is shown in Fig. 4, where the interaction "radii" of the various liquids are plotted in comparison to the "radius" of PVB. If the "radius" of the liquid is greater than that of PVB, it is not a solvent for PVB, as in the case of toluene. The lower the "radius" in comparison to PVB, the higher the solubility. By comparing Fig. 4 with Fig. 3, it is clear that the reason the viscosity decreases is due to enhanced solubility. Once the PVB is fully solvated, the excess liquid is available for dispersion of the solids.

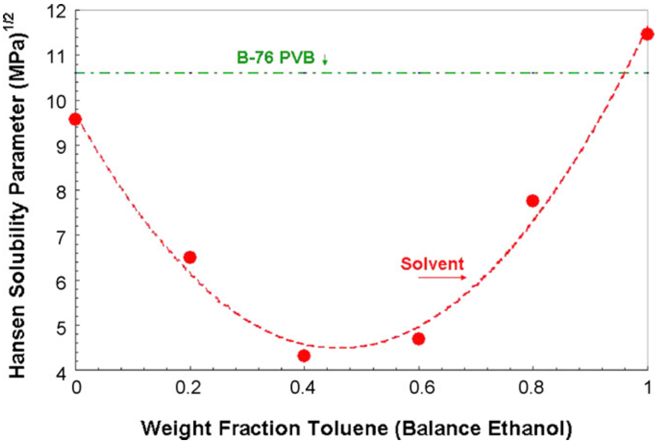

Fig. 4. Calculated Hansen solubility interaction "radii" (Ra) for toluene/ethanol mixtures in comparison to B-76.[20]

The solubility data only qualitatively explain the data since the minimum viscosities for low hydroxyl PVB occurs near a mass ratio of 4:1 toluene to ethanol ratio, whereas the minimum in viscosity is close to a 2:3 ratio for high-hydroxyl PVB. It is therefore tempting to tape cast near the maximum solubility of PVB in toluene/ethanol since an azeotrope exists at 68 wt.% ethanol–32 wt.% toluene. All slips displayed Newtonian behavior with viscosities in the range of 2500–2800 mPa s for 62 vol.% solids slips. When these tapes were cast, it was much easier to get crack-free tapes for all grades of PVB when the toluene/ethanol mass ratio was 4:1 than when it was 2:3. High-hydroxyl (B-98 and B-90) PVB resulted in crack-free tapes for 4:1 toluene/ethanol ratios at dried thicknesses of 0.7 mm, whereas low hydroxyl and low molecular weight B-79 cracked at this same thickness. The tape made with B-76 (low hydroxyl content but high molecular weight) did not crack at thickness up to 600 μm and it took high power on the stereomicroscope to see the fine surface cracks in the thickest cast (≈730 μm). Three (B-90, B-98, and B-76) of the four PVB binders looked excellent at dried thicknesses of 500–600 μm. These data suggest that there are other factors besides the solubility of the binder which affect cracking.

Toluene and ethanol have similar evaporation rates.[22] Fig. 5 shows the results of the slip evaporation rate measurements, which were made under the same conditions as a tape would experience during uncovered drying. The data in Fig. 5 show that the evaporation rate of liquid decreases in order B-90 > B-76, B-98 > B-79. While the evaporation rate was normalized for area and total amount of evaporating liquid (using the height of the doctor blade), the area fraction of liquid decreases in order of B-90 > B-76, B-98 > B-79 explaining the differences in evaporation rate. It therefore does not appear that evaporation rate, due to differences in molecular weight, is the reason for the cracking of tapes made using B-79, and the absence of cracking from the other three binders.

The amount of solvent required to maintain a constant viscosity in the 2–2.5 Pa s range is a function of the solids content in the tape, the molecular weight of the binder, and the hydroxyl content of the PVB as shown in Fig. 6. Lower solvent usage occurs with lower molecular weight, lower hydroxyl content PVB, and lower solid content tapes. This translates to higher costs not only in dealing with solvents which are evaporated in the tape casting process, but also in the cost of the raw materials to make the tape, as shown in Fig. 7. There is a strong driving force to minimize the amount of binder and to choose a binder which allows for easy solvation. This selection, however, is dependent on the mechanical properties of the tape produced.

