FABRICATION OF PIEZOELECTRIC CERAMIC/POLYMER COMPOSITES BY INJECTION MOLDING.

Leslie J. Bowen and Kenneth W. French,
Materials Systems Inc.
53 Hillcrest Road, Concord, MA 01742

Abstract

Research at the Materials Research Laboratory, Pennsylvania State University has demonstrated the potential for improving hydrophone performance using piezoelectric ceramic/polymer composites. As part of an ONR-funded initiative to develop cost-effective manufacturing technology for these composites, Materials Systems is pursuing an injection molding ceramic fabrication approach. This paper briefly overviews key features of the ceramic injection molding process, then describes the approach and methodology being used to fabricate PZT ceramic/polymer composites. Properties and applications of injection molded PZT ceramics are compared with conventionally processed material.

Introduction

Piezoelectric ceramic/polymer composites offer design versatility and performance advantages over both single phase ceramic and polymer piezoelectric materials in both sensing and actuating applications. These composites have found use in high resolution medical ultrasound as well as developmental Navy applications. Many composite configurations have been constructed and evaluated on a laboratory scale over the past thirteen years. One of the most successful combinations, designated 1-3 composite in Newnham's notation [1], has a one-dimensionally connected ceramic phase (PZT fibers) contained within a three-dimensionally connected organic polymer phase. Hydrophone figures of merit for this composite can be made over 10,000 times greater than those of solid PZT ceramic by appropriately selecting the phase characteristics and composite structure.

The Penn State composites were fabricated [1] by hand-aligning extruded PZT ceramic rods in a jig and encapsulating in epoxy resin, followed by slicing to the appropriate thickness and poling the ceramic. Aside from demonstrating the performance advantages of this material, the Penn State work highlighted the difficulties involved in fabricating 1-3 composites on a large scale, or even for prototype purposes. These are:

1) The requirement to align and support large numbers of PZT fibers during encapsulation by the polymer.

2) The high incidence of dielectric breakdown during poling arising from the significant probability of encountering one or more defective fibers in a typical large array.

Over the past five years several attempts have been made to simplify the assembly process for 1-3 transducers with the intention of improving manufacturing viability and lowering the material cost. Early attempts involved dicing solid blocks of PZT ceramic into the desired configuration and back-filling the spaces with a polymer phase. This technique has found wide acceptance in the medical ultrasound industry for manufacturing high frequency transducers [2]. More recently, Fiber Materials Corp. has demonstrated the applicability of its weaving technology for fiber-reinforced composites to the assembly of piezoelectric composites [3]. Another exploratory technique involves replicating porous fabrics having the appropriate connectivity [4].

For extremely fine scale composites, fibers having diameters in the order of 25 to 100 µm and aspect ratios in excess of five are required to meet device performance objectives. As a result, these difficulties are compounded by the additional challenge of forming and handling extremely fine fibers in large quantities without defects. Recently, researchers at Siemens Corp. have shown that very fine scale composites can be produced by a fugitive mold technique. However, this method requires fabricating a new mold for every part [5].

This paper describes a new approach to piezoelectric composite fabrication, viz: Ceramic injection molding. Ceramic injection molding is a cost-effective fabrication approach for both Navy piezoelectric ceramic/polymer composites and for the fabrication of ultrafine scale piezoelectric composites, such as those required for high frequency medical ultrasound and nondestructive evaluation. The injection molding process overcomes the difficulty of assembling oriented ceramic fibers into composite transducers by net-shape preforming ceramic fiber arrays. Aside from this advantage, the process makes possible the construction of composite transducers having more complex ceramic element geometries than those previously envisioned, leading to greater design flexibility for improved acoustic impedance matching and lateral mode cancellation.

Process Description

Injection molding is widely used in the plastics industry as a means for rapid mass production of complex shapes at low cost. Its application to ceramics has been most successful for small cross-section shapes, e.g. thread guides, and large, complex shapes which do not require sintering to high density, such as turbine blade casting inserts. More recently, the process has been investigated as a production technology for heat-engine turbine components [6,7].

