Development of Fine-Scale Piezoelectric Composites for Transducers

Ahmad Safari, Victor F. Janas, and Amit Bandyopadhyay
Dept. of Ceramic and Materials Engineering, Rutgers, State University of New Jersey, Piscataway, NJ 08855

Piezoelectric ceramic/polymer composites, also known as piezocomposites, have been developed over the past two decades for electromechanical transducers to be used in both military and civilian applications. Recently, the thrust in these transducers is toward high operating frequencies, requiring fine-scale (< 200- μm ceramic-phase dimension) piezocomposites. Methods for processing these fine-scale piezocomposites are discussed. Current capabilities, as well as strengths and weaknesses of each method, are compared. The fundamentals of medical imaging and the importance of spatial scale in composite performance are reviewed. Several processing methods demonstrated composites with fine-scale ceramic phases (< 50 μm), and others have shown the potential to form composites with a ceramic scale of under 20 μm.

Introduction

Piezoelectricity is defined as the ability of certain materials to develop an electrical charge proportional to a mechanical stress (Jaffe et al., 1971). The piezoelectric response may be either direct or converse. For the direct piezoelectric response, the electrical polarization is proportional to the stress applied to the material. In the converse effect, material strain is proportional to the electric field applied across the material.

This quality of piezoelectric materials has led to their use in transducers which convert electrical energy to mechanical energy, and vice versa. These electromechanical transducers have found applications where they are used in either passive or active modes. In the passive mode such as in a hydrophone, or underwater listening device, the transducer only receives signals. In the active mode, such as in ultrasonic medical imaging, the transducer sends an acoustic pulse into the body and receives back reflected signals. Other applications include microphones, speakers, phonograph pickups, ignitors, accelerometers, strain gages, nondestructive evaluation, microactuators, and micromotors. Other than in medical ultrasonic imaging, medical applications for ultrasonic transducers include osteosynthesis, lithotripsy, thrombolysis, and transdermal drug administration. In 1995, the total U.S. market for ultrasonic technology was approximately $3.3 billion, and is expected to grow at between 5 and 10% through the rest of the decade.

A number of monolithic materials exhibit piezoelectric behavior. These include ceramics and polymers, as well as composites of ceramics with polymers. Table 1 from Gururaja (1994) summarizes the advantages and disadvantages of each type of material. Ceramics with lead zirconate titanate (PZT) being the most extensively used are less expensive and easier to fabricate than polymers or composites. They also have relatively high dielectric constants and good electromechanical coupling. However, they have a high acoustic impedance, and are therefore a poor acoustic match to water, the media through which it is typically transmitting or receiving a signal. Also, since they are stiff and brittle, monolithic ceramics cannot be formed onto curved surfaces, limiting design flexibility in the transducer. Finally, they have a high degree of noise associated with their resonant modes.

Piezoelectric polymers (Brown, 1992; Furukawa, 1990) such as poly(vinylidene fluoride) or poly(vinylidene fluoride-trifluoroethylene) copolymer are acoustically well matched to water, are very flexible, and have few spurious modes. However, applications of piezoelectric polymers are limited by their low electromechanical coupling, low dielectric constant, and high cost of fabrication.

Conflicting desires in optimum transducer physical and electromechanical properties have led researchers to look at composite materials. Piezocomposites, consisting of a piezoelectric ceramic in an inactive polymer, have shown superior

Correspondence concerning this article should be addressed to A. Safari.
Current address of A. Bandyopadhyay: Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164.

Table 1. Advantages (+) and Disadvantages (−) of Piezoelectric Ceramics, Polymers, and Composites (Gururaja, 1994)

Parameter	Ceramic	Polymer	Ceramic/Polymer Composite
Acoustic Impedance	High (−)	Low (+)	Low (+)
Coupling Factor	High (+)	Low (−)	High (+)
Spurious Modes	Many (−)	Few (+)	Few (+)
Dielectric Constant	High (+)	Low (−)	Medium (+)
Flexibility	Stiff (−)	Flexible (+)	Flexible (+)
Cost	Cheap (+)	Expensive (−)	Medium (+)

properties when compared to single-phase materials. As shown in Table 1, composites combine high coupling, low impedance, few spurious modes, and an intermediate dielectric constant. In addition, they are flexible and moderately priced.

The connectivity, or microstructural arrangement of component phases in the composite, first discussed by Newnham et al. (1978), and later amended by Pilgrim et al. (1987), is a critical parameter for the electromechanical performance of the composite. Connectivity is defined as the number of dimensions in which a phase is self-connected. For a composite containing two phases, there are sixteen connectivity patterns, as shown on Figure 1. They range from 0-0 where neither phase is self-connected to 3-3, where each phase is self-connected in three dimensions. In this convention, the first digit refers to the active (piezoelectric ceramic) phase, while the second digit refers to the soft polymer or inactive phase. Though Figure 1 shows only 10 structures, the sixteen connectivities arise from the structures labeled [0-1], [0-2], [0-3], [1-2], [1-3], and [2-3]. These structures each refer to two microstructural agreements. For example, the [1-3] structure represents both 1-3 and 3-1 connectivities, remembering that the first digit refers to the ceramic, while the second digit refers to the polymer.

Over the last two decades, researchers have looked for different routes to process piezocomposites and improve their properties. Most of the work has been limited to the connectivities which are easier to form, namely 0-3 (ceramic particle filled polymer), 1-3 (unidirectional laminates of ceramic fiber), 2-2 (laminated sheets of ceramic and polymer), 3-0 (porous ceramic), 3-1 and 3-2 (drilled ceramic), and 3-3 (ceramic/polymer networks). There are several excellent review articles (Safari, 1994; Smith, 1989; Gururaja et al., 1987) on processing techniques used to form piezocomposites with a variety of connectivities.

