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R&E-93-R-005



DEMONSTRATION AND FABRICATION OF
LARGE AREA 1-3 PZT COMPOSITE PANELS

Quarterly report for:

Contract No. N00014-92-C-0186

Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

August 20, 1992 to February 28, 1993

from:

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INTRODUCTION

Fiber Materials, Inc. (FMI[®]) has been contracted by the Office of Naval Research (contract #N00014-92-C-0186) to develop actuator/sensor technology for smart structures through economical and automated fabrication of large area 1-3 piezocomposite advanced materials.

This one year program, predicated on lead zirconate titanate (PZT) rod delivery provided by the sponsor, will fabricate a 2 meter x 2 meter x 5 millimeter test array containing 15 volume percent PZT rods. Since the start of the program, August 20, 1992, the 2 m x 2 m 1-3 piezocomposite test array has evolved by direction of the technical sponsor into the following configuration.

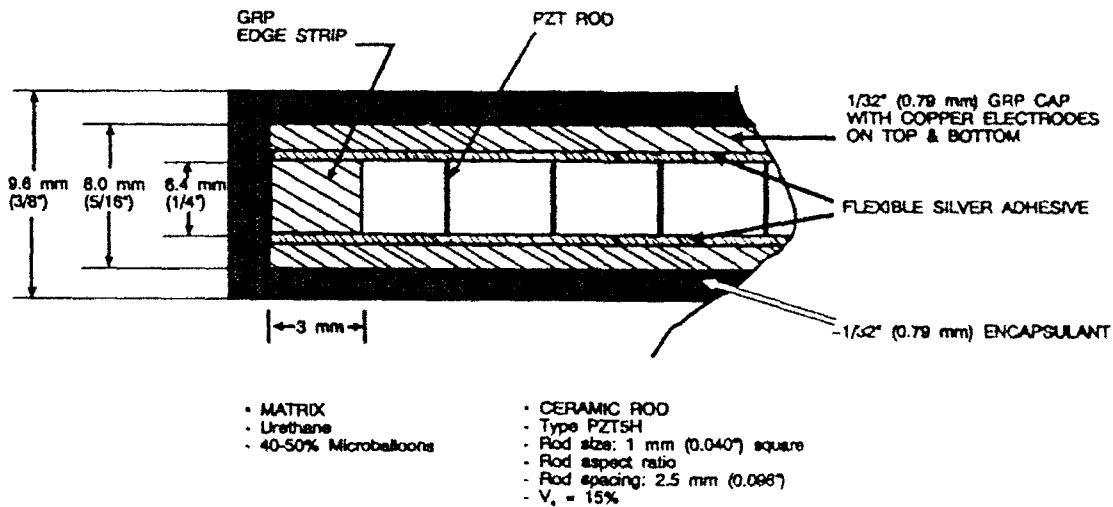


Figure 1

FMI is a registered trademark of Fiber Materials, Inc.

The 2 m x 2 m test array will be comprised of 16 tiles .5 m x .5 m x 5 mm with the configuration represented in Figure 1. Test samples of the prototype array configuration have been included by direction of the program technical monitor. The test samples will involve the following:

- (4) 4" x 4" piezocomposite panels to be delivered to Bob Ting at NRL Orlando for evaluation.
- (2) 10" x 10" piezocomposite panels to be delivered to Wayne Reader at Vector Research for evaluation.

The work presented in the following sections represents FMI's efforts into the fulfillment of its contract and input into the evolution of the 1-3 piezocomposite array configuration.

PREFORM TOOLING

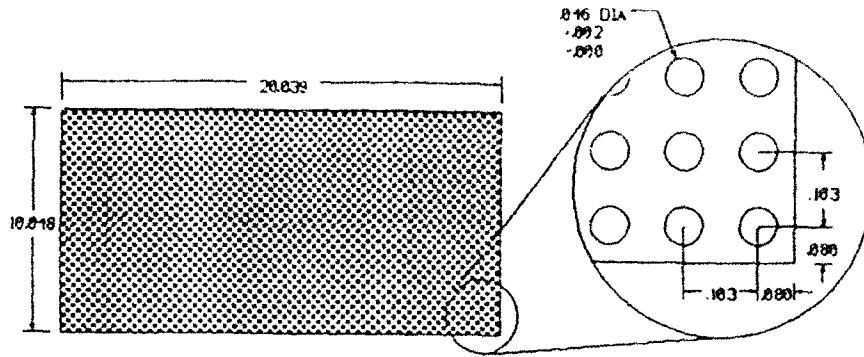
Preform tooling was designed to provide for both manual and automatic insertion of PZT rods for the fabrication of 1-3 piezocomposite panels. The tooling design, illustrated in Figure 2, employs thin copper plates with precise holes as rod guides so that the PZT rods can be positioned and their locations maintained during resin impregnation. The copper plates were patterned by photolithography and chemically etched to provide very precise hole diameters and locations.