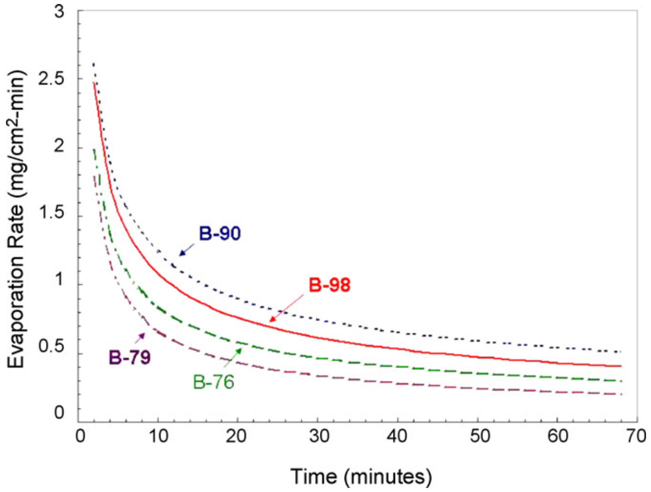

Fig. 5. Evaporation rate as a function of drying time for LSCo slips made with a toluene/ethanol mass ratio of 4.

3.2. Mechanical behavior of tapes

Table 3 lists mechanical properties of tapes as a function of PVB type and solids loading after the solvent has been removed. The B-79 binder was not cast at 75 vol.% solids since it showed cracking at 62 and 70 vol.% solids. The difference between 62 and 70 vol.% cracking for the B-79 binder was the nature of the cracks, which were fine and homogeneously dispersed at 62% solids and larger and more widely spaced at 70 vol.% solids. This resulted in improved mechanical properties at higher solids loading for this tape, but it was clear that this binder was not suitable for casting thick tapes at high solids contents. It is apparent

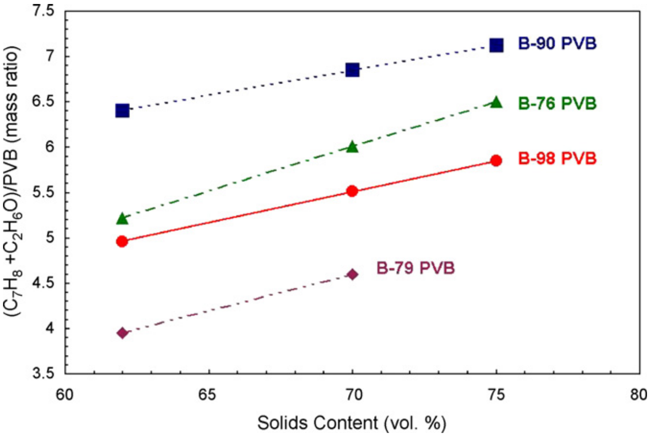

Fig. 6. Liquid (toluene:ethanol at a 4:1 ratio) to binder ratios for four different PVB types as a function of volume fraction of LSCo.

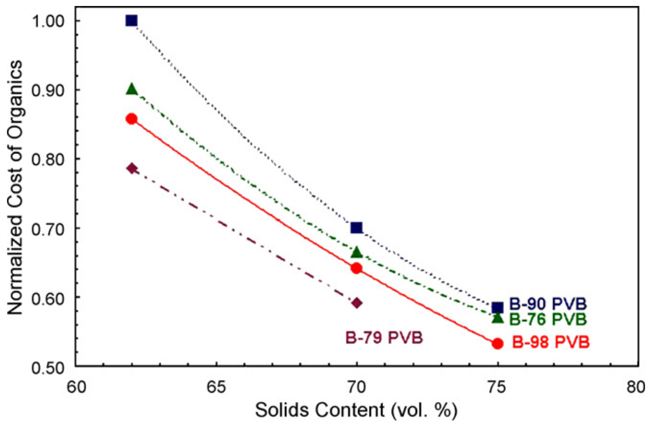

Fig. 7. Normalized cost of organics (binder, plasticizer, toluene, and ethanol) required to cast one square meter of 250 μm thick green tape as a function of the solids content. Symbols are triangles, diamonds, squares, and circles for PVB types B-76, B79, B-90, and B-98, respectively.

that the green tape properties are controlled by the binder since the ceramic particles are not interlocked, as shown by a green microstructure displayed in Fig. 8. SEM images of 75 vol.% LSCo tape cast with B-76 binder are displayed in Fig. 8 showing micrographs at either 3 kV (a–c) or 1.5 kV (d) accelerating voltage. Images are side of tape in contact with air (a) or polyester (b–d) during drying. Image (c) was taken with backscattered imaging. The binder at the tape surface is more visible at lower accelerating voltages, since the binder is evaporated by the electron beam. More binder is expected to be on the side of the tape in contact with the polyester, since the binder is soluble in the moving front of liquid which progresses towards the polyester side of the tape as the drying continues. Backscattered imaging (see Fig. 8c) shows darker regions for the binder, compared to the brighter perovskite. It is still difficult in the backscattered mode to distinguish between the surface porosity and the binder. Secondary imaging at low accelerating voltage clearly shows the binder present.