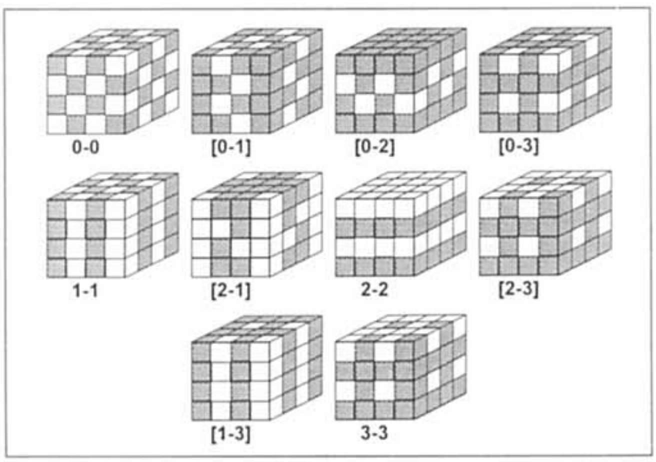

Figure 1. Connectivities for a two-phase solid.
After Newnham et al. (1978).

As mentioned earlier, one of the applications of piezoelectric transducers is in ultrasonic medical imaging, a critical diagnostic tool widely used by physicians. The popularity of this diagnostic tool lies in its ability to produce real-time, high resolution three-dimensional images of internal soft body tissue without the use of potentially hazardous ionizing radiation. As shown in Figure 2, the process utilizes an electromechanical transducer operating in the active, or pulse-echo mode. The transducer transmits ultrasonic pulses into the body. The pulses reflect off of internal structures, and are received by the transducer as faint echoes. A more detailed discussion on the finer points of biomedical imaging can be found elsewhere (Hagen-Ansert, 1989; Sprawls, 1987).

In medical imaging applications, the drive has been toward operating at frequencies between 1 and 30 MHz (Gururaja, 1994; Smith, 1989; Gururaja et al., 1985a,b) to improve lateral resolution while minimizing acoustic clutter and lateral vibrational modes. In review articles by Janas and Safari (1995) and Smith (1992), methods for forming fine-scale piezoelectric ceramic/polymer composites for high frequency applications are discussed. Since then, several newer forming methods have been demonstrated. This article discusses the newer methods, as well as reviews the better known methods for processing fine-scale piezocomposites. The capabilities, strengths, and weaknesses of each method are presented. Prior to discussions on the processing techniques, the importance of spatial scale in composite performance is reviewed.

Importance of Spatial Scale

Piezocomposites with 1-3 connectivity have been shown to be well suited for medical imaging applications (Gururaja,

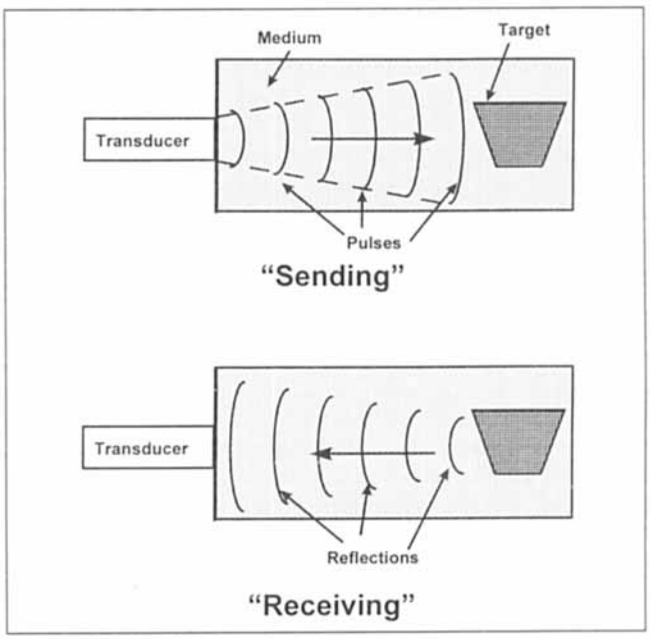

Figure 2. Pulse-echo operation of transducers in ultrasonic medical imaging.

1994; Smith, 1989). Here, active piezoelectric ceramic rods (or fibers) are continuous in one direction (z-axis), while the polymer phase is self-connected in all three directions. This type of connectivity reduces the transverse clamping effect in the active element and shows higher dielectric constant in the thickness mode even with 20 to 30 vol. fraction of ceramics in the composites. These composites show the highest sensitivity in the pulse-echo mode and the low acoustic impedance required for good matching to the human body.

This spatial scale of the composite plays a key role in the transducer's application and performance. The attainable resolution of the transducer is limited by the wavelength of the ultrasonic pulse transmitted into the body. The relationship between the pulse wavelength (λ) and its frequency (f) is given by

$$\lambda = V/f \tag{1}$$

where V is the velocity of sound in the propagating media. In the human body, V is approximately 1,500 m/s.

Equation 1 shows that increasing the composite's frequency of oscillation decreases the wavelength, thereby increasing the resolution of the transducer. According to the equation, in the frequency range of 1.5–30 MHz, the resolution varies from 1.5 mm to 50 μm. In medical imaging, the frequency range for various application are: obstetrical 2–5 MHz, adult heart 3 MHz, child heart 5 MHz, pediatric and peripheral vascular 5–7.5 MHz, eye 10 MHz, intracardiac and intravascular up to 30 MHz (Gururaja, 1994).

Increased resolution, however, must not come with a loss of homogeneity or a gain in spurious modes of behavior. Composite transducers are typically used at their thickness resonant mode frequency. Their performance is adversely affected by cross-talk in the composite structure (Janas and Safari, 1995; Gururaja, 1994; Smith and Auld, 1991; Auld, 1989; Smith et al., 1989). The cross-talk comes from the periodicity of the structure. For a given periodicity, there is a spectrum of resonant standing Lamb waves, which are located at wave numbers $n\pi/d$, where d is the periodicity of the ceramic phase, and $n = 1, 2, 3, \ldots$ In a 1-3 composite, the values of d are shown in Figure 3 for unit cell edge (f_{l1}) and diagonal (f_{l2}) rods. These standing wave resonances detract from the thickness resonance (f_t) if they are located too close to it. If, however, the Lamb wave resonances are at least two times higher than the thickness mode oscillations, then the thickness resonance vibrations are uniform in the plate. The frequency of the Lamb wave resonances increase as f_{t1} and f_{t2} decrease, while the thickness resonance is only a function of the plate thickness (f_t). Thus, fine-scale phases result in the composite behaving as a uniform medium in the region of its fundamental thickness-mode frequency.

