PROCESSING OF NOVEL PIEZOELECTRIC TRANSDUCERS VIA SFF

A. Safari, S. C. Danforth, R. K. Panda, T. F. McNulty, F. Mohammadi and A. Bandyopadhyay
Department of Ceramic and Materials Engineering
Rutgers University, Piscataway, NJ 08855-0909

Abstract

Piezoelectric ceramics and ceramic/polymer composites exhibiting conventional and novel designs were fabricated using Solid Freeform Fabrication (SFF) techniques. SFF is used to develop and optimize numerous transducer designs with simple and complex shapes without using any part specific tools or dies. Fused Deposition of Ceramics (FDC), Fused Deposition Modeling (FDM™), and Sanders Prototyping (SPI) techniques were used to develop lead-zirconate-titanate (PZT) novel ceramic structures via: (1) direct fabrication and (2) indirect fabrication routes. For the direct fabrication route, green PZT ceramic preforms consisting of 50-55 volume fraction of powder with RU binders were prepared by FDC and used for piezocomposites. For the indirect route, SPI and FDM™ techniques were used build the polymer prototype or mold, and the ceramic parts were fabricated from the molds/prototypes using (a) lost mold and (b) soft tooling processes. Among the various ceramics and composites processed via the direct and indirect processes are dome shaped actuators, 3D honeycomb, ladder, annular, rods, tubes and various oriented PZT fiber structures. This presentation will review the processing routes for design, development and optimization of piezoelectric ceramics and ceramic/polymer composites for transducer applications.

Introduction

Piezoelectricity, discovered in Rochelle salt in 1880 by Jacques and Pierre Curie [1], is the term used to describe certain crystalline materials that have the ability to develop an electric charge that is proportional to an applied mechanical stress and vice versa. Piezoelectric materials show piezoelectric behavior due to their unique crystal structures. All natural crystals are grouped into 32 point groups which can be divided into two sub-groups: (1) crystals with a center of symmetry or centrosymmetric, and (2) crystals with no center of symmetry or non-centrosymmetric. Of the twenty-one non-centrosymmetric point groups, twenty of them show the piezoelectric behavior along unique directional axes. The piezoelectric effect is observed in a variety of materials including single crystals, ceramics, and polymers [2-4]. Among them, piezoelectric ceramics and ceramic polymer composites have found wide applications in consumer, automotive, medical and aerospace industries. The U.S. market for piezoelectric ceramic components was estimated to be ~$150 million in 1996 with a 10% growth rate per year, while the Japanese market for these components is > $500 million [5]. At Rutgers University, structural, piezoelectric, bio ceramics and composites have been processed using various SFF techniques [6-8]. Functional ceramic prototypes have been manufactured directly using the Fused Deposition of Ceramics (FDC) process. Ceramics and ceramic/polymer composites have also been manufactured via the indirect processing routes using either the lost mold or the soft tooling technique. In this work, novel piezoelectric ceramics and composites were developed and optimized via solid freeform fabrication techniques for improved electromechanical properties.

Processing

Indirect Process: The indirect fabrication route utilizes a lost mold technique. In this process, sacrificial molds having a negative of the desired structures were manufactured via Sanders Prototype MM6-PRO system (SPI Inc., Wilton, NH). The MM-6PRO is a liquid to solid inkjet plotter, which deposits the polymer onto a movable Z-platform. The main advantages of the SP technique include a very high resolution (a mold wall thickness of ~100 μm can be easily obtained) with a good surface finish due to finer Z-direction resolution. A high solids loading PZT ceramic slurry, with a solids loading of ~52 vol% was specially developed to infiltrate the polymer molds, thus avoiding cracking in the sample during drying and the subsequent binder burn out process.