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Statement A per telecon Stephen Newfield
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PZT COMPOSITE TOOLING PLATE



MATERIAL: .010 THICK COPPER
TOLERANCES: +/- .002 UNLESS SPECIFIED
QUANTITY: 100

Figure 2

Both PZT rods and copper tooling holes were designed to a tight tolerance so that all rods would fit into the holes with minimum deviation from the vertical position. As shown in Figure 3, a photochemically etched copper plate was bonded to an aluminum base plate, .080" spacers attached, and a second copper plate bonded to the spacers. This provides preform tooling for the manual and automatic insertion of PZT rods for fabrication of 10" x 20" piezocomposite panels. After resin impregnation and cure, the tooling plates will be machined away.

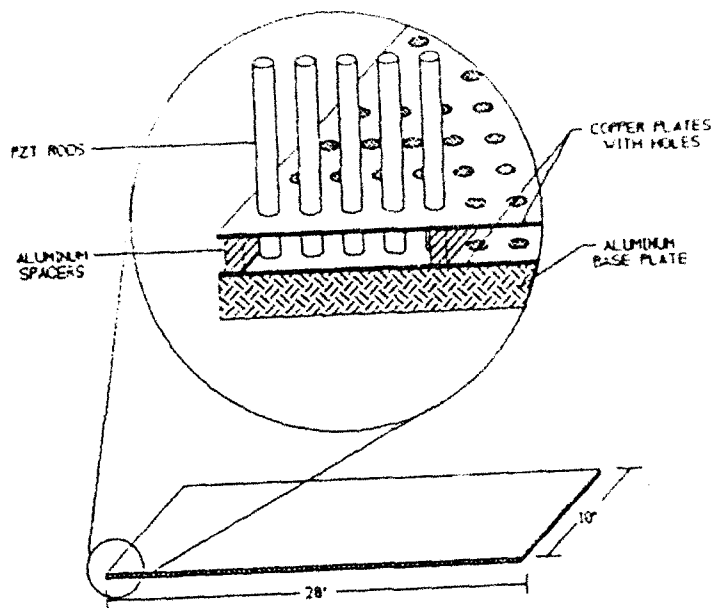


Figure 3

The fabrication of this preform tooling was completed during the first quarter of this program. The copper tooling plates, base plates and spacers were designed, built and have been ready for assembly since mid December 1992. Subscale parts were fabricated with non-compliant PZT rods to evaluate rod insertion and resin impregnation techniques.

PZT RODS

Early in the first quarter, Ceramics Process Systems (CPS), who was contracted by the sponsor to supply the PZT rods to FMI, reviewed their PZT rod manufacturing capabilities with FMI and a specification (Figure 4) was agreed upon for the 600,000 PZT-5H rods.

Figure 4

PZT ROD REQUIREMENTS

Cross-section:	Round
Dimensions:	Round: 1.14 mm diameter
Tolerances:	+/- .025 mm
Length:	12.70 mm minimum
Perpendicularity:	+/- .025 mm
Camber:	.025 mm TIR maximum
Amount:	600,000

The first sample shipment of PZT-5H rods, powder lot #127C, were received at FMI on 2 December 1992 for evaluation of the mechanical and piezoelectric properties. Ten PZT-5H rods were electroded on each end, poled by corona discharge, seasoned for 24 hours and tested to determine piezoelectric properties. An additional 30 rods were measured to check physical dimensions. The results are listed in Figure 5. The piezoelectric properties of these rods were low, with an average d_{33} value of 185 pC/N, K_{33} of 0.23 and dielectric constant of 1570. The dimensional results showed a large standard deviation for diameter, rod length and camber.

At the request of CPS and the sponsor, several PZT powder lots were evaluated for piezoelectric properties using pellets made from each lot. Of the four lots evaluated, d_{33} values ranged from an average of 85 to 511 pC/N. A sampling of rods from the best powder lot (Lot #127D) was received 18 February 1993 and evaluated. The results are shown in Figure 6. These results showed a significant improvement in piezoelectric properties from the previous powder lot #127C, with an average d_{33} of 421, K_{33} of 0.47 and dielectric constant of 2187.

Figure 5

CPS PZT-5H RODS
TESTED 04 DECEMBER 1992

PIEZOELECTRIC PROPERTIES:

DENSITY (g/cc)	DIELECTRIC CONSTANT	K33	Nt (m-Hz)	d33 (pC/N)
7.0	1570	0.23	1592	185

DIMENSIONAL PROPERTIES:

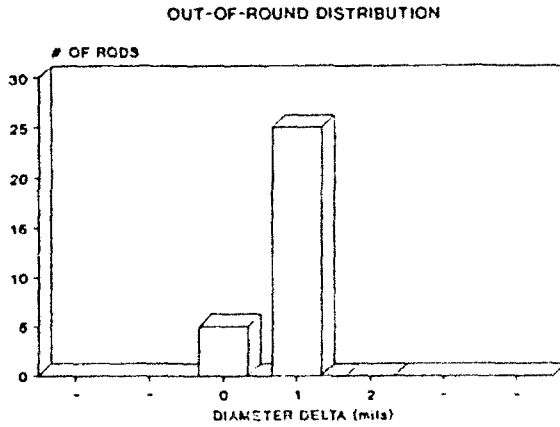
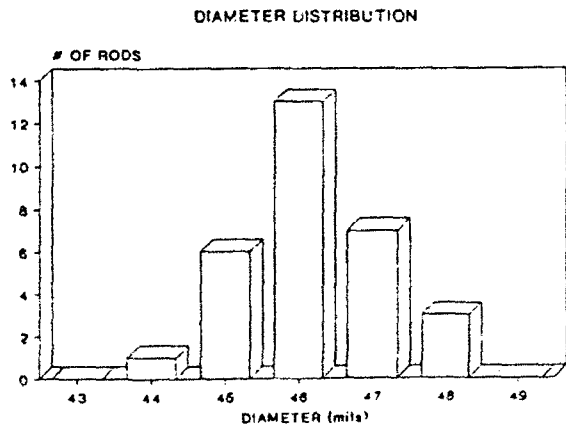
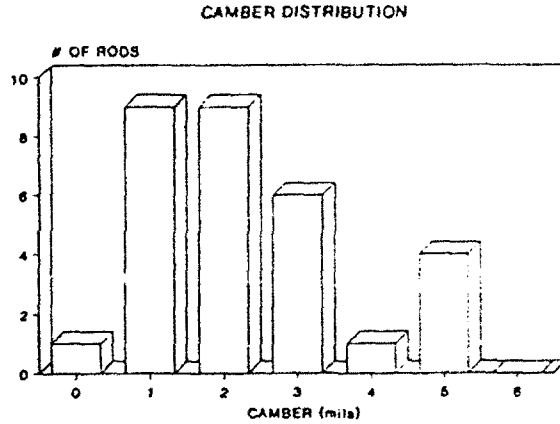
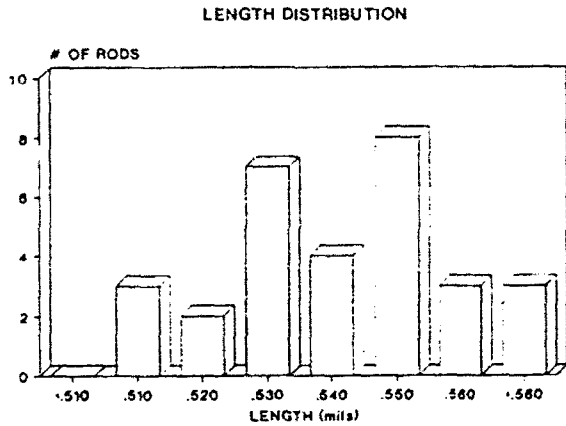


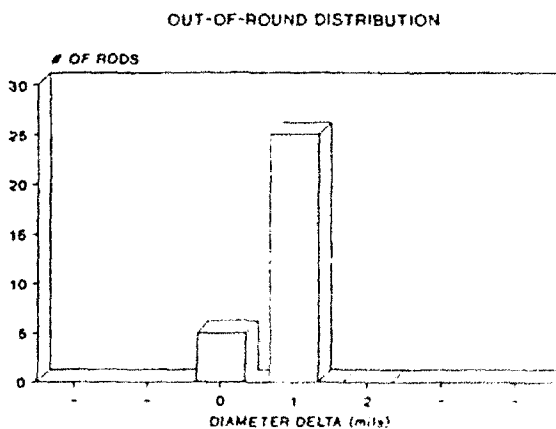
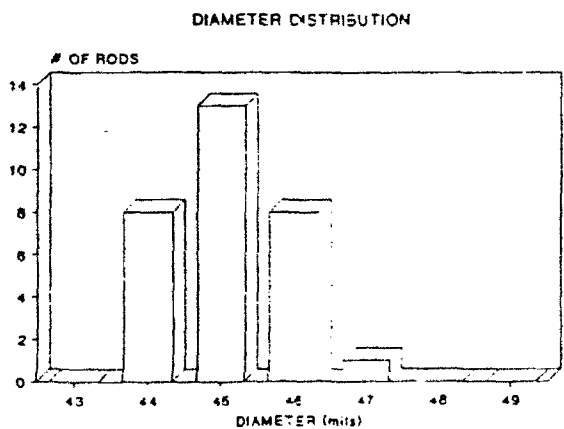
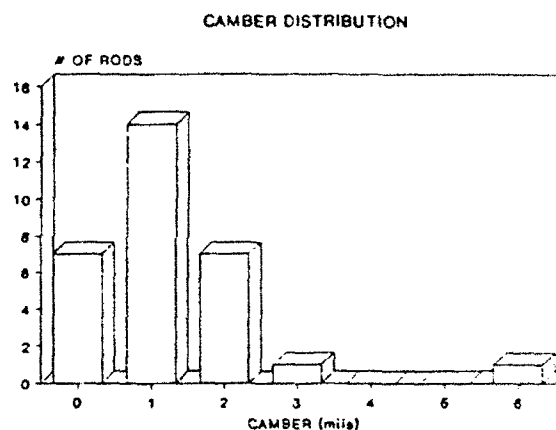
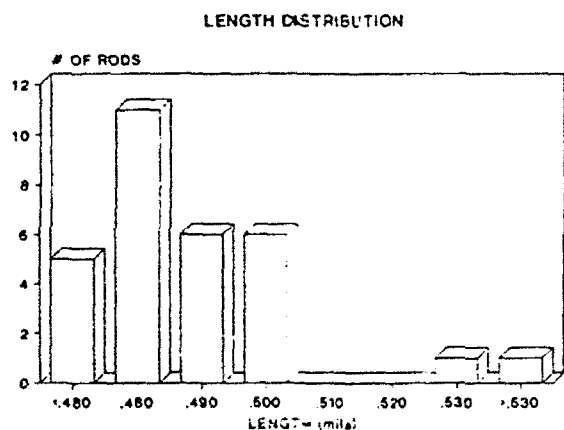
Figure 6