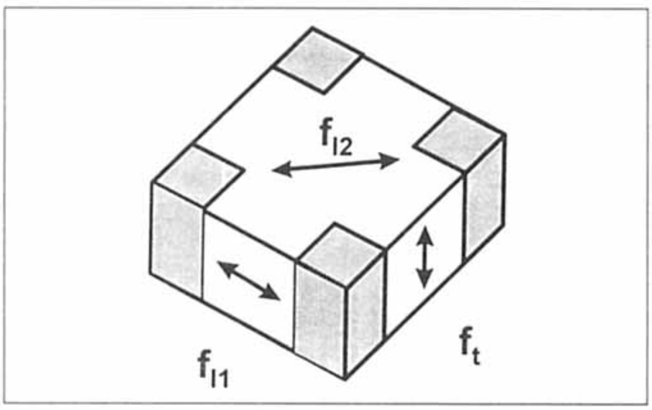

Figure 3. Thickness and surface stop-band modes in 1-3 piezoelectric ceramic/polymer composites.
After Auld (1989).

In summary, fine-scale piezocomposites increase the resolution of medical imaging transducers without increasing spurious modes of behavior or the loss of property homogeneity. In the remainder of the article, methods of forming fine-scale piezocomposites will be discussed.

Fine-Scale Forming Techniques

Different methods of forming fine-scale piezocomposites are reviewed in the following subsections. Process and typical characteristics for composites formed using each method will be described. In each case, current capabilities and typical properties will be presented with their advantages and limitations. In general, composites with a ceramic loading of between 20 and 30 vol. % are desired. At this loading, they have very high sensitivity, and the low density required for acoustic matching.

Rod placement

An early technique used to create fine-scale piezocomposites was demonstrated by Klicker et al. (1981). The technique uses ceramic rods placed in a polymer matrix. The rods were formed by extrusion and subsequent firing of a PZT powder/binder paste. As shown in Figure 4, fired rods were

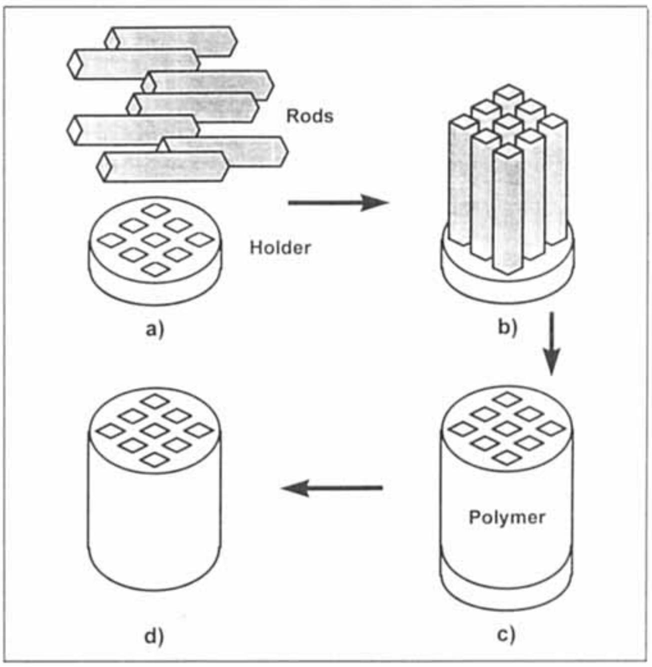

Figure 4. Rod placement ("pick and place") technique for formation of 1-3 composites.
(a) Ceramic rods and fixture prior to process; (b) rods in fixture; (c) embedded polymer; (d) final composite (1-3 connectivity).

aligned in a fixture consisting of a perforated plate. The entire structure was then embedded in epoxy, and composite formation completed by cutting away the brass fixture. The volume fraction of PZT in the composite was varied by varying the spacing of the holes in the brass plates.

An automated method for placing PZT rods has been developed by Fiber Materials, Inc. (Batha, 1992; McAllister, 1987). The equipment, known as the Ultraloom, accurately places PZT rods in the radial, axial, and circumferential directions in a woven glass cloth. It is a three-axis computer controlled machine to define the surface of the preform and is used mainly for making preforms for carbon-carbon composites.

The advantages of the rod placement method, also known as the "pick and place" method, are its flexibility in forming composites with a range in ceramic phases, phase dimensions, and spacing. If the transducer contains both transmitting and receiving sections, then overall response will be improved. Also, a range in spacing of the ceramic elements results in a transducer with a dispersed resonant frequency (Sanchez et al., 1990), or a transducer which can operate at several resonant frequencies (Bui et al., 1989). Finally, a gradient in ceramic volume fraction serves to reduce the side lobes in the direction perpendicular to the imaging plane, reducing out-of-plane artifacts (Smith, 1992).

Though the "pick and place" processing technique has these advantages, it also has a number of limitations. First, the fine ceramic rods used in this process are formed by extrusion. Extrusion of fine ceramic structures requires proper ceramic paste rheology, die design, and delicate heat treating. Though rods of approximately 100 μm diameter have been formed (Parish, 1995), extrusion of finer rods will require a leap in extrusion technology. Another limitation to the "pick and place" process is that the process is time-consuming. As the PZT rods become finer, the number of rods required per unit area rapidly increases. Finally, the individual fibers are fragile, and therefore have a high breakage rate in handling.

Dice and fill

The simple approach of piezocomposite forming known as "dice and fill" was first reported by Savakus et al. (1981). In this approach, shown in Figure 5, a series of parallel cuts are made into, though not through, a block of fired PZT ceramic. After the first series of cuts are made, a composite with 2-2 connectivity is made by backfilling the structure with polymer, and separating the composite from the base. If the block is rotated 90°, and a second series of parallel cuts are made, a composite with 1-3 connectivity is formed.

The simplicity of the dice and fill technique has made it the standard commercial method of forming 1-3 composites for medical imaging. Rods as small as 100 μm on each side are routinely formed (Lubitz et al., 1993). The minimum rod size is a function of both the accuracy of the dicing saw, and the ability of the ceramic to survive the process. The minimum spacing of the poles is limited to the width of the dicing saw blade. Silicon wafer blades as fine as 25 μm are the current blade limit. Dicing at this fine scale, however, is time-consuming.

Alternatives to dicing using a saw blade include laser (Ohara et al., 1994) and ultrasonic (Ohara et al., 1993) cutting. The disadvantage of these techniques is that they both cut tapered grooves. The taper results in a ceramic volume fraction gradient across the thickness of the composite.