Direct Process: In the direct technique, the piezoelectric ceramic structures were fabricated via Fused Deposition of Ceramics (FDC). Ceramic loaded filaments with a diameter of 1.75 mm were first extruded from a compounded mixture containing 52 volume % PZT-5H powder in a thermoplastic binder system. These filaments formed the input material for the Stratasys™ FDM™ 3D-Modeler (Stratasys Inc., Eden Prairie, MN). The ceramic loaded filaments were fed into a liquifier heated to a temperature between 170 to 210^{0}C. The liquifier extrudes a road of material through a 250 μm nozzle, depositing it onto a foam substrate attached to a fixtureless platform capable of moving in the Z direction. The liquifier moves in the X - Y plane based on the shape of the part to be built. After depositing the first layer, the fixtureless platform moves down the height of one layer, and the next layer is built on top of it. These steps are repeated until the whole structure is made. The final dimensions of the green ceramic part were about 25.4mm x 25.4mm x 10mm. The parts were then removed from the foam substrate for further processing.

Soft tooling: Soft tooling is a process in which flexible polymer molds are fabricated by encasing a prototype in a suitable polymer material. After the prototype is removed from the mold, the mold is then used to cast duplicates in a fashion similar to injection molding (IM), using IM ceramic / thermoplastic compounds. Although not a new process, it has yet to find usage in the transducer community because of the difficulty in producing suitable prototypes used for the creation of new molds. With the advent of SFF, a new technique has been created that will facilitate the quick and easy production of silicone molds. In this work, 1-3 composite designs were created using commercial CAD-based programs such as Auto-CAD™ and Pro-Engineer. These designs were used in conjunction with a Sanders Prototype rapid prototyping system to produce prototypes. The prototypes were then used to create molds by encasing them in silicone room temperature vulcanizing (RTV) rubber. Upon removal of the prototype, the molds were used to cast multiple duplicates with a custom designed PZT / thermoplastic compound. Several variables were explored for the fabrication of parts via soft tooling technique including:

1. optimization of the CAD designs,
2. testing of a variety of RTV rubbers to determine which materials are suitable for use in various part geometry, and
3. development of a thermoplastic binder with specific rheological, mechanical, and thermal properties.

Before any molds were made, suitable prototypes were designed. Key variables in the design of suitable prototypes are factors such as pole diameter and aspect ratio, pitch, base thickness, and pole taper. Designs were optimized to facilitate the flow of the materials inside the mold and for easy release after casting. Once the part design was complete, the .stl file was saved and transferred to the Sanders Prototype machine. Designs went through several iterations before good quality prototypes were made.

Various RTV silicone rubbers were tested in order to gain some insight into which material or materials work best for the production of flexible polymer molds. Two important material properties for mold-making are viscosity and flexibility. Several molds were fabricated using different RTV silicone rubbers with properties ranging from low viscosity and high flexibility to high viscosity and low flexibility.

Development of thermoplastic binder formulation was performed concurrently. Several important factors governed the material selection. It is important that the developmental PZT/thermoplastic compound exhibits a low viscosity at the operating temperatures of around 200^0C. The compound must also exhibit sufficient strength to allow for easy part removal once molded. The binder formulation should gradually decompose at temperatures up to about 500^0C to facilitate easy binder removal. Finally, the binder formulation should be hydrophobic to avoid complications in casting due to atmospheric humidity changes. A developmental binder was formulated which meets most of the existing criteria. The formulation consists of a major and minor binder, fluidizer, tackifier, and plasticizer in the appropriate proportions. For this work, PZT-5H powder was coated with a surfactant, and compounded with the binder formulation in a 60 volume % PZT5H solids loading. This formulation was used to cast multiple 12.5x12.5 mm green preforms using an RTV silicone rubber mold.

Post processing: The green parts, made either by indirect, direct or soft tooling techniques, were slowly heated to 550^0C and held for 1 hour to allow the organic components to evaporate. The temperature was then increased to 780^0C, with a dwell of 1 hour at that temperature, to provide enough bisque strength to the parts for mechanical handlability. The bisque fired samples were then placed in an alumina crucible with excess lead source, heated at 3.5^0C/minute to 1285^0C, and held at that temperature for 1.5 hours for sintering. The sintered samples were embedded in a standard Spurr Epoxy (Ernest F. Fullam Inc., Latham, NY) and cured in an oven at 70^0C for 12 hours.