Even though particle packing appeared to improve (based on microscopic observations) with increasing solids content, the strength and ductility are controlled by the binder in between the ceramic particles. This is illustrated by the decrease in Young's modulus with increasing solids content. The Young's modulus of the dense perovskite is over two orders of magnitude greater than that of the binder, yet modulus decreases with increasing LSCo content due to the lower concentration of the binder and the increase in porosity in the tapes (see Table 3). Similar trends are observed for yield strength, ultimate tensile strength, and ductility.

Not surprisingly, the total porosity increases as the solids content increases (see Table 4, where 100 minus %T.D. is the percent porosity in the green tape). What is surprising, however, is the lower open porosity at 75 vol.% solids compared with 70 vol.% solids (see Table 4). This can only happen as the plasticized binder seals off the internal pores. Since all three tapes were made from the same lot of powder, it is not due to particle size distribution. Warm pressing (65 °C/60 MPa/2 min) closes porosity, as expected, regardless of the tape properties.

The main concern with increasing solids content was the worry that higher solids content would result in less binder at the surface to help with bonding. Surprisingly, the higher solids content materials appear to bond nearly as well as lower solids content, and perhaps bond better without pressure. This is unexpected and deserves further attention. It is possible that capillary forces may help wick some of the solvent away from the interface, but open porosity is similar to that in 62 vol.% tapes (see Table 4). Hellebrand[6] suggests that total porosity in the 25–35% range is desired for interlocking laminates. Using Table 4, the 70–75 vol.% compositions are close to the optimum range as described by Hellebrand. Lower porosity, as is the case when the solids content is only 62 vol.%, is not as desirable.

Fig. 9 shows that the strength of heat-bonded tape at room temperature is a linear function of binder content in the range investigated. It was necessary to get the binder to flow by laminating at an elevated temperature. Bonding at 85 °C resulted in improved strength compared with laminating at 65 °C for all three solids loadings. Higher temperature decreases porosity, which improves the strength. For unlaminated tape, both the Young's modulus and strength at room temperature decrease after an annealing in the 65–85 °C temperature range. Young's modulus, for example, decreases by a factor of 4–5 for high-hydroxide 62 vol.% tapes and strength degrades by 30–40% after the annealing treatment. Fig. 9 clearly indicates that the advantage gained by heat laminating in reducing porosity outweighs the loss in strength expected due to annealing, which relaxes residual stresses. The strength data displayed in Fig. 9

Table 3
Room temperature tensile tape property comparison.

PVB	Solids content (vol.%)	Young's (GPa)	Yield stress modulus (MPa)	UTS (MPa)	Energy/area (mJ/mm^2)	Max. strain (%)
B-79	62	0.13	0.3	1.1	2	11.0
B-79	70	0.20	0.4	3.4	21	18.5
B-76	62	0.30	0.8	7.7	65	25.8
B-76	70	0.19	0.5	3.9	21	16.1
B-76	75	0.21	0.5	3.6	22	18.8
B-98	62	0.78	2.3	12.5	85	18.1
B-98	70	0.45	1.2	8.2	41	16.7
B-98	75	0.34	0.9	7.0	29	14.5
B-90	62	0.95	2.7	13.3	104	19.3
B-90	70	0.65	1.9	10.2	59	18.1
B-90	75	0.52	1.2	6.3	30	12.5