CPS PZT-5H RODS
TESTED 18 FEBRUARY 1993

PIEZOELECTRIC PROPERTIES:

DENSITY (g/cc)	DIELECTRIC CONSTANT	K33	Nt (m-Hz)	D33 (pC/N)
7.2	2187	0.47	1554	421

DIMENSIONAL PROPERTIES:



Rod physical dimensions improved as shown by the tighter diameter distribution and reduced camber measurements. Although the dimensional quality of this last batch of rods is acceptable for manual rod insertion, further improvement will be needed for automated rod insertion. The delay in providing PZT rods has put FMI behind schedule in preform fabrication (see Figure 7).

ONR PROGRAM STATUS

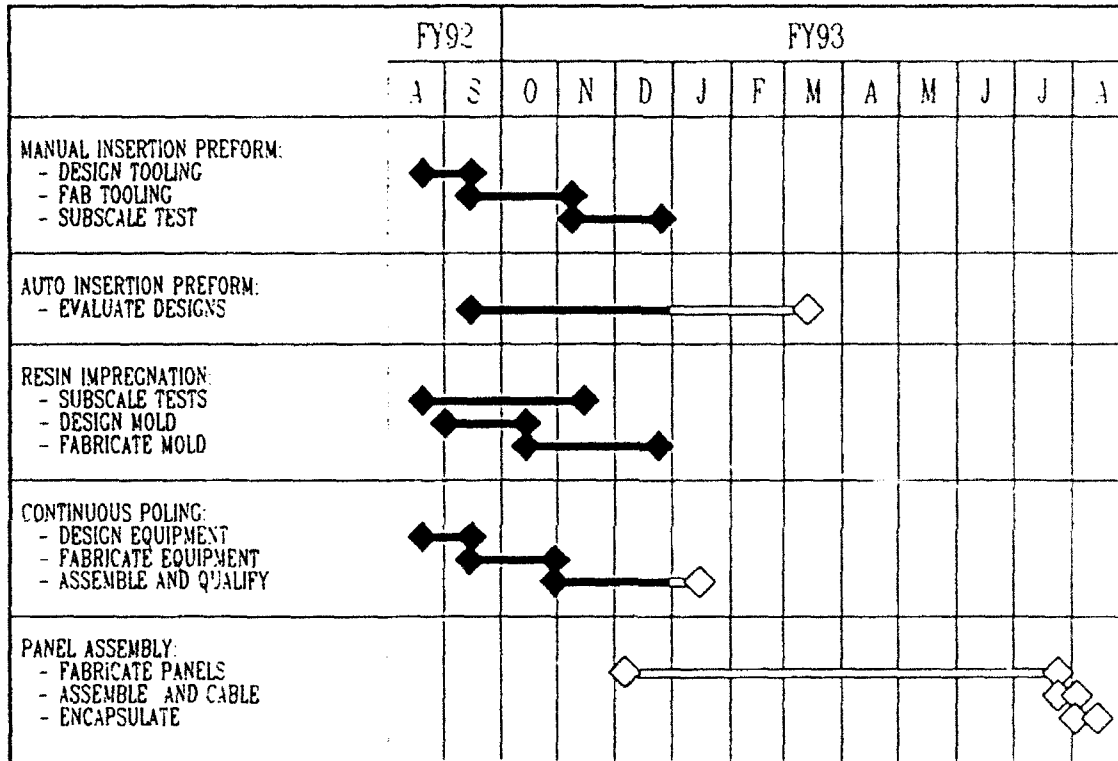


Figure 7

AUTOMATIC ROD INSERTION

Of all the steps involved in piezocomposite fabrication, rod insertion is the most time consuming. While the Ultraloom[®] allows precise positioning of each PZT rod, this automated cycle requires up to 15 seconds per insertion. Since fabrication of the 2 m x 2 m panel will utilize almost 600,000 rods, work has

Ultraloom[®] is a registered trademark of Fiber Materials, Inc.

been conducted to modify the Ultraloom insertion system to accommodate multiple rods in each cycle. The modification significantly improves the efficiency of the insertion system.