The composites prepared with direct, indirect or soft tooling were cut, polished and electroded the top and the bottom surfaces with an air dried silver paint and poled in a corona poling apparatus using 25 kV at 65^0C for 15 minutes. Electromechanical properties of composites including dielectric constant (K), the charge coefficient (d_{33}), and the planar and thickness mode coupling coefficients (k_p and k_t) were measured. Scanning electron microscopy of the structures was carried out using an AMRAY 1400 SEM.

Results and Discussion

Indirect Process: Sacrificial polymer molds having a negative of the desired ceramic structure were made via the indirect technique, using the Sanders MM6-PRO equipment. Pro Engineer™ software was used to make a mold design that had 3-dimensional interconnected porosity. The ceramic structure obtained from these scarificial molds is shown in Figure 1. It shows uniform square PZT rods with ~ 600 μm sides separated by a spacing of ~600 μm. As shown in Table 1, 3-3 piezoelectric ceramic/polymer composites made from this structure gave good dielectric properties with a thickness coupling coefficient of 62%.

Direct Process: Using the direct technique, a variety of composites were made, where the ceramic rods were oriented at different angles to the poling direction. The specimens were fabricated to give a ladder type structure (*Type A*) as shown in Figure 2. This structure could be poled along many directions that will generate different electromechanical properties. The *type A* structure was poled along the Z-direction [001] perpendicular to the fiber direction. The ceramic connectivity was through the joints of the rods in the specimen. This structure can be poled in another way if it is rotated such that either the [100] or [010] direction of Figure 2 coincides with the poling axis. In *type B* composites, 50 % of the rods are continuous along the poling axis while the rest of the rods are continuous along the axes perpendicular to it. Yet another type of structure (*Type C*) can be obtained when the composite is poled along the [110] direction. In these structures, the rods are oriented at $\pm \theta^0$ to the poling direction. Figure 3 shows a SEM micrograph of an oriented fiber composite where the rods make an angle of ± 15 ° with the poling axis.

A comparison of the properties of *Type A*, *Type B* and *Type C* structures is shown in Table 1. The measured charge coefficient, d_{33}, of most of the oriented composites (*Type C*) is higher than the ladder structures (*Type A and Type B*). The d_{33} rises as the angle of orientation to the vertical poling axis increases. A maximum d_{33} of 510 pC/N is observed for an orientation angle of ± 30° to the poling axis. The d_{33} value decreases on further increasing the orientation angle. A value of 175 pC/N was obtained for a composite with fibers oriented at ± 75° to the poling axis. The thickness mode coupling coefficient, k_t, remain nearly constant for the samples with different orientations. The high values of d_{33} for these composites could be due to a contribution from the actual d_{33}, d_{31} and d_{15} components.

Monolithic dome shaped actuators has also been processed via FDC. The SFF approach is useful for a precise control on curvature, diameter and the size of these actuators compare to the conventionally processed curved shaped actuators such as Rainbow (**R**educed **a**nd **in**ternally **b**iased **o**xide **w**afer). The later was first produced with thin slices (0.5 mm) of lead lanthanum zirconate titanate (PLZT) ceramics by placing them between a carbon block and a zirconia plate in a preheated furnace at 975°C for 45 minutes under reduced atmosphere. While still hot, the assembly is air quenched to room temperature. The reaction caused by the carbon block leaves a reduced surface layer with excess lead. The internal stress due to the reduced layer gives dome shape geometry to the original ceramic disk. Displacement and generative force in RAINBOW actuators are related to the thickness and the curvature of the disc that is difficult to control in conventional processing. Dome-shaped actuators with various sizes and curvature have been produced by FDC. The green ceramic parts were fabricated via FDC using filaments loaded with 52 volume % of PZT-5H ceramic powders. Figure 4 shows the SEM micrograph of the sintered dome shaped actuator processed via FDC. Electromechanical properties of the sintered discs are currently being evaluated.

