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Tape Casting for Lead Zirconate Titanate (PZT) Multilayer Composites

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INTRODUCTION

Tape casting is a process for making thin flat ceramic pieces by using a scraping blade or "doctor blade" to evenly coat a smooth surface with a slip[1]. The slip is a mixture of powder, solvent, binder, and other organics which result in a paint like consistency after they are mixed.

The tapes is cast into thicknesses ranging from 1 to 50 mils on a smooth surface , which is usually made of Mylar, and left to dry.

Once the tape has dried it can be cut into several different shapes and sizes, and then fired to form two dimensional flat packages [2]. These pieces in the green state can also be punched and machined to produce the products which can be used in electronic substrates and packages.

In our project tape casting was used to cast Lead Zirconate Titanate (PZT) and polymer flat pieces for piezoelectric transducer devices used in medical applications.

Previous work had been done on making the thin stacked PZT layers by using a diamond blade saw to cut wafers, but due to saw's in producing thicknesses smaller than 1mil, it was decided to use the process of tape casting

ABSTRACT

In this project tape casting was used to make not only thin flat PZT ceramic pieces ranging in casting thicknesses of 2mils to 75 mils , but also polymer tapes of varying thicknesses for use in laminating the fired PZT parts together.

The slip formulation was varied for each tape to determine the optimum organic and solvent content necessary to produce a tape which had a minimum shrinkage upon drying and deformability upon handling. Variations in the casting technique were also performed to find the optimum milling time, deairing length, and the most suitable casting surface for the PZT and polymer tapes.

SLIP FORMULATION

Powder: In a ceramic tape the particle size and surface area are important parameters which must be considered If the particle sizes are too small and the surface area is too large then the particles will agglomerate in the slip and once cast will produce an unevenly dispersed tape .

The Lead Zirconate Titanate powder that was chosen for this project has an average particle size of 1.23 +/- 0.02 microns, and a B.E.T. surface area of $1.86 m^2/g$. The particle sizes being small means that an organic dispersant must be added to the slip to prevent agglomeration. The surface area is not vary large , but the small value could also mean that the dry powder is already agglomerated.

This PZT's small particle size means that upon sintering it is highly reactive compared to the larger particle powders, thus lower sintering temperatures. This particular powder will sinter at a low temperature of 1275 ^oC.

Binder: This is an organic polymer which is added to the slip to hold the PZT particles together when they dry. Several characteristics that the binder must have are that it forms a flexible tape, it is dissolvable in an organic solvent, it is not affected by ambient conditions, and that upon burnout it leaves little to no residual ash [1].

Some binders and their properties that were considered for this project are listed in Table1. The binders which were chosen for the PZT tapes were the polyvinyl butyral resins B-76 and B-79, because of the products uniform shrinkage upon heating which will minimize surface defects in the tape. These binders burned out at a temperature of approximately 550 °C in air and leave an ash content of less than 0.75%. This low burnout temperature with low ash content, and uniform shrinkage minimized any additional defects from being introduced into our slip formulation.

TABLE I. POSSIBLE BINDER SYSTEMS

Binder	Solvents
Polyvinyl butyral [a]	Ethanol-Toluene (60:40)
Polyacrylate esters	Mixed Phthalate Esters
Nitrocellulose	Dibutyl Phthalate
Polyvinyl Chloride	Tricresyl Phosphate

Note: data from reference [3]

[a] Butvar Type B-76 and B-79, Monsanto Company, St.Louis. Mo.

Solvents: The Polyvinyl Butyral tapes can have many possible solvent systems which will dissolve the binder. The Ethanol-Toluene (60:40) system was chosen because it is an azeotrope mixture in which the vapor has the same composition as the liquid. This results in an even evaporation of the two solvents, and thus even drying of our tape.

Plasticizers: Plasticizers are used to obtain a degree of flexibility in the tape so that it can be handled without it cracking. The recommended plasticizer which is also dissolvable in our solvent system is Monsanto's Sanitizer 160, and is composed of Butyl Benzyl Phthalate. This plasticizer is typically used in the floor tile industry to aid in processing.

Deffloculant: When the small PZT particles are added to the solvent they tend to agglomerate or stick together. An organic dispersant is added to the slip to keep the particles evenly dispersed in the tape upon casting, and thus prevent such problems as cracking of the dried tape due to uneven shrinkage.

