

# Processing of Piezocomposites via Solid Freeform Fabrication (SFF) Techniques

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## Abstract

Fused Deposition and Sanders prototyping were used to manufacture PZT-polymer composites with various architecture for transducer applications. Two separate processing routes, direct and indirect, were utilized to make these composites. In the direct processing route, Fused Deposition of ceramics (FDC) was used to form green ceramic structures. For the indirect processing route, molds of the negative of the structures were made using FDM™ and Sanders prototyping techniques. Molds were infiltrated with a PZT slurry and dried. These structures were subjected to a binder burn out cycle to remove the mold polymer and binder. Structures were sintered and infiltrated with an acoustic epoxy, cut, polished and poled for electro-mechanical characterization. Among the various composites produced via the direct and indirect processes were: 3D honeycomb, 3-3 ladder, 2-2 annular and 1-3 rods. Composites with features as fine as 50  $\mu\text{m}$  were manufactured and characterized. Properties of piezoelectric composites produced by SFF techniques compared to conventionally processed composites.

## I. Introduction

Piezoelectric materials have the ability to convert electrical energy into mechanical energy and vice versa. These materials are used as ultrasonic transducers in two different modes, active and passive. In the active mode, the piezoelectric material only receives signals while in the passive mode, it will both send and receive signals. The various applications for these transducers include: medical imaging, hydrophones, microphones, phonographic pick-ups, speakers, strain gages, ignitors, nondestructive evaluation, and medical applications such as osteosynthesis, lithotripsy, and transdermal drug administration. The total US market for ultrasonic technology was \$3.3 billion in 1995, and was projected to grow to ~\$5.0 billion by year 2000[1].

Several ceramic and polymer materials exhibit piezoelectric behavior. Among the ceramic materials lead zirconate titanate (PZT) is being the most extensively used material in piezoelectric transducers. Piezoelectric ceramics have a relatively large value of  $d_{33}$ , the longitudinal piezoelectric charge coefficient, but their hydrostatic charge coefficient ( $d_h$ ) and voltage coefficient ( $g$ ) are low. Moreover, there is a poor acoustic match between the ceramic and the media through which it is transmitting or receiving a signal[2]. Piezoelectric polymers have low density and higher  $g_h$  values with good acoustic matching, but they have low electromechanical coupling coefficients ( $k_p$  and  $k_t$ ), with relatively high cost of fabrication and poling[3]. Piezocomposites consisting of a piezoelectric ceramic in an inactive polymer combine the desired piezoelectric sensitivity and dielectric constants of piezoceramics and low density and greater flexibility of polymers. These composites have shown better

electromechanical properties than monolithic materials. Various composite structures with innovative architectures have been explored over the last two decades. The connectivity or the microstructural arrangements of the ceramic and the polymer phase/s in the piezocomposites is a critical parameter for the electromechanical performance of the composites[4]. Numerous processing routes have been explored to fabricate composites with various connectivities including, 0-3, 1-3, 2-2 and 3-3. Here, the first digit refers to the number of dimensions in which the piezoelectric ceramic phase is connected and the second digit refers the same for the polymer. One of the applications for these composites is in ultrasonic imaging for medical applications where the imaging resolution can be increased by operating these transducers at higher frequencies. An increased operating frequency usually increases the noise to signal ratio which can be minimized by using fine scale piezoelectric transducers[5]. Some of the processing techniques developed for processing piezoelectric ceramic/polymer composites with numerous connectivities are listed in Table 1.