The injection molding process used for PZT molding is shown schematically in Figure 1. By injecting a hot thermoplastic mixture of ceramic powder and organic binder into a cooled mold, complex shapes can be formed with the ease and rapidity normally associated with plastics molding. Precautions, such as hard-facing the metal contact surfaces, are important to minimize metallic contamination from the compounding and molding machinery. For ceramics, the binder must be removed nondestructively, necessitating high solids loading, careful control of the binder removal

CH3080-0-7803-0465-9/92$3.00 ©IEEE

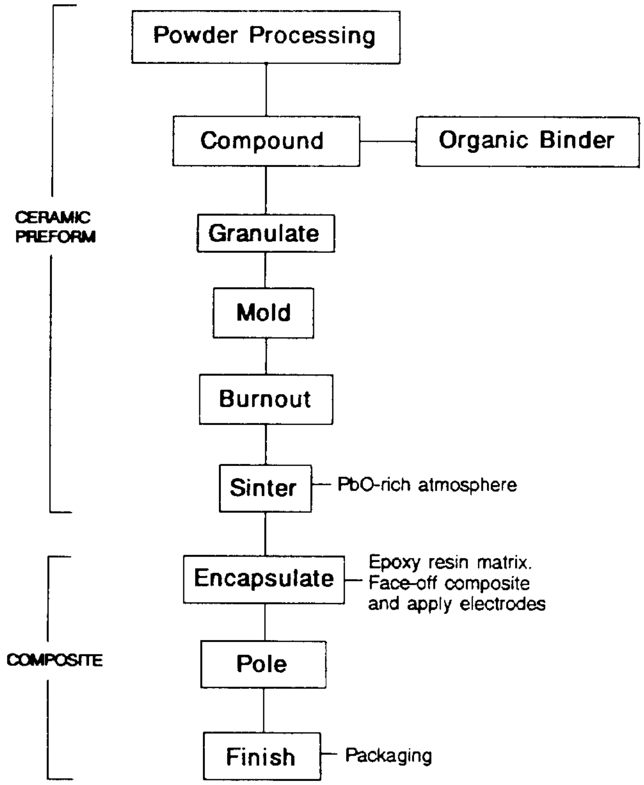

Figure 1: Injection Molding Process Route.

process, and proper fixturing. Once the binder is removed, the subsequent firing, poling and epoxy encapsulation processes are similar to those used for conventional PZT/polymer composites [1]. Thus, the process offers the following advantages over alternative fabrication routes: Complex, near net-shape capability for handling many fibers simultaneously; rapid throughput (typically seconds per part); compatibility with statistical process control; low material waste; flexibility with respect to transducer design (allows variation in PZT element spacing and shape); and low cost in moderate to high volumes. In general, because of the high initial tooling cost, the ceramics injection molding process is best applied to complex-shaped components which require low cost in high volumes.

Composite Fabrication and Evaluation

The approach taken to fabricate 1-3 piezoelectric composites is shown in Figure 2a, which illustrates a PZT ceramic preform concept in which fiber positioning is achieved using a co-molded integral ceramic base. After polymer encapsulation the ceramic base is removed by grinding. Aside from easing the handling of many fibers, this preform approach allows broad latitude in the selection of piezoelectric ceramic element geometry for composite performance optimization. Tool design is important for successful injection molding of piezoelectric composites. The approach shown in Figure 2b uses shaped tool inserts to allow changes in part design without incurring excessive retooling costs. Figure 2c shows how individual preforms are configured to form larger arrays.

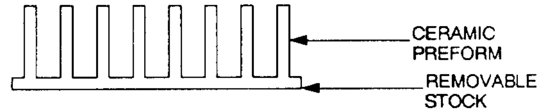

Figure 2a: Preform Configuration (Approx. 400 ceramic elements)

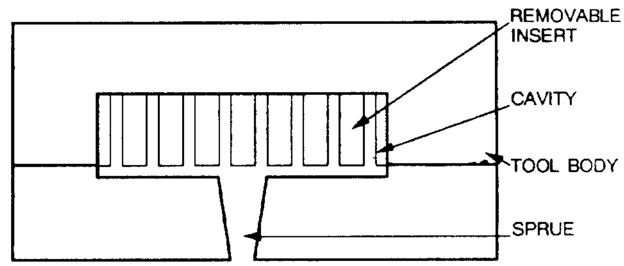

Figure 2b: Injection Molding Tool Configuration

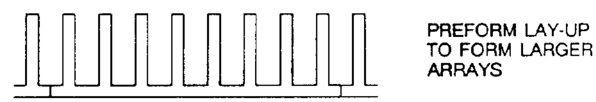

Figure 2c: Large Area Composite Arrays made from Preforms

Figure 2: Preform Approach to Composite Fabrication.