Release Agent: The majority of our tape casting was done on a glass surface. To prevent the tape from sticking to this surface a release agent was added to the slip. It was found that by adding small amounts of Polyethylene Glycol with a molecular weight of 400 that the tape released easily from the glass at all thicknesses cast.

SLIP PREPARATION AND CASTING

The PZT tapes that were made involved a casting process which had two steps. The first stage required mixing the solvent, powder, and dispersant together and milling them on a ball mill with 15-20 zirconia media balls for 24 hours. This process was done to ensure adequate dispersal of the small PZT particles before addition of the binder, which would inhibit any further dispersal.

The second stage involved the addition of the binder, plasticizers, and release agent to the slip. This stage is then milled for 3-4 hours, or until all of the binder is dissolved. Figure 2 shows this process for the PZT slip formulation.

Once the slip is done mixing it is poured into a cup and then deaired by using a vacuum pump for several seconds. If the slip is cast with bubbles, the tape will develop defects known as pin holes upon drying. These pinholes inhibit even densification of the sintered ceramic piece.

Then the slip is taken to the tape casting machine where it is poured, cast by the doctor blade, and then left to dry in an open air system. Figure 1 shows a flow chart of this process.

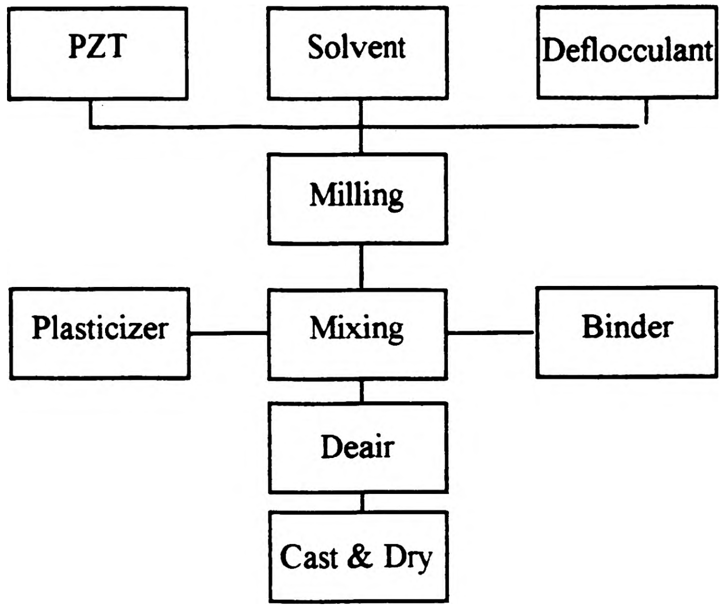

Figure 1. Flow Chart of Tape Casting

LEAD ZIRCONATE TITANATE TAPE FORMULATION

The PZT tapes were cast using a two stage system of mixing and milling. Previous work had been done to optimize the slip formulation and Table II shows the results.

TABLE II. PZT SLIP FORMULATION

Process	Material	wt.%
Stage 1	PZT[a]	61.7
	Ethanol	21.8
	Toluene	10.3
	Menhaden Fish Oil	0.6
Stage 2	B-76[b]	3.8
	S-160[c]	0.9
	Polyethylene Glycol 400	0.9

[a] PZT Type USH-27, Ultrasonic Powders, South Plains, NJ

[b] Butvar Type B-76, Monsanto Company, St.Louis, MO

[c] Sanitizer 160, Monsanto Company, St.Louis,Mo

LEAD ZIRCONATE TITANATE TAPE CASTING

Once the slip has been milled ,it is then poured into a wax coated cup to deair in a vacuum chamber for a few seconds to remove the entrapped air within the slip. Initial slip deairings had problems with forming a scum layer on top of the slip due to solvent evaporation. The scum layer had to be removed before casting to prevent the doctor blade from becoming blocked. This was accomplished by filtering the slip just before casting with a metal screen.

The deairing process was further optimized by using several short deairing in combination with tapping the cup to bring the bubbles to the surface of the slip. This process removed the bubbles and avoided the scum layer, thus eliminating the need for an extra filtering process.

A second formulation was tried with replacing the B-76 with B-79 to see if there was a difference in the slips properties. The B-79 has a lower molecular weight than the B-76 and produces slips with lower viscosities. The lower viscosity can be helpful when removing the bubbles in the deairing process by producing less resistance against the bubble when it is evacuated to the top of the slip.