The foundation for the modifications lies in the concept of a multiple rod dispenser that can be attached to the existing insertion arm. Several different approaches are currently under evaluation, but all will lead to the basic scenario of a series of rods loaded onto a grooved holder, aligned to the holes in the copper screen tooling and lowered into place.

One insertion approach builds on a rod dispenser loading mechanism developed by Dr. Kahn et al under a related program being conducted at NRL. A schematic of this system is presented in Figure 8. This set-up consists of a single row of rods loaded onto a holder with each pass through the rod bin. The holder is then fed to the Ultraloom positioning head which lines up the rods with the tooling and inserts the rods into the appropriate holes. Since the rods supplied by CPS are round in cross-section, rod handling issues are simplified and offer potential for high-speed automation not achievable with the more difficult to handle square cross-section PZT rods that FMI has used in the past.

SCHEMATIC OF AUTOMATED ROD INSERTION

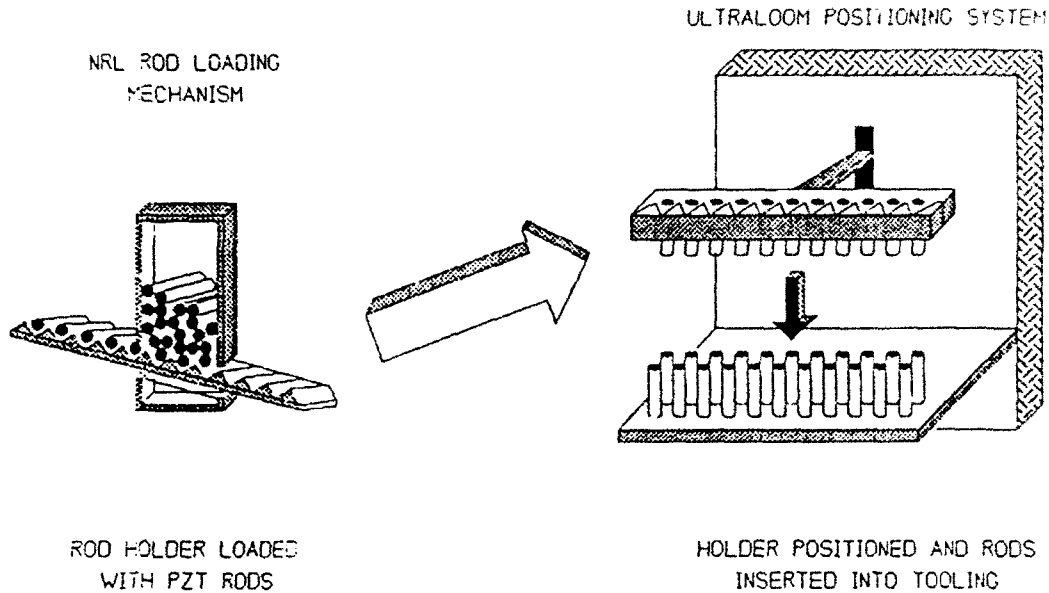


Figure 8

Another approach involves the use of a slightly different rod holder which is designed to hold many rows at a time. Loading of such a holder is achieved through a method similar to that just described or may incorporate a vibratory bowl and conveyor system that has been used on the Ultraloom in the past.

Work in this quarter has focused on rod handling issues and the identification of the most effective rod holder groove shape. Three different groove configurations were selected for evaluation and are illustrated in Figure 9. Since one goal of this program is to speed up the insertion process without sacrificing the precision of the Ultraloom, the rod holders have been designed with the following factors in mind.

- ability to hold rods in position
- ease of filling each groove with rods
- machinability and cost
- feasibility for scale-up to .5 m x .5 m demonstration tiles
- durability

INSERTER GROOVE SHAPES

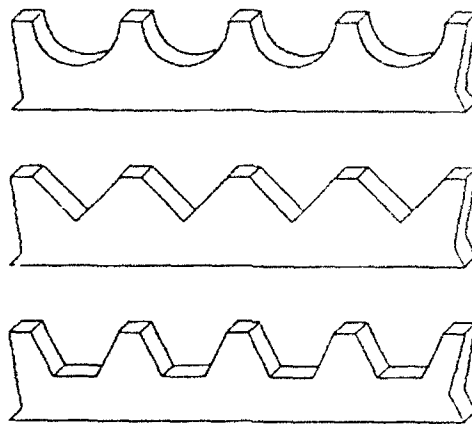


Figure 9

The dimensions of these rod holders have been specified to position the rods at 2.6 mm spacing, center-to-center. This is dictated by the rod volume loading of the composite. Each of the different groove shapes was sized to allow precise location of each rod with minimal movement within the groove. Once the rods are loaded into the trays and the holder capped for insertion, no shifting of the rods can occur. Only with such tight tolerances can the precision of the original Ultraloom mechanism be reproduced in a high speed, high volume insertion operation.