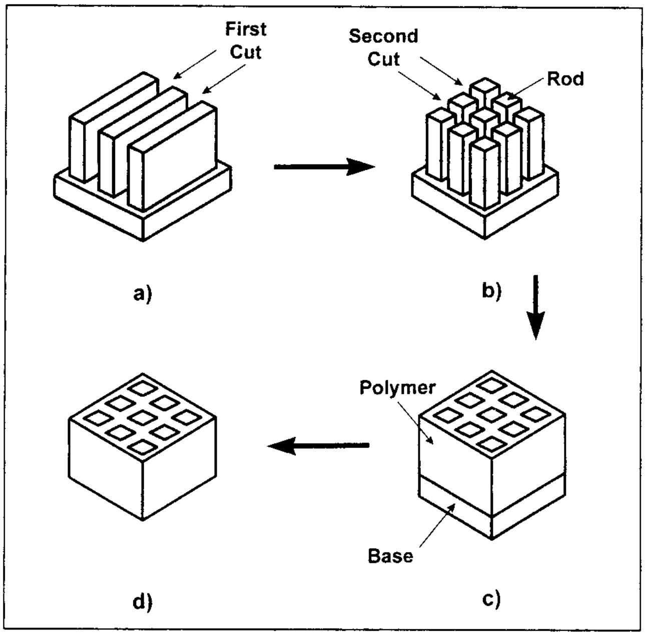

Figure 5. Dice and fill method of forming piezoelectric ceramic/polymer composites.

(a) Ceramic block after first cut (2-2 connectivity); (b) after second cut (1-3 connectivity); (c) embedded a polymer; (d) final composite after base removal.

Injection molding

Fine-scale piezocomposites with 1-3 and 2-2 connectivities have also been formed via injection molding (Gentilman et al., 1994, 1995, 1996). The process is shown in Figure 6. In this process, PZT ceramic is mixed with a thermoplastic and injection molded on standard equipment into preforms containing hundreds of sheets or rods. The preforms are then heat treated to remove the binder, sintered, filled with a desired polymer, and poled. Preforms with rods (1-3 connectivity) as small as 70 μm diameter, or sheets (2-2 connectivity) 25 μm wide have already been reported with an ultimate goal of decreasing the rod diameter to 25 μm.

The process can form composites with a variety of rod size, shape, and spacing. The injection molding process is simple, and therefore fast. Processing of small area transducers is adaptable to mass production. In addition, the small, individual panels can be arrayed together to form large area composites. Multiple ceramic phase composites can also be formed by injection molding panels containing different ceramics, and arraying them to form the final composite. The limitation of injection molding is the lengthy and relatively expensive process of forming the injection molding mold.

Lost mold

The lost mold technique (Safari et al., 1996; Lubitz et al., 1992, 1993) is currently under development as a method of forming fine-scale piezocomposites. In the process, shown in

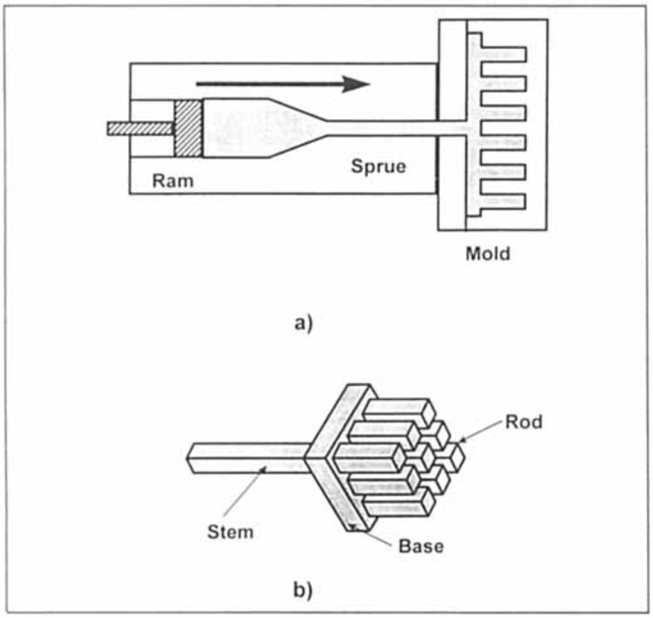

Figure 6. Injection Molding Method of forming 1-3 piezoelectric ceramic/polymer composites.

(a) Injection fill mold; (b) remove ceramic preform from mold.

Figure 7, a sacrificial mold which is the negative of the desired composite structure is filled with a PZT/binder slurry or gel. The mold and the binder are burned out, and the structure is sintered to full density. The sintered structure is filled with a polymer phase to form the composite. Rods as fine as 80 μm diameter have been reported with honeycomb structures as small as 10 μm wall thickness demonstrated (Lubitz et al., 1993).

There are several ways to form the sacrificial mold used in the process. The mold may be manufactured by the LIGA (lithography, galvanoforming, and plastic molding) process (Lubitz et al., 1992, 1993), or by punching or laser drilling holes into a plastic film or sheet (Safari et al., 1996).

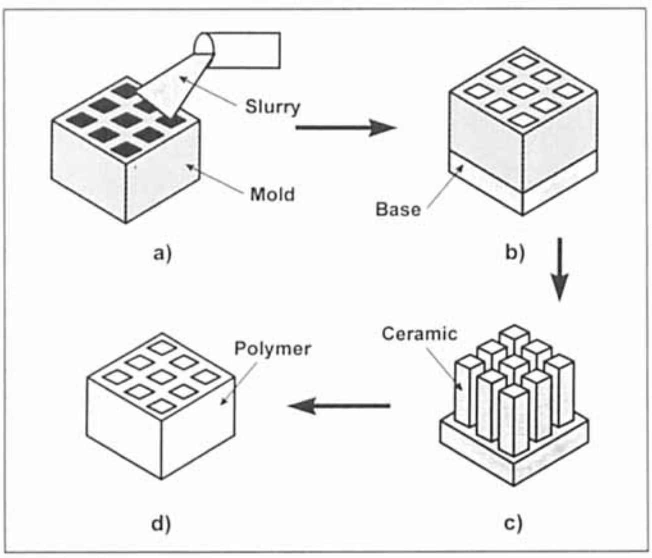

Figure 7. Lost mold method of forming 1-3 piezoelectric ceramic/polymer composites.