Soft Tooling: Figure 5 (a) and (b) shows the wax prototype, mold and four copies of the green ceramic structures processed via soft tooling technique. Sintered ceramic preforms fabricated via soft tooling technique consist of 25 poles of 800 μm diameter and a pole to pole pitch of 2 mm. For these structures, the volume fraction of PZT ceramics is approximately 15 % in the composite form, as shown in Figure 6. Figure 7 is an SEM micrograph of a single ceramic pole after sintering. The poles are very dense, and exhibit a 10:1 aspect ratio. Table 1 lists some of the average physical and electromechanical properties of composites fabricated via soft tooling. Although only conventional composite designs have been manufactured to this date, this technique has shown great potential for use in the production components with more complex architectures, such as random orientation, polar orientation, or volume fraction gradients.

Conclusions

In this work, Solid Freeform Fabrication (SFF) techniques such as Fused Deposition (FD) and Sanders Prototype (SP) were used to form a variety of novel piezoelectric ceramic/polymer composites. The indirect and the direct methods for the development of piezoelectric composites were discussed. The composites made via lost mold and direct FDC techniques gave excellent electromechanical properties. The properties of oriented fiber composites were found to greatly depend on the orientation of the rods with the poling axis. Theoretical modeling of the oriented structures is in progress to predict the structure with the best electromechanical properties.

Acknowledgments

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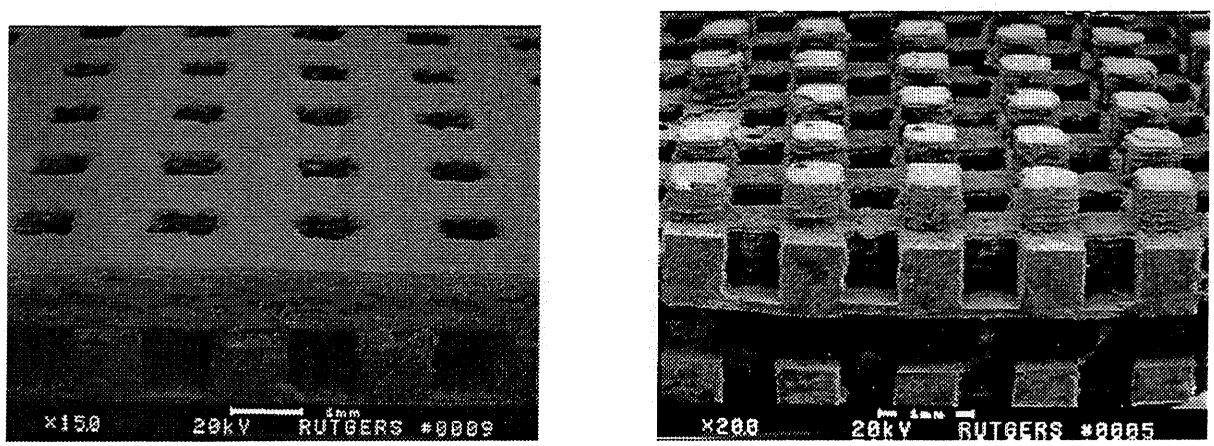


(a) (b)

Fig. 1 : Scanning Electron Micrograph (SEM) of (a) polymer mold and (b) 3-3 sintered PZT-5H ceramic structures obtained using the indirect technique.

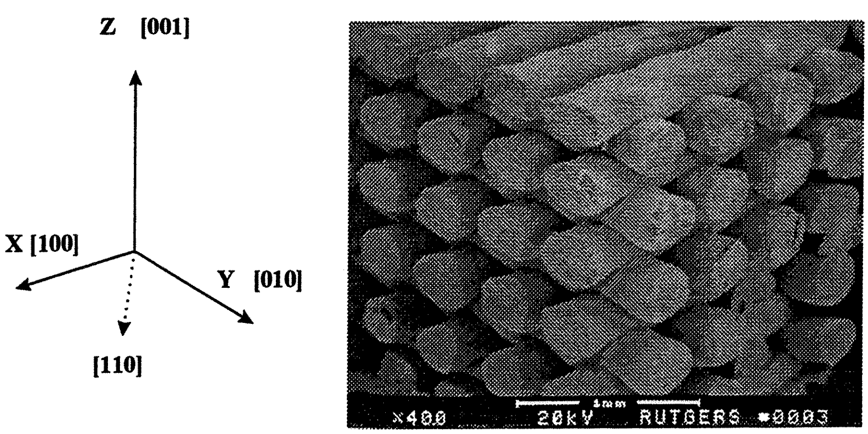


Fig 2 : SEM of sintered PZT-5H ladder type structure (*Type A*) obtained by direct deposition technique.