Twelve steel single row rod holders were fabricated, four of each shape. Relative effectiveness of each was evaluated and compared in the course of rodding a 101 mm x 101 mm x 6.4 mm part. Rods were loaded onto a tray, then positioned on the

tooling and inserted using a manual operation that simulates the automated procedure. By positioning and loading 35 rods at a time, these trays in themselves offer a 30-fold improvement over single rod insertion rates. Initial experiments were hampered by variations in the diameters and straightness of the PZT rods, but CPS has made significant improvements in these areas. As better quality rods become available next quarter, a more detailed sequence of mechanical handling and dispensing operations will be identified and optimized. This in turn will facilitate translating the manual operation into an automated process through modifications and additions to the Ultraloom equipment.

10" X 20" RTM MOLD

A Resin Transfer Molding (RTM) tool was designed to fabricate piezocomposite panels up to 10" x 20" x .75". The tool is shown in Figure 10. The design concept is based on the RTM tool developed for the 4" x 4" piezocomposites. The PZT rods are fixed in a base and located in the tool cavity. The top plate is bolted to the bottom plate with O-rings providing for an air tight seal. Air is evacuated from the tool with a vacuum pump and then the resin injected into the tool under pressure. After the mold cavity is completely filled with resin and all voids eliminated, the vacuum pump and resin lines are disconnected. The piezocomposite is cured at room or moderate temperature to complete the molding operation.

RESIN TRANSFER MOLD

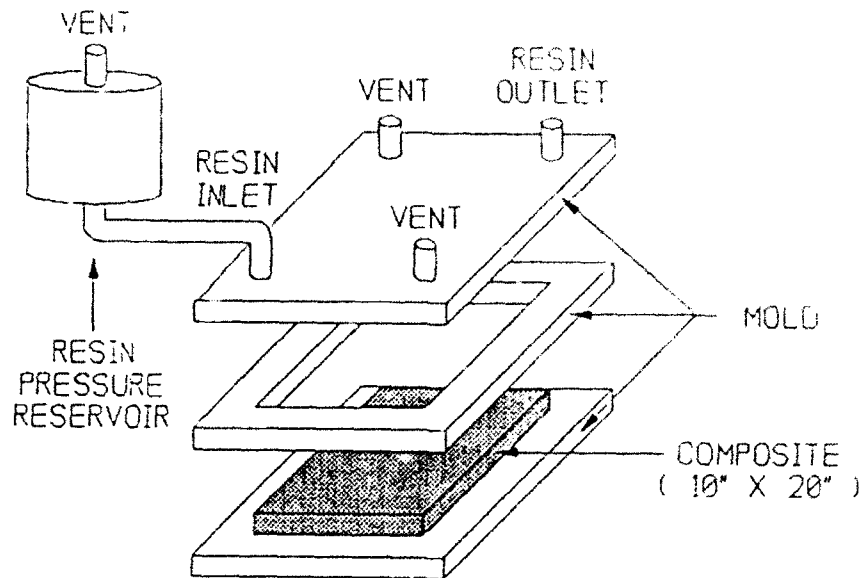


Figure 10

Several design changes were introduced in the RTM mold. The top plate is clear acrylic so that resin flow and void elimination can be studied during the resin injection operation. The acrylic plate was designed so that the center deflection will be minimal at full vacuum. The holes in the top plate are located at the center and four corners. This arrangement will permit flexibility in attaching resin inlet and vacuum lines to the tool. One system would be to inject the resin at the center and evacuate the air from the four corners. If smaller piezocomposites are desired, part of the tool cavity can be filled with an aluminum plate. The multiple holes in the top plate will still allow for resin inlet and vacuum lines. Ports that are not needed can be sealed with plugs. Another tool feature is that the cavity is formed by four rails, two side and two end rails. The rail thickness is equal to the cavity depth. This design allows changing the cavity depth by changing just the

rails and not the entire tool. Another advantage is that piezocomposite demolding is simplified through tool dismantling.

A resin transfer study has been conducted to debug the system using a simple resin system. Best results were achieved when a partial vacuum was coupled with back pressure on the resin. The pressure vessel was equipped with an acrylic top. This allowed the resin mixture to be degassed within the vessel rather than in a desiccator and eliminated a second degassing step, the transfer of the resin from the desiccator to the pressure vessel.

MATRIX RESIN DEVELOPMENT

During the previous quarter, effort was devoted to exploring those variables that contribute to near net shape molding of piezocomposites using a resin transfer process. The matrix resins used in this work consisted of HD68 (soft), HD77 (medium) and HD85J (hard) epoxy formulations. Successful small scale (e.g. 4" x 4") moldings were made from non-reinforced as well as reinforced piezocomposites having Z direction rods.

Matrix resin development has continued during this quarter with the emphasis shifting away from epoxy systems toward urethane systems containing Expancel thermoplastic microballoons. This redirection of the matrix resin effort was made by the program technical monitor during the December quarterly review meeting.