(a) Fill mold with slip; (b) full mold before heat treatment; (c) after heat treatment; (d) completed composite.

The process has the capability of forming composites with a variety of rod size, shape, and spacing. In addition, the process is simple, following standard ceramic processing techniques. Development of ceramic slurries with submicron sized particles allow in forming structures finer than 10 μm.

The limitations of the "lost mold" technique include the inability to form multiple ceramic phase composites. This is because the method of filling the mold allows only single ceramic phase slurries/gels.

Tape lamination

Fine-scale piezoelectric ceramic/polymer composites with 1-3 or 2-2 have also been formed by starting with thin PZT sheets. The thin sheets may be formed by tape casting (Runk and Andrejco, 1975). The ceramic sheets are either laminated with a passive material (Stevenson, 1994; Smith, 1989, 1992), or stacked with a spacer support placed between each layer, and filled with a passive polymer (Janas et al., 1995). This technique, shown in Figures 8a and 8b, yields a composite with 2-2 connectivity. Tapes as thin as 20 μm, separated by polymer layers as thin as 6 μm, have been incorporated into composite structures.

Composites with a 1-3 connectivity may also be created dicing the 2-2 stack perpendicular to the thickness direction of the tapes (Janas et al., 1995), as shown in Figures 8c and 8d. The diced stack is reinfiltrated with a matrix to complete 1-3 composite formation.

The advantages of the tape forming method include flexibility in forming composites with multiple ceramic phases, phase dimensions, and/or spacing. By varying the composition or the spacing of the tapes in the stack, composites with multiple active phases or volume fraction gradients could be

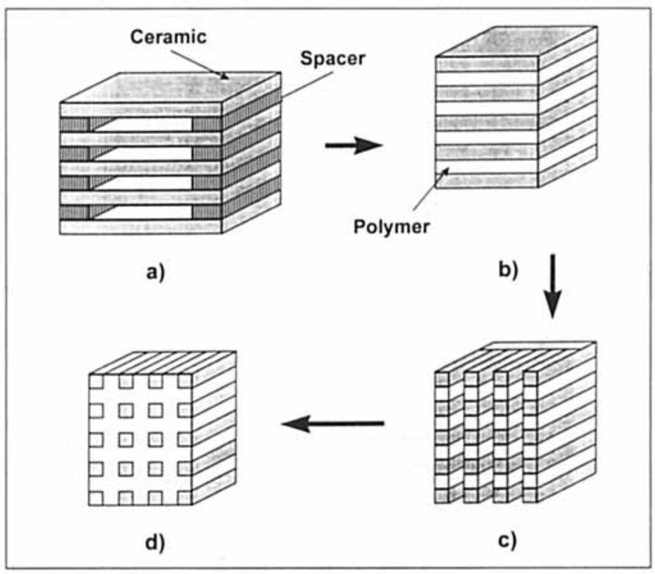

Figure 8. Tape casting method of forming 2-2 and 1-3 piezoelectric ceramic/polymer composites.

(a) Stacked tape separated by spacers; (b) polymer filled stack with spacers removed (2-2 connectivity); (c) diced stack; (d) polymer filled diced stack (1-3 connectivity).

formed. Ceramic phase composition could be altered from sheet to sheet in the stack.

The major drawbacks to the tape forming method are the challenges in forming and handling the flat, fully dense ceramic tapes. As thickness is decreased below 20 μm, breakage is high during firing and handling of the tapes.

Fiber processing

Fine PZT fibers (20 μm) have been used to form fine-scale piezoelectric fiber/polymer composites with connectivities such as 1-3, 2-3, 3-3 via the traditional textile processes of braiding, weaving, and knitting (Safari et al., 1996; McNulty et al., 1995). Three different methods have been used to produce PZT fibers, and sol-gel processing, the relic process and the viscous suspension spinning process (VSSP). The sol-gel technique (Yoshikawa et al., 1994; Selvaraj et al., 1992) relies on viscosity changes caused by hydrolization and polycondensation of a metal alkoxide and/or metal salt precursor solution. At the proper viscosity, the gel is spun into fibers, which are dried and fired to complete fiber formation. In the relic process (Ting, 1996; Livneh, 1995), activated carbon fibers were saturated with a precursor solution of metal salt or alkoxide. After drying, the fibers were heated to remove the carbon and to cause the constituents to react to form PZT.

Continuous PZT fibers have also been made by the viscous suspension spinning process (VSSP) (Cass, 1991). In the process, calcined PZT powder is loaded into a rayon fiber precursor solution, mixed, and extruded into an acid bath through a spinneret. The fibers are washed, dried, and fired to complete the process.

Weaving of the sized PZT fibers has resulted in numerous possibilities for composite microstructures. Scale-up to mass production is feasible, and other phases may be incorporated into the fiber architecture during its fabrication to form multiple ceramic phase composites. However, techniques for increasing the fiber strength for textile processing need further development.

Co-extrusion

The forming of fine-scale piezoelectric ceramic/polymer composites with 1-3 or 2-2 connectivities has recently been demonstrated using a co-extrusion process (Griffith, 1995). In this process, shown in Figure 9, ceramic powder is mixed with a thermoplastic polymer and extruded to a sheet or a rod geometry. The green ceramic sheet or rod is then laminated with a carbon-filled thermoplastic sheet. The laminates are then co-extruded to reduce the size of the ceramic and carbon rich phases. The extrudate may be bundled together and extruded again to further reduce the phase sizes. Composites with layers as fine as 8 μm have been made with this process.

The main advantages of the coextrusion method are its simplicity, and the ability to form multiple ceramic phase composites. Control of 1-3 rod periodicity, however, is difficult in this method.