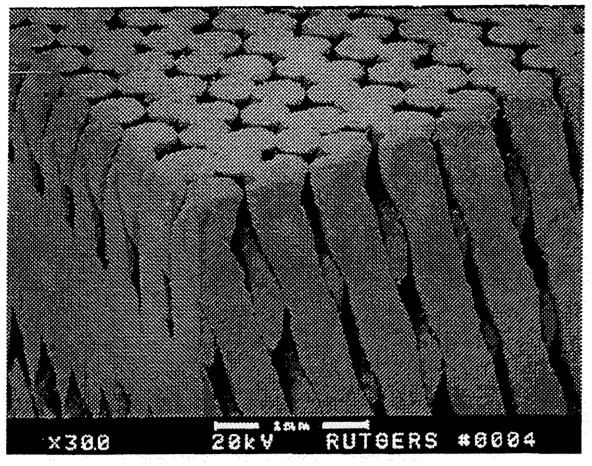


Figure 3 : SEM of the an oriented structure (*Type C*) where the PZT rods are aligned at $\pm 15°$ to the poling axis.

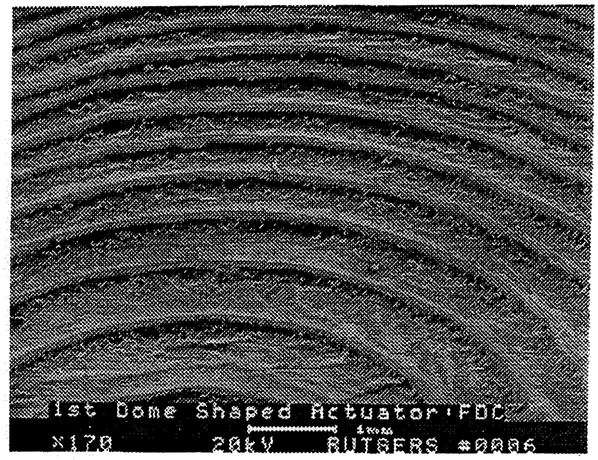
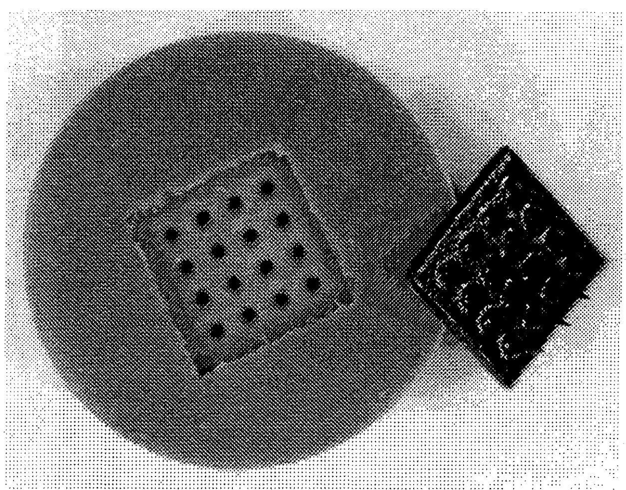
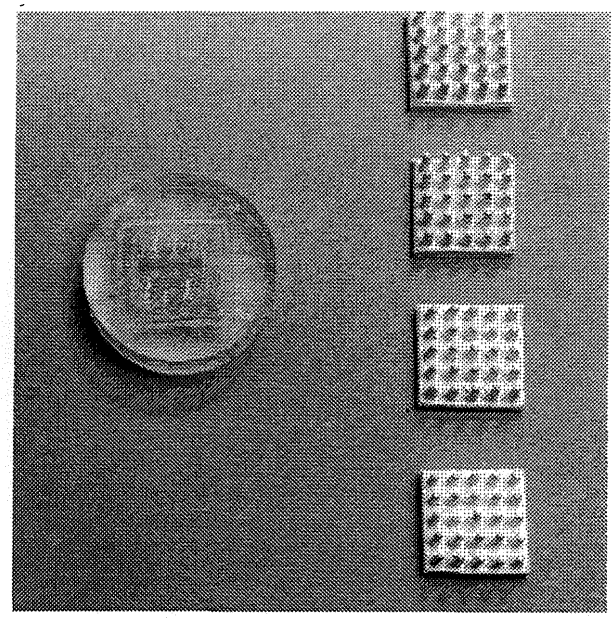