In practice, material and molding parameters must be optimized and integrated with injection molding tool design to realize intact preform ejection after molding. Key parameters include: PZT/binder ratio, PZT element diameter and taper, PZT base thickness, tool surface finish, and the molded part ejection mechanism design. In order to evaluate these process parameters without incurring excessive tool cost, a tool design having only two rows of 19 PZT elements each has been adopted for experimental purposes. Each row contains elements having three taper angles (0, 1 and 2 degrees) and two diameters (0.5 and 1mm). To accommodate molding shrinkage, the size of the preform is maintained at 50x50mm to minimize the possibility of shearing off the outermost fibers during the cooling portion of the molding cycle.

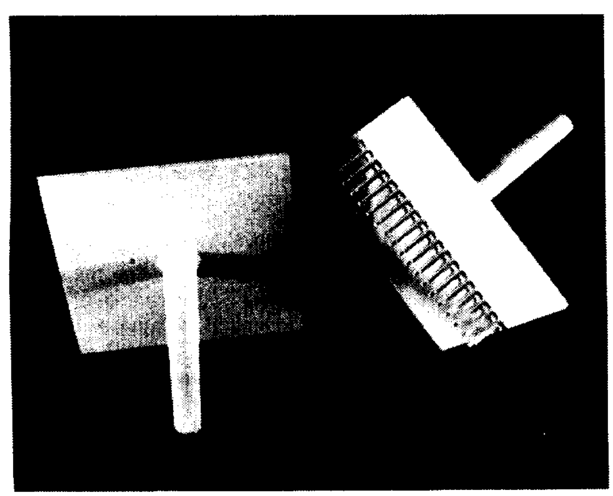

Figure 3: Injection Molded 1-3 Composite Preforms.

Figure 3 shows green ceramic preforms fabricated using this tool configuration. Note that all of the PZT elements ejected intact after molding, including those having no longitudinal tapering to facilitate ejection. Slow heating in air has been found to be a suitable method for organic binder removal. Finally, the burned-out preforms are sintered in a PbO-rich atmosphere to 97-98% of the theoretical density. No problems have been encountered with controlling the weight loss during sintering of these composite preforms, even for those fine-scale, high-surface area preforms *which are intended for high frequency* ultrasound.

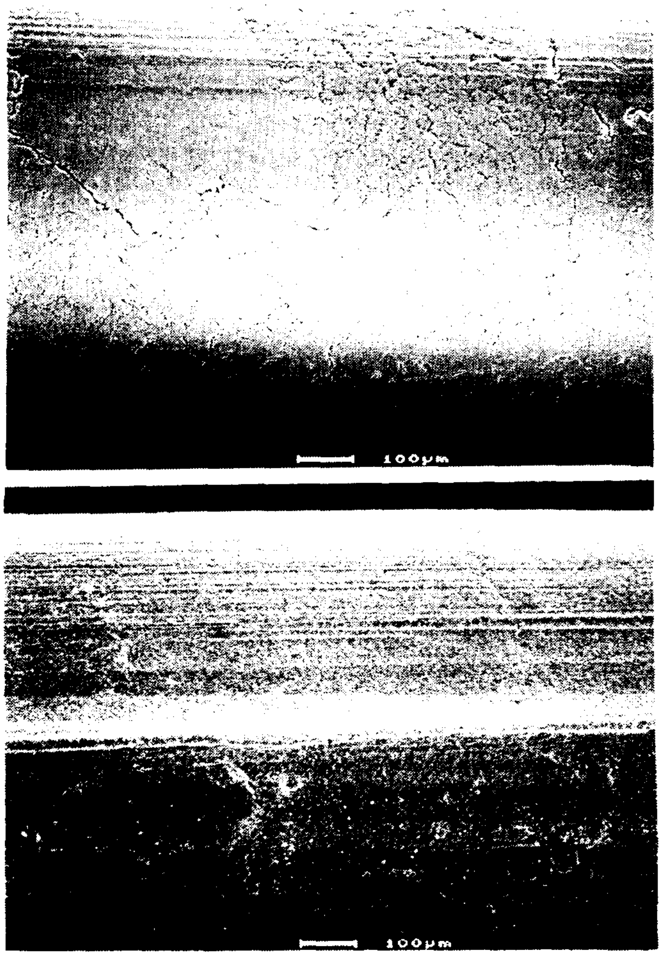

Figure 4: Scanning Electron Micrographs of As-molded (Upper) and As-sintered (Lower) Surfaces of PZT Fibers.