Solid freeform fabrication (SFF)

Recently, fine-scale piezoelectric ceramic polymer composites with numerous connectivities were also formed using solid freeform fabrication (SFF) or rapid prototyping techniques (Bandyopadhyay et al., 1996). Several SFF techniques have been developed over the last decade to fabricate polymer, metal, and ceramic parts directly from a CAD data description of the part. These structures are made without using any part specific tooling, dies, or molds. Among the various SFF techniques, stereolithography or SLA, selective laser sintering or SLS, fused deposition modeling or FDM, laminated object manufacturing or LOM, and 3-D printing are some of the most commonly used ones (Bourell et al., 1990). Direct and indirect processing routes can be used to process fine-scale piezoelectric ceramic polymer composites. Figure 10 shows the different steps involved in direct and indirect

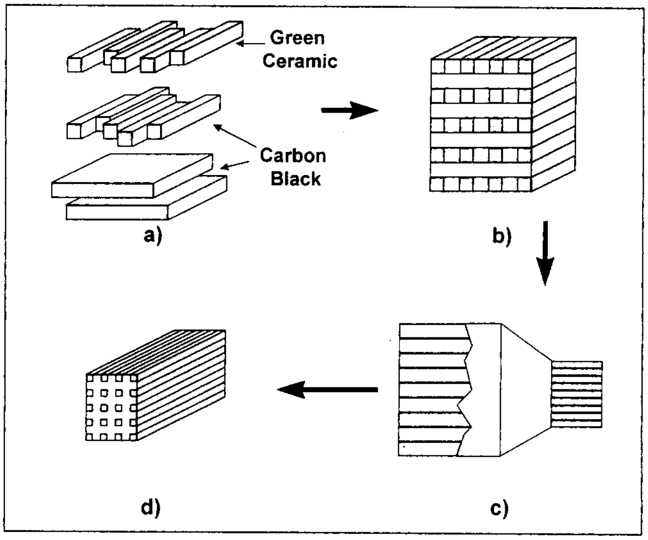

Figure 9. Piezoelectric ceramic/polymer composite formed by coextrusion.

(a) Preforms; (b) laminate; (c) extrusion; (d) 1-3 composites.

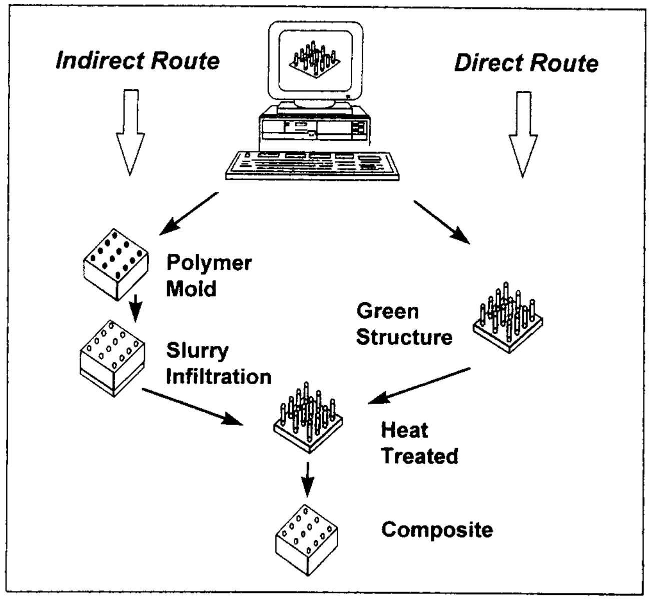

Figure 10. Fused deposition (FD) process for forming piezoelectric ceramic/polymer composites.

Both direct and indirect techniques shown.

processing routes for the fabrication of the piezoelectric ceramic polymer composites. In the direct processing route, green PZT ceramic structures can be formed directly from a CAD file using one of the SFF techniques. Green ceramic structures are then heat treated to burn the binder out and sinter the ceramic. For the indirect processing routes, a polymer mold, that is, the negative of the desired structure, can be formed using an SFF technique. The mold is infiltrated with a PZT slurry or gel and dried. The structure is heat treated to remove the mold and the binder, and sinter the ceramic. FDM and Sanders prototype techniques were used to form 1-3, 2-2, 3-3 ladder, and 3-D honeycomb structures via direct and indirect processing routes. Structures as fine as 50 μm were reported using these techniques (Bandyopadhyay et al., 1997).

The main advantages of the SFF techniques include: (1) rapid prototyping of functional quality piezoelectric ceramic polymer composites with various connectivities; (2) fabrications of composites with controlled phase periodicity to vary the volume fractions and micro- and macro-structures, which are not possible with most of the conventional processing techniques.

The major drawback of these techniques is large-scale production. Though one of a kind part or a small lot production is cost-effective, large-scale production of parts using SFF techniques are not.

Flextensional actuators

Flextensional actuators known as "moonies" (Onitsuka et al., 1995; Sugawara et al., 1992) have recently been developed. Shown in Figure 11a, Moonies are formed by sandwiching a PZT disk between two metal end caps which have dome shapes machined into them. The special design results in enhanced sensitivity and displacement for the Moonie structures. Moonie actuators have already been manufactured commercially in large quantities.

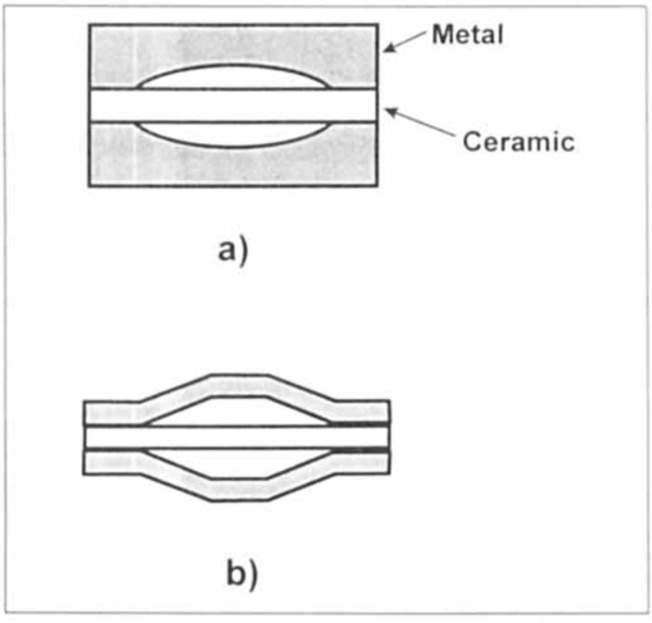

Figure 11. Flextensional actuators.
(a) Single Moonie; (b) single Cymbal.

Another new generation of actuators called "cymbal" was systematically modified from Moonies where a new endcap was designed using finite-element analyses. Figure 11b shows the cymbal actuators. These actuators are relatively easy to assemble, and showed a higher generative force and displacement compared to standard Moonie design. These actuators may be stacked to further enhance their overall performance.