In this work, solid freeform fabrication (SFF) methods were used to make piezoelectric composites with novel architectures. Over the last decade, several SFF methods have been developed as techniques to fabricate polymer, metal or ceramic structures on a fixtureless platform directly from a CAD file[6]. During design verification or product development stage, SFF techniques offer great flexibility to manufacture prototypes with various shapes, sizes and functionality. For example, 1-3 piezocomposites are widely used for transducer applications and they are fabricated using various techniques including, injection molding, dice and fill, tape lamination and lost mold[5]. In conventional processing, a change in design for 1-3 piezocomposites is not only cost intensive, but also very time consuming. SFF techniques offer the possibility of processing these 1-3 piezocomposites with different rod spacing, rod size, rod geometry or a volume fraction gradient in ceramic materials from surface to inside with superior properties at a similar cost of production with no extra time for processing. The Fused Deposition process, commercialized by Stratasys™ Inc. (Eden Prairie, MN), and the ink jet printing process, commercialized by SPI (Wilton, NH), were used for this work. Indirect and direct processing routes were used for processing these piezoelectric ceramic/polymer composites. In the indirect processing route, a polymer mold or the negative of the structure was fabricated using SFF techniques. The mold was infiltrated with ceramic slurry, dried and then heat treated to remove the mold polymer and the binder. In the direct processing route, a green ceramic structure was directly formed using Fused Deposition of Ceramics (FDC) and then heat treated to remove the binder[7]. The structures were then sintered and back filled with an epoxy to form the composite.

This paper focuses on fabrication of PZT/polymer composites with 1-3 (using MM6-Pro, Sanders Prototype), 2-2 and 3-3 connectivities (using Fused Deposition technique). Physical and electromechanical characterization of these composites are presented, and advantages of the SFF approach are highlighted.

## II. Processing

The Fused Deposition and Sander Prototype processes were used to form piezoelectric ceramic/polymer composites. These composites were processed via two different routes: (a) direct and (b) indirect. Both methods are schematically shown in Fig. 1. In the direct

processing route, FDC was used with a PZT powder loaded polymer filament as the feed material for a direct layered manufacturing of the 3D green ceramic structure. Commercially available polymer/wax was used to create the molds for the indirect process. Piezoelectric ceramic/polymer composite structures were processed via lost mold technique[8]. In both the indirect and the direct routes, the final composite was formed by embedding the ceramic structure in an acoustic epoxy, and then electroding and poling them. Physical and electromechanical properties were then evaluated.

## **II.a Direct Fused Deposition of Piezoelectric Ceramic/Polymer Composites**

The 3-3 ladder structures with various orientations were built using the direct manufacturing technique with filaments of thermoplastic binder filled with PZT powder. A commercially available spray dried PZT-5H powder (Morgan Matroc Inc., Cleveland, OH) was used. Filaments were fabricated with 52 volume percent solids loading in a six-component thermoplastic binder system. Compounding or mixing of the powders with binders was done at 100°C using a Haake Rheocord System 40 (Passaic, NJ) at 100 rpm for one hour at a stabilized torque. The compounded mix was granulated before filament fabrication. Filaments of 1750 (+/- 50)  $\mu\text{m}$  in diameter were fabricated using an Instron capillary rheometer at a temperature of 65-75°C using a constant cross head speed of 1 mm/minute. A 3D Modeler™ by Stratasys™, Inc. (Eden Prairie, MN) was used for Fused Deposition of Ceramics (FDC) process. The liquifier temperature was maintained between 140-200°C while the temperature of the surrounding environment was in the range of 30-40°C. After processing, the green part was removed from the foam bed for further processing.

## **II.b Indirect Processing of Piezoelectric Ceramic/Polymer Composites**

In this process, polymer molds having the negative of the desired structures were formed via Sanders Prototype and FDM™. Molds were built using Stratasys™ commercial investment casting wax or ICW-04 and SPI's commercial wax. A ceramic slurry containing a high solids loading (45 volume %) of lead zirconate titanate (PZT) developed for the lost mold technique used to infiltrate the polymer molds[9]. The high solids slurry minimized cracking in the samples during solvent drying and binder burnout. Excess ceramic slurry on the top acted as a base for the structure after the burnout of the mold.