Figure 4 illustrates the surfaces of as-molded and as-sintered fibers, showing the presence of shallow fold lines approximately 10µm wide, which are characteristic of the injection molding process. The fibers exhibit minor grooving along their length due to ejection from the tool. Figure 5 shows the capability of near net-shape molding for fabricating very fine scale preforms; PZT element dimensions only 30µm wide have been demonstrated. The as-sintered surface of these elements indicates that the PZT ceramic microstructure is dense and uniform, consisting of equiaxed grains 2-3µm in diameter.

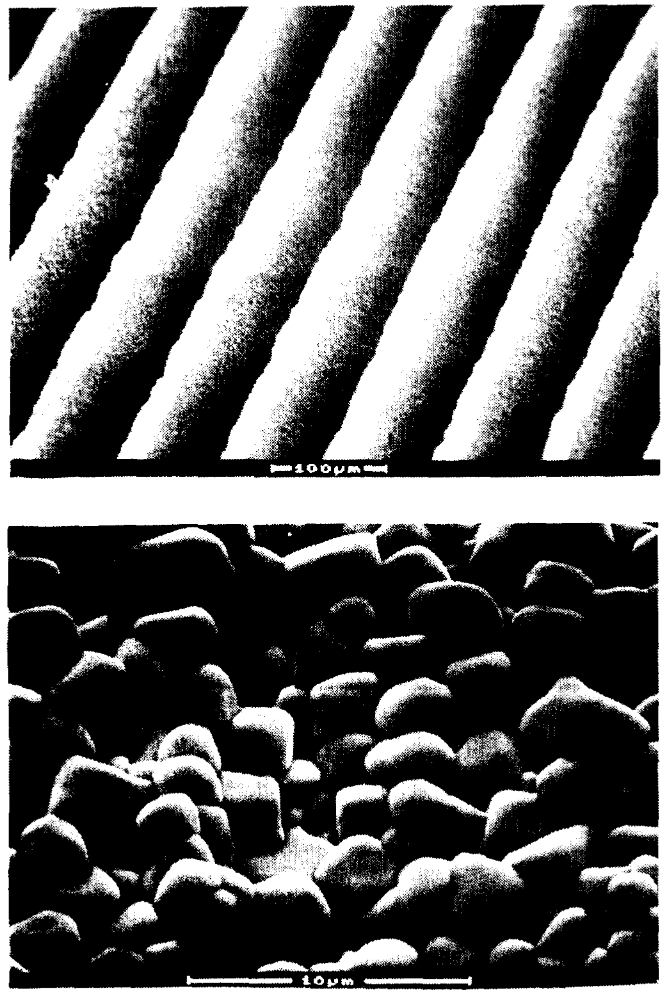

Figure 5: Fine-scale 2-2 Composite formed by Near Net-shape Molding (Upper Micrograph). As-sintered Surface (Lower Micrograph).

In order to demonstrate the lay-up approach for composite fabrication, composites of approximately 10 volume percent PZT-5H* fibers and Spurrs epoxy resin were fabricated by epoxy encapsulating laid-up pairs of injection molded and sintered fiber rows followed by grinding away the PZT ceramic stock used to mold the composite preform. Figure 6 shows composite samples made from freshly-compounded PZT/binder mixture and from reused material. Recycling of the compounded and molded material appears to be entirely feasible and results in greatly enhanced material utilization.

Table 1 compares the piezoelectric and dielectric properties of injection molded PZT ceramic specimens with those reported for pressed PZT-5H samples prepared by the powder manufacturer. When the sintering conditions are optimized for the PZT-5H formulation, the piezoelectric and dielectric properties are comparable for both materials. Since the donor-doped PZT-5H formulation is expected to be particularly sensitive to iron contamination from the injection molding equipment, the implication of these measurements is that such contamination is negligible in this injection molded PZT material.