Summary

Methods for processing fine-scale piezoelectric ceramic/polymer composites were reviewed. Fine-scale composites allow higher frequency pulses to be used in medical imaging applications. The fineness of spatial scale influences the maximum operating frequency of the transducer.

Different fine-scale processing methods include: rod placement, dice and fill, lost mold, injection molding, tape lamination, fiber processing, co-extrusion, and solid freeform fabrication. Most of the methods have demonstrated the ability to form composites with fine-scale ceramic phases (between 50 and 100 μm), and others have shown the potential to form composites with a ceramic scale of under 20 μm.

Acknowledgments

The authors would like to acknowledge the financial support of the Office of Naval Research, contract numbers N00014-93-1-1059 and N00014-94-1-0588, which made this work possible.

Literature Cited

Auld, B. A., "Waves and Vibrations in Periodic Piezoelectric Composite Materials," *Mat. Sci. Engr.*, **A122**, 65 (1989).

Bandyopadhyay, A., R. Panda, V. F. Janas, M. K. Agarwala, S. C. Danforth, and A. Safari, "Processing of Piezocomposites by Fused Deposition Technique," *J. Amer. Cer. Soc.*, **80**(6), 1366 (1977).

Bandyopadhyay, A., R. K. Panda, V. F. Janas, S. C. Danforth, and A. Safari, "Processing of Piezocomposites by Fused Deposition Technique," *Solid Freeform Fabrication Symp. Proc.*, Univ. of Texas at Austin, 265 (1996).

Batha, H. D., "Demonstration and Fabrication of Large Area 1-3 PZT Composite Panels," ONR Contract No. N00014-92-C-0186 (1992).

Bourell, D. L., J. J. Beamen, H. L. Marcus, and J. W. Barlow, "Solid Freeform Fabrication, An Advanced Manufacturing Approach," *Solid Freeform Fabrication Proc.*, J. J. Beamen, H. L. Marcus, D. L. Bourell, and J. W. Barlow, eds., Univ. of Texas at Austin, 1 (1990).

Brown, L. F., "Ferroelectric Polymers: Current and Future Ultrasonic Applications," *Proc. IEEE Ultrasonics Symp.*, 539 (1992).

Bui, T., H. L. W. Chan, and J. Unsworth, "Development of a Multi-frequency Ultrasonic Transducer Using PZT/Polymer 1-3 Composites," *Ferroelectric Lett.*, **10**, 97 (1989).

Cass, R., "Fabrication of Continuous Ceramic Fiber by the Viscous Suspension Spinning Process," *Amer. Ceram. Bull.*, **70**(3), 424 (1991).

Dogan, A., K. Uchino, and R. E. Newnham, "Composite Piezoelectric Transducer with Truncated Conical Endcaps "Cymbals," IEEE Trans. on Ultrasonics Ferroelectric and Frequency Control, in press (1997).

Furukawa, T., "Recent Advances in Ferroelectric Polymers," *Ferroelectrics*, **104**, 229 (1990).

Gentilman, R. L., D. F. Fiore, H. T. Pham, W. Serwatka, B. Pazol, C. Near, P. McGuire, and L. J. Bowen, "1-3 Piezocomposites Smart Panels for Active Surface Control," *SPIE Proc.*, **2721**, Soc. of Photo-Optical Engs. (1996).

Gentilman, R. L., D. F. Fiore, H. T. Pham-Nguyen, W. Serwatka, and L. J. Bowen, "Manufacturing of 1-3 Piezocomposite SonoPanel™," SPIE Proc., **2447**, Soc. of Photo-Optical Engs., 274 (1995).

Gentilman, R. L., D. F. Fiore, H. T. Pham, K. W. French, and L. J. Bowen, "Fabrication and Properties of 1-3 PZT-Polymer Composites," *Ferroic Materials: Design, Preparation, and Characteristics*, Vol. 43, A. S. Bhalla, K. M. Nair, I. K. Lloyd, H. Yanagida, and D. A. Payne, eds., Amer. Cer. Soc., 239 (1994).

Griffith, M. L., A. R. Barda, and J. W. Holloran, "Microfabrication of Ceramics by Co-Extrusion," Paper SXIX-69-95, Meeting and Exposition of Amer. Cer. Soc. (1995).

Gururaja, T. R., "Piezoelectric Transducers for Medical Ultrasonic Imaging," *Amer. Cer. Soc. Bull.*, **73**(5), 50 (1994).

Gururaja, T. R., A. Safari, R. E. Newnham, and L. E. Cross, "Piezoelectric Ceramic-Polymer Composites for Transducer Applications," *Electronic Ceramics*, L. M. Levinson, ed., Marcell Dekker, New York, p. 92 (1987).

Gururaja, T. R., W. A. Schulze, L. E. Cross, R. E. Newnham, B. A. Auld, and J. Wang, "Piezoelectric Composite Materials for Ultrasonic Transducer Applications. Part I: Resonant Modes of Vibration of PZT Rod-Polymer Composites," *IEEE Trans. on Sonics and Ultrasonics*, **SU-32**(4), 481 (1985a).

Gururaja, T. R., W. A. Schulze, L. E. Cross, and R. E. Newnham, "Piezoelectric Composite Materials for Ultrasonic Transducer Applications. Part II: Evaluation of Ultrasonic Medical Applications," *IEEE Trans. on Sonics and Ultrasonics*, **SU-32**(4), 499 (1985b).

Hagen-Ansert, S. L., *The Textbook of Diagnostic Ultrasonography*, The C. V. Mosby Co., St. Louis (1989).

Jaffe, B., W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics*, R.A.N. Publishers, Marietta, OH (1971).

Janas, V. F., T. F. McNulty, F. R. Walker, R. P. Schaeffer, and A. Safari, "Processing of 1-3 Piezoelectric Ceramic/Polymer Composites," *J. Amer. Cer. Soc.*, **78**(9), 2425 (1995).

Janas, V. F., and A. Safari, "Overview of Fine-Scale Piezoelectric Ceramic/Polymer Composite Processing," *J. Amer. Cer. Soc.*, **78**(11), 2945 (1995).