The B-79 tapes produced fewer holes due to bubbles in the final tape over the B-76 tapes, but the difference was not significant. Also, once the deairing process was changed to eliminate the extra filtering step there became little if any change in quantity of holes in the dried tape.

The differences in shrinkage can be seen in Figure 2, which is a graph of PZT-7 , which has the B-76, and PZT-7c, which has the B-79. It can be seen that upon drying there is little deviation between the green thicknesses in relation to the cast thicknesses. Those variations that do exist can be related to the rate of evaporation being either fast or slow. Faster drying results in less time for the tape to creep on the glass surface, and thus thicker tapes.

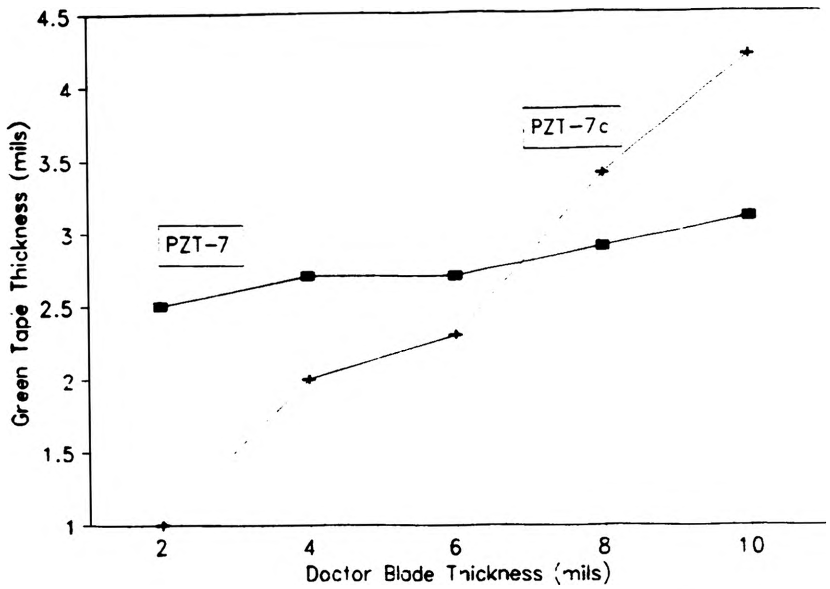

Figure 2. Graph of PZT-7(B-76) and PZT-7c(B-79)
Cast and Green Thicknesses

As you can also see from Figure 2 , the relationship between the cast thicknesses with the doctor blade and the dry thicknesses is not a linear relationship. This can be attributed also to the varying drying rates between the tapes. The PZT was successfully cast at thicknesses from 2mils to 45mils, but further studies must be done to optimize the processing techniques which will result in reproducible and predictable data when casting the PZT tapes.

LAMINATION

The first trials for laminating together the sintered PZT pieces for use in making multilayer composites were done by using a liquid epoxy. This process was rejected because it was extremely difficult to control the epoxy thicknesses between the sandwiched layers .

It was then decided to try to tape cast slips of the dissolved binders in a solvent system. The dried tapes of even thickness were cut into uniform pieces, placed between the PZT layers, and then heated to the binder's softening point to glue the layers together. Thus many layers were sandwiched together at even interval with less hassle.

Polyvinyl Butyral was first chosen to be cast in an Ethanol / Toluene solvent system. The PVB (B-76) and solvent were the only materials in the slip formulation . Other additives such as plasticizers and release agents were not used as to avoid lowering the softening point temperature. The slip was then left on the ball mill for approximately 3 hours to allow the binder time to dissolve.

Dearings were done to remove the large amount of bubbles. Unfortunately it seemed that by using a vacuum to remove the bubbles , the solvent evaporation under the reduced pressure only created more bubbles. After many trials it was found that by just letting the sealed container with the slip sit for a couple of hours, the bubbles came out on their own. Since there were no particles in the slip that might settle out upon setting, this seemed to be the easiest process for bubble removal.

The Polyvinyl Butyral tapes came out clear and were cast at several thicknesses from 2 to 35 mils. Unfortunately the PVB tapes were later rejected because of their softening point being too close to the operating temperature of the transducer device.

Acryloid Resins were next tried because of their higher softening temperatures, but due to their high viscosities, which made it difficult to remove the entrained air, it was impossible to get a good cast tape from the slips.