## **II.c Firing**

A three-stage binder burnout cycle in air was developed for the polymers in the structure. The specimens were heated from room temperature to 350°C at a rate of 1°C/min. and held for 1 hour to allow most of the polymer mold to evaporate. The temperature was then increased to 550°C at a rate of 1.5°C/min. and held for 2 hours to burnout the binder. A third soak at 800°C for 1 hour, with a heating rate of 3.5°C/min., was necessary to impart sufficient bisque strength to the ceramic structures for mechanical handlability. The specimens were cooled to room temperature, and sealed in a crucible containing an excess lead source. The specimens were then heated at a rate of 3.5°C/min to 1285°C, and held for 1 hour to sinter the PZT ceramic.

## II.c Characterization

The sintered samples were embedded in Spurr epoxy (Ernest F. Fullam Inc., Latham, NY) and cured in an oven at 70 °C for 12 hours in air. After removing the base and polishing both of the sides parallel to each other, the volume percent of PZT ( $V_{PZT}$ ) in the composite was calculated. The polished surfaces were then coated with silver paint and the composite specimens were poled in a corona poling apparatus at 70°C, 25 kV for 20 min., with a needle to specimen separation of 4.5 cm. 3-3 composites were poled perpendicular to the ceramic roads/mold X-Y plane and 1-3 composites were poled parallel to the rod length. The electromechanical properties were measured after aging the specimens for a minimum of 24 hours. The capacitance ( $C_p$ ) and the dielectric loss factor ( $\tan \delta$ ) were measured, before and after poling, at 1kHz using a RLC digibridge (Model 1689M, Gen. Rad. Inc., Boston, MA). The  $d_{33}$  coefficient of each composite was measured at 100 Hz using a piezo  $d_{33}$  meter (Model CPDT-3300, Channel Products Inc., Cleveland, OH). The composite impedance behavior versus frequency at resonance was used to measure the series and parallel resonant frequencies. Using these values, the electromechanical coupling coefficients were calculated[9]. Scanning electron microscope (Model 1400 SEM, Amray Corporation) pictures of the ceramic structures were taken after sputter coating them with gold.

## III. Results and Discussion

Various composites architectures were fabricated using both direct and indirect processing routes and three of them, 1-3, 3-D honeycomb and 3-3 ladder structures were characterized.

### III a. Piezocomposites Processed via Indirect Processing Route

1-3 PZT ceramic/polymer composites were fabricated via the indirect processing route. Molds of 1" X 1" X 0.1" were created using Sanders Prototype. A .stl file for cross-hatch pattern was used to create these molds with a road width of 100  $\mu\text{m}$  and an inter road gap of 150 to 350  $\mu\text{m}$ . Fig. 2a shows an SEM micrograph of the mold for 1-3 structure fabricated by Sanders Prototype. The figure shows a mold wall thickness of 100  $\mu\text{m}$  and an inter road gap of 350  $\mu\text{m}$ . Sanders prototype uses two different nozzles to deposit build and support materials and a milling operation to adjust the layer thickness. During fabrication of these molds, due to milling operation, some of the support materials went inside the holes. These small chips of the support materials can also be observed from Fig. 2a. Fig. 2b shows the 1-3 PZT ceramic structure processed from one of these molds via lost mold technique. The rod surfaces are not smooth because of the entrapment of the support materials inside the holes. The figure shows square rods of 300  $\mu\text{m}$  width separated by gaps of 70-90  $\mu\text{m}$ . Volume fraction of PZT ceramic ( $V_{PZT}$ ) was 48% for this 1-3 composite. Similar structures with different rod widths, spacings and volume fractions of ceramic were also fabricated using these molds. Table II shows the properties of these composites processed via SFF techniques.

Composites with various novel architectures were processed via Fused Deposition. A "3-D honeycomb" piezoelectric ceramic/polymer composite structure (3-3 connectivity) was one of them. Molds for 3-D honeycomb structures were fabricated using Stratasys™ 3-D Modeler™.