Klicker, K. A., J. V. Biggers, and R. E. Newnham, "Composites of PZT and Epoxy for Hydrostatic Transducer Applications," *J. Amer. Cer. Soc.*, **64**(1), 5 (1981).

Livneh, S., V. F. Janas, and A. Safari, "Development of Fine Scale PZT Ceramic Fiber/Polymer Shell Composite Transducers," *J. Amer. Cer. Soc.*, **78**(7), 1900 (1995).

Lubitz, K., A. Wolff, and G. Preu, "Microstructure Technology," *Proc. IEEE Ultrasonics Symp.*, 515 (1993).

Lubitz, K., A. Wolff, and G. Preu, "New Piezoelectric Composites for Ultrasonic Transducers," *Ferroelectrics*, **133**, 21 (1992).

McAllister, L. E., "Multidirectionally Reinforced Carbon/Graphite Matrix Composites," *Engineered Materials Handbook, Vol. 1, Composites*, ASM International, Metals Park, OH, 915 (1987).

McNulty, T. F., V. F. Janas, and A. Safari, "Novel 1-3 Piezoelectric Ceramic/Polymer Composites Using the Honeycomb Support Method," *J. Amer. Cer. Soc.*, **78**(11), 2913 (1995).

Newnham, R. E., D. P. Skinner, and L. E. Cross, "Connectivity and Piezoelectric-Pyroelectric Composites," *Mat. Res. Bull.*, **13**, 525 (1978).

Ohara, Y., M. Miyayama, K. Koumoto, and H. Yanagida, "PZT-Polymer Composite Fabricated with YAG Laser Cutter," *Sens. & Actu. A.*, **40**, 187 (1994).

Ohara, Y., M. Miyayama, K. Koumoto, and H. Yanagida, "Partially Stabilized Zirconia-Polymer Composites Fabricated with an Ultrasonic Cutter," *J. Mater. Sci. Lett.*, **12**, 1279 (1993).

Onitsuka, K., A. Dogan, J. F. Tressler, Q. Su, S. Yoshikawa, and R. E. Newnham, "Metal-Ceramic Composite Transducer, The 'Moonie'," *J. Intelligent Mater., Sys. and Structures*, **6**, 447 (1995).

Parish, M. V., personal communication (1995).

Pilgrim, S. M., R. E. Newnham, and L. L. Rohlfing, "An Extension of the Composite Nomenclature Scheme," *Mat. Res. Bull.*, **22**, 677 (1987).

Runk, R. B., and M. J. Andrejco, "A Precision Tape Casting Machine for Fabricating Thin Ceramic Tapes," *Ceram. Bull.*, **54**(2), 199 (1975).

Safari, A., "Development of Piezoelectric Composites for Transducers," *J. Phys. III France*, **4**(7), 1129 (1994).

Safari, A., V. F. Janas, and R. K. Panda, "Fabrication of Fine-Scale 1-3 Pb $(Zr_xTi_{1-x})O_3$ Ceramic/Polymer Composites Using a Modified Lost Mold Method," SPIE Proc., **2721**, Soc. of Photo-Optical Engs., Bellingham, WA, 251 (1996).

Safari, A., V. F. Janas, and B. Jadidian, "Incorporation of Piezoelectric $Pb(Zr_xTi_{1-x})O_3$ Fibers into Ceramic/Polymer Composites," SPIE Proc., **2721**, Soc. of Photo-Optical Engs., Bellingham, WA, 240 (1996).

Sanchez, M. S., F. R. M. D. Espinosa, and J. L. S. Emeterio, "Multi-frequency (1-3) Piezoelectric Composites," *Proc. IEEE Int. Symp. on the Applications of Ferroelectrics*, p. 73 (1990).

Savakus, H. P., K. A. Klicker, and R. E. Newnham, "PZT-Epoxy Piezoelectric Transducers: A Simplified Fabrication Procedure," *Mater. Res. Bull.*, **16**, 677 (1981).

Selvaraj, U., A. V. Parasadarao, S. Komarneni, K. Brooks, and S. Kurtz, "Sol-Gel Processing of PbTiO3 and $Pb(Zr_{0.52}\ Ti_{0.48})O_3$ Fibers," *J. Mater. Res.*, **7**(4), 992 (1992).

Smith, W. A., "New Opportunities in Ultrasonic Transducers Emerging From Innovations in Piezoelectric Materials," *New Developments in Ultrasonic Transducers and Transducer Systems*, SPIE Proc., **1733**, 3 (1992).

Smith, W. A., and B. A. Auld, "Modeling 1-3 Composite Piezoelectric: Thickness Mode Oscillations," *IEEE Trans. on Ultrasonics, Ferroelectrics, and Frequency Control*, **38**(1), 40 (1991).

Smith, W. A., "The Role of Piezoelectric Composites in Ultrasonic Transducers," *Proc. IEEE Ultrasonics Symp.*, 755 (1989).

Smith, W. A., A. Shaulov, and B. Auld, "Design of Piezocomposites for Ultrasonic Transducers," *Ferroelectrics*, **91**, 155 (1989).

Sprawls, P., Jr., *Physical Principles of Medical Imaging*, Chap. 25 and 26, Aspen Publishers, Rockville, MD (1987).

Sugawara, Y., K. Onitsuka, S. Yoshikawa, Q. C. Xu, R. E. Newnham, and K. Uchino, "Metal Ceramic Composite Actuators," *J. Amer. Cer. Soc.*, **74**(4), 996 (1992).

Stevenson, J. W., M. R. Reidmeyer, and W. Huebner, "Fabrication and Characterization of PZT/Thermoplastic Polymer Composites for High-Frequency Phased Linear Arrays," *J. Amer. Cer. Soc.*, **77**(9), 2481 (1994).

Ting, S. M., V. F. Janas, and A. Safari, "Relic Processing of Fine-Scale, Large Area Piezoelectric Ceramic Fiber/Polymer Composites," *J. Amer. Cer. Soc.*, **79**(6), (1996).

Yoshikawa, S., U. Selvaraj, P. Moses, Q. Jiang, and T. Shrout, "Pb(Zr, Ti)O3 [PZT] Fibers—Fabrication and Properties," *Ferroelectrics*, **154**, 325 (1994).

Manuscript received Oct. 28, 1996, and revision received Mar. 14, 1997.