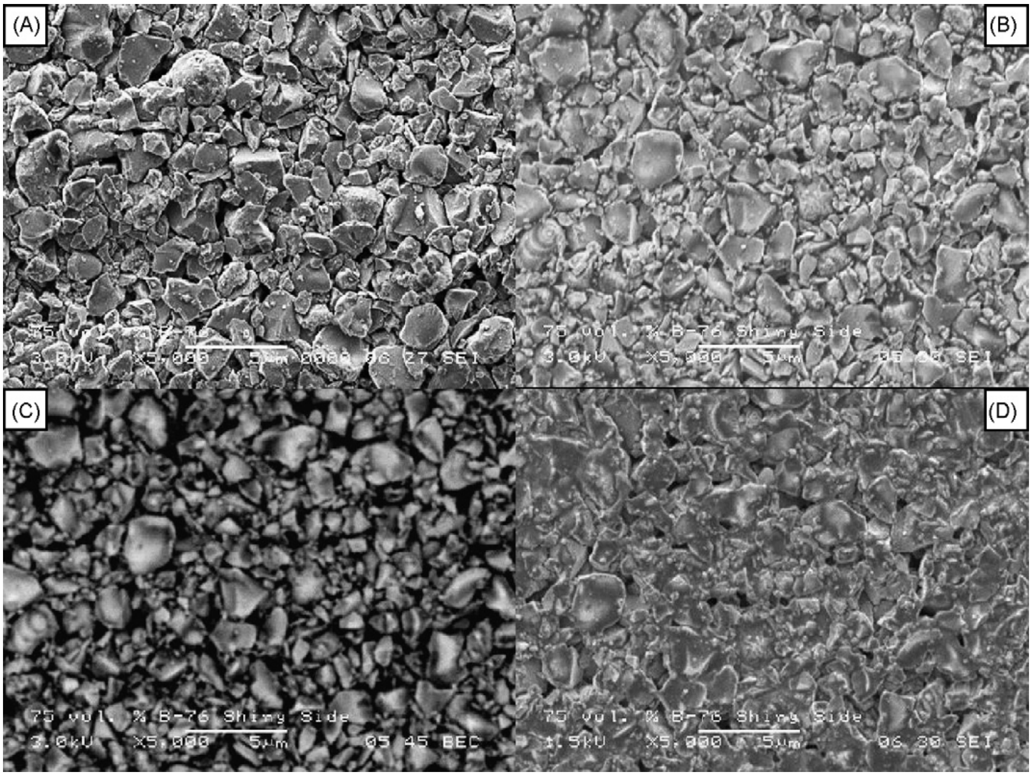

Fig. 8. SEM images of 75 vol.% LSCo tape cast with B-76 binder showing images at either 3 kV (a–c) or 1.5 kV (d) accelerating voltage. Images are side of tape in contact with air (a) or polyester (b–d) during drying. Image (c) was taken with backscattered imaging. All markers are 5 μm.

Table 4
Tape green density and porosity comparison.

PVB	Solids content (vol.%)	Pressed[a]	Green density		Porosity(%)	
			(g/cc)	%T.D.	Open	Total
B-79	62	No	4.02 ± 0.03	90.6	1.2 ± 0.1	9.4
		Yes	4.24 ± 0.05	95.5	0.8 ± 0.2	4.5
B-79	70	No	3.91 ± 0.02	80.1	9.9 ± 0.3	19.9
		Yes	4.03 ± 0.05	82.5	7.5 ± 1.0	17.5
B-76	62	No	3.95 ± 0.04	89.0	1.6 ± 0.2	11.0
		Yes	4.09 ± 0.08	92.1	0.9 ± 0.4	7.9
B-76	70	No	3.76 ± 0.03	77.0	11.1 ± 0.7	23.0
		Yes	3.95 ± 0.06	80.9	7.7 ± 0.9	19.1
B-76	75	No	3.89 ± 0.01	75.6	2.8 ± 0.1	24.4
		Yes	4.00 ± 0.05	77.6	4.1 ± 0.3	22.4
B-98	62	No	3.87 ± 0.07	86.9	1.5 ± 0.1	13.1
		Yes	4.09 ± 0.11	91.8	0.9 ± 0.2	8.2
B-98	70	No	3.78 ± 0.01	77.4	1.7 ± 0.1	22.6
		Yes	3.86 ± 0.10	79.0	8.5 ± 0.9	21.0
B-98	75	No	3.82 ± 0.01	74.1	1.9 ± 0.2	25.9
		Yes	3.93 ± 0.04	78.1	1.8 ± 0.1	21.9
B-90	62	No	3.87 ± 0.04	86.9	1.6 ± 0.1	13.1
		Yes	4.03 ± 0.05	90.5	1.3 ± 0.2	9.5
B-90	70	No	3.60 ± 0.01	73.7	18.3 ± 0.3	26.3
		Yes	3.82 ± 0.04	78.2	12.9 ± 1.5	21.7
B-90	75	No	3.71 ± 0.02	72.0	1.8 ± 0.7	28.0
		Yes	3.85 ± 0.03	74.8	1.7 ± 0.2	25.2

[a] Pressed at 65 °C/60 MPa/2 min.