Fig. 3a shows the optical micrograph of the top view of a typical mold for 3-D honeycomb structure and Fig. 3b shows an SEM micrograph of the sintered ceramic structure prior to epoxy infiltration. The PZT ceramic structure is a honeycomb structure where uniformly spaced holes are connected in all three directions. The holes were created when the sacrificial polymer was evaporated during heat treatment. The volume fraction of the ceramic phase in these structures can be varied by changing the diameter of the holes, the spacing between the holes, or both the hole diameter and spacing. Several 3-D honeycomb composites were fabricated with 10 to 60 volume percent PZT ( $V_{\text{PZT}}$ ). It has been observed that as the volume fraction ceramic increases, both the relative dielectric constant  $K$  and the piezoelectric charge coefficient  $d_{33}$  increase[10]. Fabrication of 3-3 composites has been reported earlier via the replamine and BURPS processes[11-12]. Measurements of electromechanical properties of 3-D honeycomb structures processed via SFF technique show superior results over conventionally processed composites due to the controlled phase periodicity inherent in these composites.

### III b. Piezocomposites Processed via Direct Processing Route

Piezoelectric ceramic/polymer composites with 3-3 ladder structures were processed via direct SFF processing by FDC and their electromechanical properties were characterized. Composites with other shapes and connectivities, such as, c-ring and 2-2 annular structures, were also fabricated via direct FDC. Miyashita et al.[13] first reported the 3-3 ladder connectivity composites made by stacking fired PZT rods. In 3-3 ladder structure, ceramic rods are placed parallel to each other in each layer and perpendicular to each other in every consecutive layers. Fig 4 shows an SEM micrograph of a typical heat treated ceramic ladder structure prepared by the direct FDC method prior to epoxy infiltration. The ladder structures were built by using a raster fill strategy with a fixed inter-road spacing. The consecutive layers were built  $90^\circ$  to one another. Ladder structures with various orientations other than  $90^\circ$  between consecutive layers were also built using this technique. It can be observed that ceramic rods with  $\sim 300 \mu\text{m}$  diameter are uniformly spaced  $\sim 250 \mu\text{m}$  apart. These composites show a significantly improved electromechanical properties compared to the conventionally processed composites. A group of various composites processed via direct and indirect SFF techniques are shown in Fig. 5. At present, piezoelectric actuators, such as, moonie, rainbow structures, are being processed via direct processing routes using PZT powder loaded thermoplastic filaments.

### Conclusions

In this work, the solid freeform fabrication (SFF) techniques such as, Fused Deposition (FD) and Sanders Prototype, were used to form a variety of piezoelectric ceramic/polymer composites. The indirect and direct methods were used to process these composites. For the indirect method, molds were made by both SFF techniques and then infiltrated with a PZT ceramic slurry. The structures were dried and heat treated to burn the mold polymer and binder out and sintered in a crucible with excess lead. For the direct FDC method, filaments of PZT powder loaded in a thermoplastic binder were used for direct fabrication of ceramic structures. Structures were heat treated to burn the binder out and sintered. Sintered structures were back

filled with desired acoustic epoxy, cut, polished and poled. Electromechanical properties were evaluated and compared with conventionally processed composites. Composites processed via SFF techniques showed excellent electromechanical properties for transducer applications.

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**Table I :** Methods for making piezoelectric ceramic/polymer composites. [5]

Processing Technique	Connectivity	Scale ( $\mu\text{m}$ )	Key Limitations
Pick and Place	1-3	>100	Slow, Breakage
Dice and Fill	2-2, 1-3	>50	Single Phase, Area
Injection Molding	2-2, 1-3, 3-1	>40	Mold Cost
Tape Lamination	2-2, 1-3	>20	Flatness
Fiber Processing	1-3, 2-3, 3-3	>20	Fiber Strength
Lost Mold	2-2, 1-3, 3-1	>50	Mold Cost
Moonie	3-0	--	Mass Production
Solid Freeform Fabrication	1-3, 2-2, 3-3	>50	Mass Production