Next Polyvinyl Formal Resins were tried. These slips used an Ethanol/ Toluene (40:60) solvent system. Any additives, such as plasticizers and release agents, were avoided in this system also for fear of lowering the softening point temperature more.

These slips were prepared the same way that the PVB slips were, but upon being cast on glass the tapes developed an "orange peel" texture on their surfaces. This was due to a problem in uneven solvent evaporation. This effect on the tapes surface stems from the slip wanting to creep on the glass before enough solvent has evaporated to give the tape a uniform shape. The uneven drying also causes internal stresses to develop in the tape which can only be relieved by the surface splitting or creating an "orange peel " like texture.

This problem was corrected by optimizing the solvent content in the slip formulation. The optimized slip formulation can be seen in Table III.

TABLE III. POLYVINYL FORMAL OPTIMIZED SLIP FORMULATION

Material	wt.%
Polyvinyl Formal Resin[a]	16.6
Toluene	53.6
Ethanol	29.8

[a]PVFTypeVinylec,ChissoNY

Also different surfaces were cast on to see if creep could be avoided. The other surface was a Teflon coated vinyl covered piece of glass. This surface worked well in releasing the tapes, but once the slip formulation was optimized it was found that glass worked just as well . Thus tapes of thicknesses ranging from 2 to 35 mils were cast for use in laminating the PZT sintered piezoelectric pieces for use in multilayer composites.

A characteristic between the PVB tapes and the PVF (polyvinyl formal) tapes was that both showed a relative linear relationship between the cast and dried thicknesses. This can be seen in Figure 3.

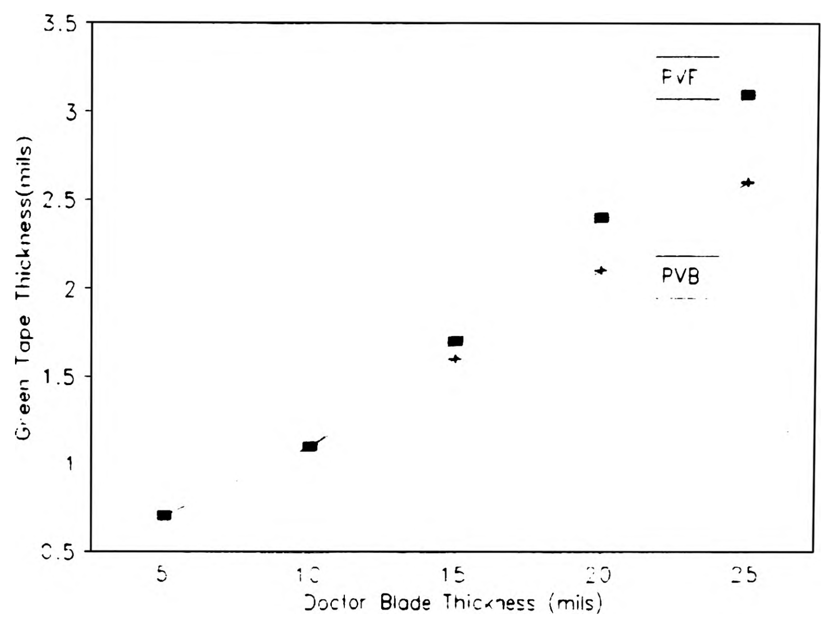

Figure 3. Graph of PVF and PVB Cast and Green Thicknesses

This can be explained by the fact that there are no solids in the slip to interfere with the drying rate. The problem with solids is in getting a homogenous mixture with the largest amount of dispersion possible. If the mix is not homogeneous then some parts of the tape will dry faster than other parts, and also dry unevenly. Since the binders are dissolved in the slip this is not a problem.

CONCLUSION

The process of tape casting Lead Zirconate Titanate and Polyvinyl Formal tapes for use in piezoelectric multilayer composites depended heavily on the slip formulation. The PZT tapes had its greatest problems with solvent evaporation being controlled. Further work must be done to optimize this, but on the good side it was found that the PZT tapes could be successfully cast at thicknesses as low as 2mils. This is a plus in processing because previous methods for making the PZT pieces could only get down to approximately 5 mils by using a diamond blade saw on the final sintered piece.

By tape casting the Polyvinyl Formal Resin for use in laminating the PZT pieces together, the problems of having uneven thicknesses between the PZT layers and ease of producing the multilayer composite were solved.

ACKNOWLEDGMENTS

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