Initial urethane studies were conducted using the recommended Conathane EN-2 system. This resin has an advantage in that it has low viscosity of only 1200 cps at room temperature, from time of initial mixing. Formulations were prepared using 50 volume percent Expancel 551DE microballoons. The microballoons were dispersed in the "B" side of the

formulation in an effort to extend the pot life of the resin system. The "A" side was then added and mixed in until homogenous system was reached. The matrix was degassed for about 1 hour @ 30 mHg but still contained entrapped air and at this point was too viscous to handle.

Trials were conducted with EN-2 using Expancel 551DU unexpanded microballoons as the filler. Mixes were prepared that degassed quite readily and had low initial viscosity when an amount of microballoons, on an equal weight basis to 551DE, was incorporated. Curing of these mixes was done at 100°C which is the recommended expansion temperature for 551DU. Using this high a cure temperature apparently caused the urethane to cure before the full expansion of 551DU microballoons.

Attempts were made to modify the "A" side of EN-2 with phenol to form a blocked isocyanate which would provide an increased pot life. While some success in extending the pot life to about 2 hours was noted, it was also apparent that the quality of the cured resin was not the same as the unmodified EN-2. This approach has since been abandoned.

Samples were solicited from several vendors in an effort to obtain urethane systems with long pot lives and low viscosities. The following products were received for evaluation:

- Desmodur N3200 and Desmophen 1150 (Bayer, Inc.)
- Polathane STE-73D, Polamine 650 and Polamine 1000 (Air Products)

Mix ratios were calculated at an isocyanate index of 1.05 with small batches of unfilled resin prepared and cured at 60°C for 16 hours. Shore D hardness was measured for each formulation and the values obtained were similar to those obtained with Conathane EN-2. Viscosity and pot life were measured on two

systems that theoretically would have the longest pot life. This data is shown Table 1. Of the two systems, the one based on Desmophen 1150/Desmodur N-3200 offered the most potential for the RTM process.

Table 1
 SCREENING OF LOW VISCOSITY AND LOG POT LIFE URETHANE SYSTEMS
 Formulation, PBW

Material	1	2	3	4	5	6
Polathane STE-730	58.3	--	52.6	45.1	--	--
Desmodur N3200	--	35.9	--	--	30.8	24.8
Polamine 650	--	--	47.4	--	69.2	--
Polamine 1000	--	--	--	54.9	--	75.2
Desmophen 1150	41.7	64.1	--	--	--	--
Gardner viscosity						
@ RT	Z, +	Y	--	--	--	--
@60°C	U-V	P	--	--	--	--
Estimated pot life						
@ 60°C, hr	1-2	4-5	--	--	--	--
Cure	16 hrs @ 60°C					
Shore D hardness @ 21°C	18	28	30	22	33	26

RTM PROCESS STUDIES

Formulations of the Desmodur N3200/Desmonphen 1150 were prepared incorporating both 40 and 50 volume percent of Expancel 551DE microballoons. Mix ratios, density, hardness of cured specimens and temperature viscosity of neat and filled formulations are shown in Table 2.

Table 2

URETHANE MATRIX RESIN FORMULATIONS (PBW)

Materials	Neat	50 Volume % microballoons	40 Volume % microballoons
Desmophen 1150	64.08	61.93	62.63
Desmodur N-3200	35.92	34.71	35.10
Expancel 5510E	--	3.36	2.27
Byk A-501	0.3	0.3	0.3
Cure	16 hrs 60°C		
Properties			
Density @ RT, g/cc	1.077	0.584	0.688
Shore D hardness @ 21°C	28	22	23
Viscosity @ 23°C, cps	3400	60800	19500

Small scale (4" x 4") RTM moldings were prepared in an effort to study the flow and rate of fill properties of the 40 and 50 microballoon volume percent formulations. Mixes containing 50 volume percent microballoons were heated to 60°C prior to transfer and filled the void space of the mold quite readily. The resulting molded parts were sectioned and examined for voids. Very few voids were detected. Likewise, 40 percent filled mixes were molded at both room temperature and 60°C with similar good result. RTM processing of piezocomposites having closely spaced PZT rods were also prepared without undue difficulty.

In an effort to estimate the pot life of the filled formulations, a viscosity study was carried out. The viscosity data obtained are shown graphically in Figure 11. From the data, it is evident that at least a 3 hour pot life is available at 60°C for both 40 and 50 percent volume filled formulations. At room temperature the 40 percent filled material should have a pot life in excess of 7 hours. This data makes the Desmodur N3200/Desmophen 1150 formulation amenable to the RTM process. Wayne Reader from Vector Research is evaluating a neat resin

sample of the formulation for room temperature modulus. FMI is waiting for the results before we proceed onward.