*Powder supplied by Morgan Matroc, Inc., Bedford, Ohio; Lot 105A.

Table 1: Properties of Injection Molded Piezoelectric Ceramics.*

Specimen Type	Relative Permittivity	Dielectric Loss (1kHz)	d33 (pC/N)
Die-Pressed	3584	0.018	745
Inj. Molded**	3588	0.018	755

*Aged 24 hours before measurement.
**Poling conditions: 2.4kV/mm, $60^{\circ}C$, 2 minutes.

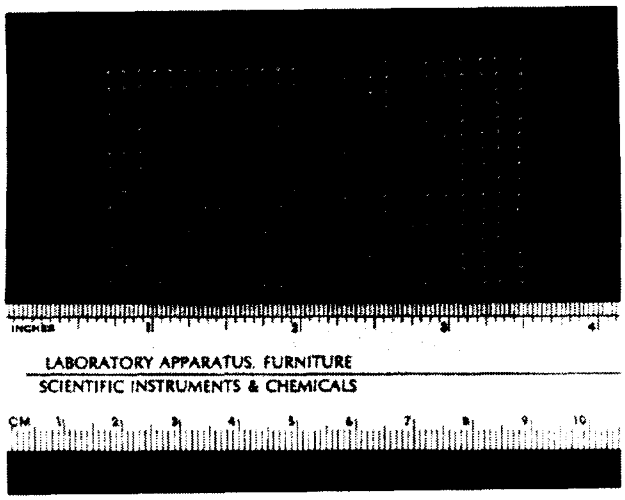

Figure 6: Injection Molded PZT Fiber/Epoxy Resin Composites prepared by the Preform Lay-up Method.

Summary

Ceramic injection molding has been shown to be a viable process for fabricating both PZT ceramics and piezoelectric ceramic/polymer transducers. The electrical properties of injection molded PZT ceramics are comparable with those prepared by conventional powder pressing, with no evidence of deleterious effects from metallic contamination arising from contact with the compounding and molding equipment. By using ceramic injection molding to fabricate composite preforms, and then laying up the preforms to form larger composite arrays, an approach has been demonstrated for net-shape manufacturing of piezoelectric composite transducers in large quantities.

Acknowledgements

This work was funded by the Office of Naval Research under the direction of Mr. Stephen E. Newfield. The authors wish to thank Ms. Hong Pham for technical assistance, and Dr. Thomas Shrout of the Materials Research Laboratory, Penn. State University for electrical measurements.

References

[1] R. E. Newnham et al, "Composite Piezoelectric Transducers," Materials in Engineering, Vol. 2, pp. 93-106, Dec. 1980.

[2] C. Nakaya et al, IEEE Ultrasonics Symposium Proc., Oct. 16-18, 1985, p 634.

[3] S. D. Darrah et al, "Large Area Piezoelectric Composites," Proc. of the ADPA Conference on Active Materials and Structures, Alexandria, Virginia, Nov. 4-8, 1991, Ed. G. Knowles, Institute of Physics Publishing, pp 139-142.

[4] A. Safari and D. J. Waller, "Fine Scale PZT Fiber/Polymer Composites," presented at the ADPA Conference on Active Materials and Structures, Alexandria, Virginia, Nov. 4-8, 1991.

[5] U. Bast, D. Cramer and A. Wolff, "A New Technique for the Production of Piezoelectric Composites with 1-3 Connectivity," Proc. of the 7th CIMTEC, Montecatini, Italy, June 24-30, 1990, Ed. P. Vincenzini, Elsevier, pp 2005-2015.

[6] G. Bandyopadhyay and K. W. French, "Fabrication of Near-net Shape Silicon Nitride Parts for Engine Application," J. Eng. for Gas Turbines And Power, 108, pp 536-539, 1986.

[7] J. Greim et al, "Injection Molded Sintered Turbocharger Rotors," Proc. 3rd. Int. Symp. on Ceramic Materials and Components for Heat Engines, Las Vegas, Nev., pp. 1365-1375, Amer. Cer. Soc. 1989.