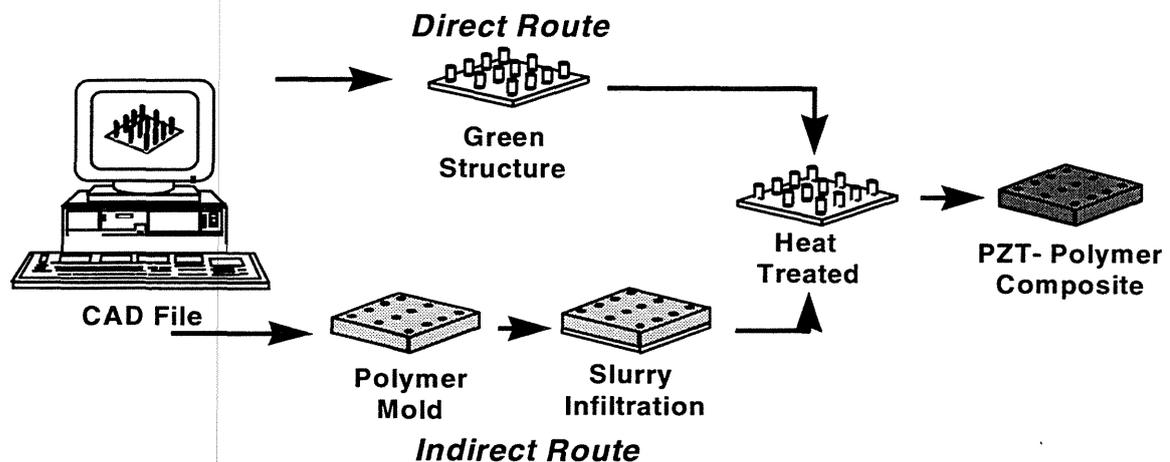


Fig. 1: Schematic of PZT/polymer composite fabrication steps using direct and indirect SFF techniques.

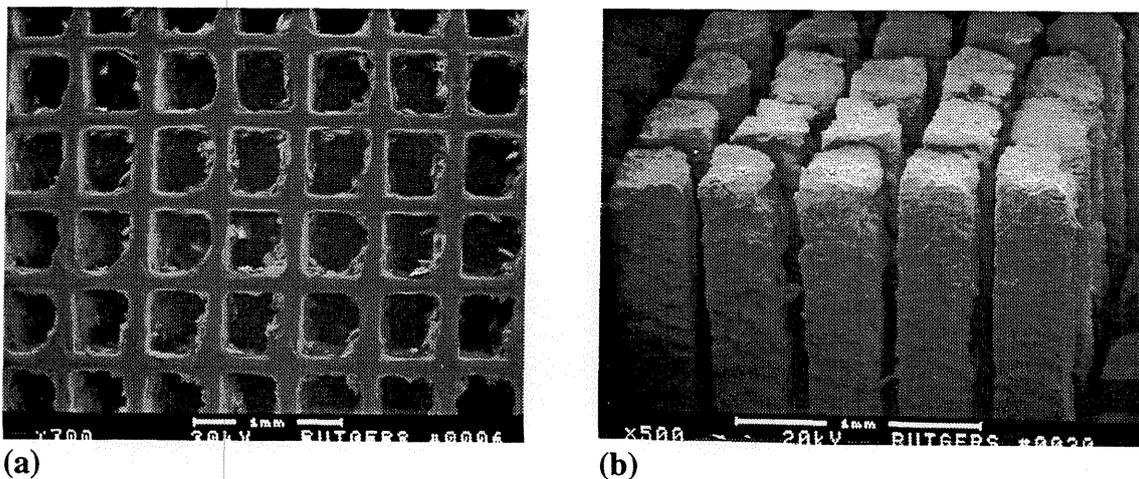
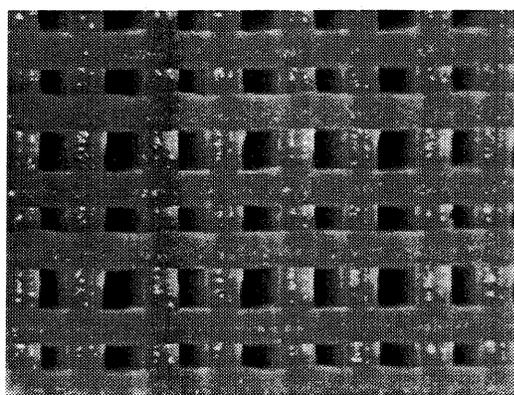