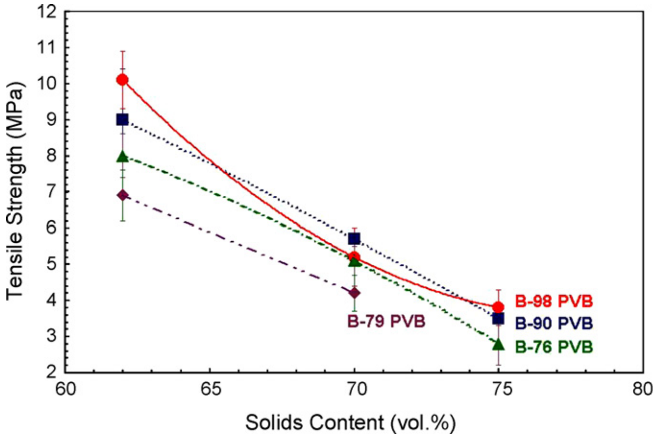

Fig. 9. Room temperature tensile pull-strength of heat-laminated (85 °C/60 MPa/2 min) bilayers of LSCo tape. Symbols are triangles, diamonds, squares, and circles for PVB types B-76, B79, B-90, and B-98, respectively. Note that fits are only used to connect data.

also indicate that tapes made with high-hydroxyl PVB data outperform those with lower hydroxide content, with the difference narrowing slightly as the volume fraction of binder in the tape decreases. The heat lamination process healed cracking in the B-76 and B-79 tapes, as expected.

3.3. Binder selection and volume loading

Plasticized polyvinyl butyral binders are excellent choices for making thick tapes, since crack-free tapes can be made at high solids content. There is strong motivation to use high solids content tapes primarily from an environmental standpoint. Higher solids content allow easier removal of organics and lessen the amount of organics to deal with from a pollution control perspective. They also result in a cost savings if the solvent is not recycled. It is obvious that choosing the optimized binder system involves a number of factors, since the quality of the finished product must come into consideration. Yield is simply one of the factors which enters into evaluating how different tapes behave during lamination. B-98 appears to be the PVB binder of choice due to its high strength, which results in crack-free tapes up to 0.8 mm in thickness at 75 vol.% solids. B-90, another high-hydroxide PVB, also could be used to make crack-free tapes, whereas tapes made with B-76 cracked at high solids contents. The improved strength associated with high-hydroxyl content (see Table 3) appears to be the reason why B-98 and B-90 resist cracking in comparison to B-76 since other factors such as Young’s modulus, porosity, viscosity of PVB are either neutral or in favor of B-76. The main advantage of the lower molecular weight B-98 PVB compared to B-90 is the reduced solvent needed to reach the same viscosity.

Mixtures of different PVB types can be used in the same slip system. One method, which makes sense is to use an easily solvated PVB, such as B-79, as the dispersant, and a higher-molecular weight, higher hydroxyl B-98 as the binder.[23] The volume loading of binder should be as low as possible to allow tape casting and lamination to occur. This study shows that solids loadings up to 75 vol.% allow thick tapes to be cast and laminated effectively using a relatively low surface area ceramic powder. The amount of binder, of course, will be dependent on the surface characteristics of the powder.

In order to better understand cracking, three 75 vol.% solids tapes were made using B-79 as the dispersant and B-98 as the binder. The toluene/ethanol ratios were 4:1, 2:3, or 0:1, with slip viscosity held constant. Only the 4:1 toluene/ethanol tape was cast crack free for dried tapes with a thickness of 0.6 mm. The total porosity in the green tape was 17% higher for the high toluene tape, suggesting that better particle packing may be partly responsible for the difficulty in making thick, crack-free tapes with a toluene/ethanol ratio which uses less solvent. In order to make crack-free, thick tapes it is helpful to have a strong, plasticized binder with plenty of porosity to lower the strain in the tapes as they dry. It is likely that crack-free tapes could be made with toluene/ethanol ratios of 2:3 using controlled drying conditions, which were not tested in this study. This would further reduce the amount of solvent used in the tape casting process.

4. Conclusions

The solubility behavior of the slips was used to partially explain the viscosity behavior, but solubility differences did not account for differences in the cracking behavior of tapes made with PVB. Initial evaporation rates did not correlate with the cracking behavior, but evaporation rates after the removal of non-solvated liquid may be important. High toluene content (toluene/ethanol = 4) was more important than PVB molecular weight in making crack-free tapes using high PVOH-content PVB as the binder in the slips. Cracking occurs for tapes made with high particle packing and weaker binders.

Binder content and type had a strong influence on the dried tape properties of LSCo tapes. The strength of both uncompacted and compacted tapes decreased with increasing solids content, since the strength was controlled by the volume fraction of binder and the porosity in the tape.

The cost of organics, coupled with the expense of recycling or disposing of solvents in a responsible way, pushes one to higher solids contents for any tapes that are produced in large quantities. B-98 appears to be the binder of choice in high-solids content thick tapes due to: (a) its ability to survive drying at high solids contents, (b) lower quantity of solvents required to achieve the same viscosity, and (c) high strength after heat lamination with acceptable solvent bonding.

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