Figure 4: SEM micrograph of the interior of a dome shaped actuator, processed via FDC.



(a)



(b)

Figure 5: (a) Prototype with soft tooling mold and (b) green PZT ceramic preforms fabricated via soft tooling mold.

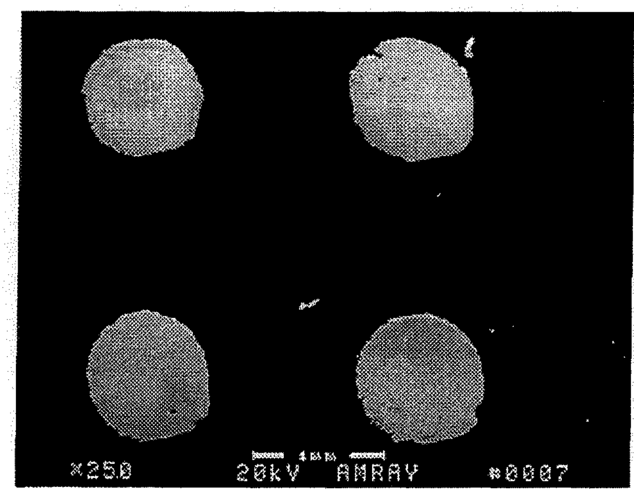


Figure 6: SEM of polished cross section

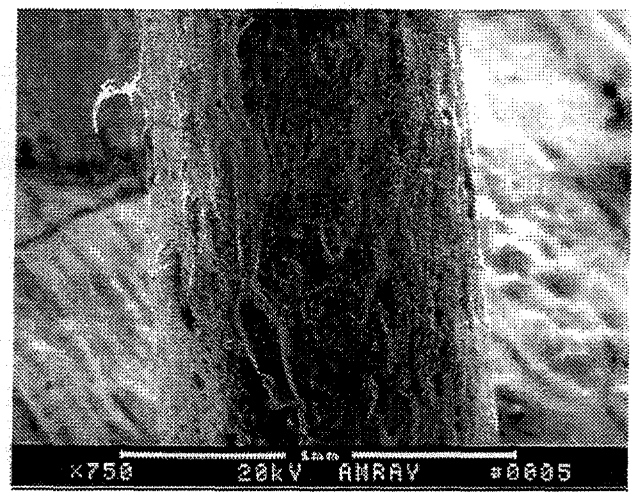


Figure 7: SEM of sintered ceramic pole

Table 1: ELECTROMECHANICAL PROPERTIES OF PIEZOELECTRIC COMPOSITES MADE BY INDIRECT, DIRECT AND SOFT TOOLING ROUTES

Technique	**Composite Type**		**Vol % PZT-5H**	**Dielectric Const. K**	**d_{33} (pC/N)**	**k_t(%)**
Indirect	3D Honeycomb		42	410	230	62
Direct	Ladder	*(Type A)*	70	1300	290	50
	Oriented (0-90°)	*(Type B)*	65	1545	300	51
	Oriented (±15°)	*(Type C)*	60	1560	350	62
	Oriented (±30°)	*(Type C)*	60	1580	510	59
	Oriented (±45°)	*(Type C)*	65	1350	390	--
	Oriented (±60°)	*(Type C)*	66	1200	225	--
	Oriented (±75°)	*(Type C)*	58	620	175	--
Soft Tooling	1-3 composite		15	320	315	63