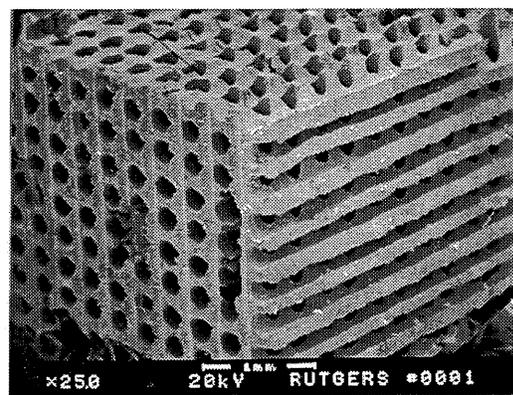
Fig 2 : (a) SEM micrograph showing a top view of a polymer mold fabricated by the Sanders Prototype.  
 (b) A 1-3 sintered ceramic structure obtained from these molds.

**Table II :** Electromechanical properties of piezoelectric composites processed via SFF and conventional techniques.

Composite Type	$V_{PZT}$ (%)	Ceramic Width( $\mu\text{m}$ )	Polymer Width( $\mu\text{m}$ )	K	$d_{33}$ (pC/N)	$k_t$ (%)	$k_p$ (%)
3-D Honeycomb	28	120	320	320	290	45	25
Ladder	70	300	200	1300	290	50	30
Ladder Angular ( $15^\circ$ )	60	250	200	1540	370	60	23
Sanders 1-3	48	300	80	970	280	66	28



(a) 500 $\mu\text{m}$



(b)

Fig 3 : (a) Optical photograph showing a top view of polymer mold made by FDM<sup>TM</sup>.  
(b) SEM micrograph of a sintered 3-D honeycomb structure obtained from these molds.

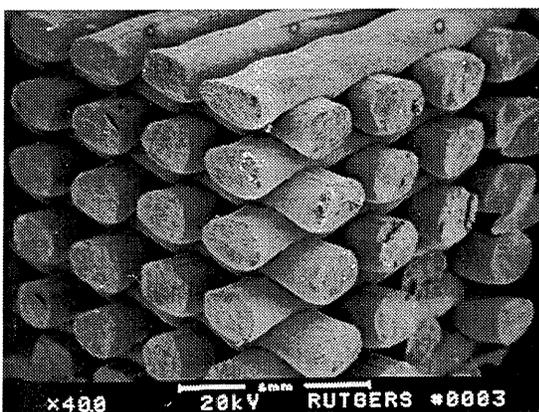


Fig 4 : SEM micrograph of a 3-3 ladder structure of sintered PZT ceramic.

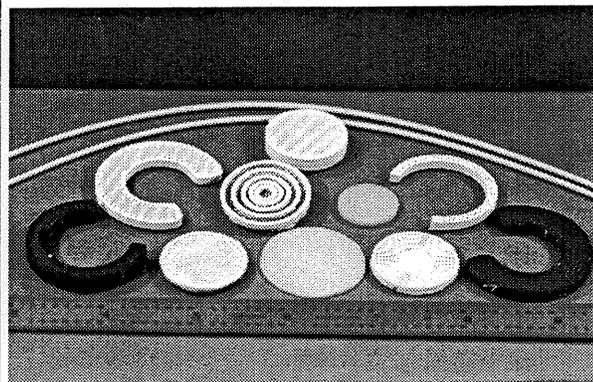


Fig. 5 : Photograph of polymer molds and PZT ceramic parts made by SFF technique.