DESMOPHEN 1150 / DESMODUR N3200 URETHANE
FILLED WITH MICROBALLOONS
POT LIFE BY VISCOSITY

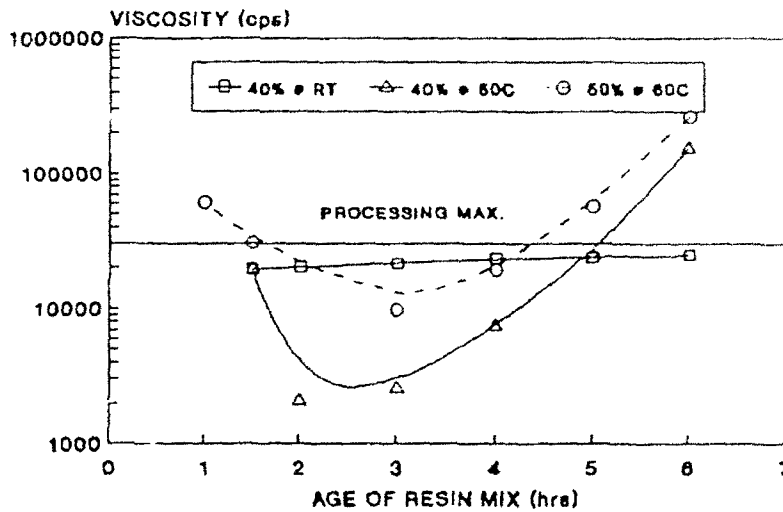


Figure 11

COMPRESSION TESTING OF FILLED URETHANE FORMULATIONS

Compression tests were performed in accordance with ASTM test method D575-91. Both 40 and 50 volume percent specimens were prepared, cured for 16 hours at 60°C and tested. The data obtained is graphically presented in Figure 12. The data shows that 40% loading by volume produces a stiffer material than a 50% volume loading of the Expancel microballoons.

DESMOPHEN 1150 / DESMODUR N3200 URETHANE
FILLED WITH MICROBALLOONS
COMPRESSION TEST AT ROOM TEMPERATURE

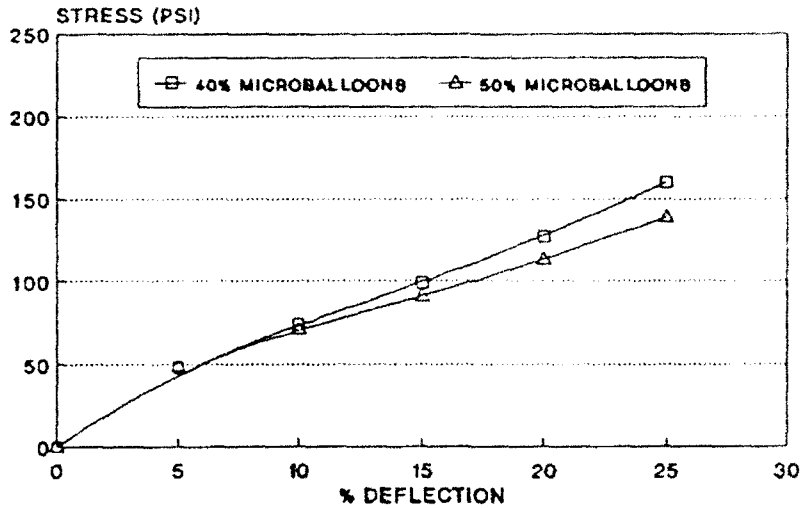


Figure 12

WATERPROOF COATING OF PIEZOCOMPOSITES

Initial work on waterproof coatings for 3.5 inch disc shaped piezocomposites involved dip coating with Conathane EN-2 and curing at room temperature for 16 hours plus 3 hours at 60°C. The composites were then tested on an HP 4274A multifrequency LCR meter for capacitance, dissipation factor, resistance and impedance. These tests were run at room temperature both dry and after immersion in seawater. The testing in seawater revealed that even with multiple dip coats of EN-2 the capacitance increased significantly, while both resistance and impedance decreased. Assuming that EN-2 had poor moisture transmission properties alternate coating materials were tried.

Among the materials tested was Saran which is known to have excellent barrier properties. The Saran was applied to the composite by wrapping and then heat shrinking into place prior to overcoating with EN-2. This approach did not solve the problem. A lacquer containing a vinylidene chloride-acrylonitrile

copolymer was developed and used to bond multiple layer of Saran to the composite. These specimens were then overcoated with EN-2 as the final sealant coat. This improved the electrical properties of composites immersed in seawater but they were still not considered acceptable. It was then assumed that the coatings were preventing penetration of seawater and it must be the influence of the seawater as a conductor that caused changes in capacitance and resistance.

Seawater acts as a partial conductor and simulates a common conductive plate being brought into contact with the waterproof coating of the composite. The coating then acts as a dielectric between two plates (e.g. electrode of the composite and the seawater) and thus creates a capacitance. Since the seawater is common to all surfaces of the immersed composite it acts to "connect" the "capacitors" that are formed across the coating, thereby adding two series capacitors across the electrodes of the composite.

For example, a composite coated with EN-2 at a thickness of 0.008 inch has a measured capacitance of 316.2 pF in air and 934.2 pF when immersed in seawater. The electrode area of the composite is 9.62 m² and the dielectric constant of EN-2 is given as 4.69 @ 1KHz. The capacitance across the EN-2 coating is,

$$C = \frac{0.225KA}{S}$$

where: c = capacitance in pF
K = dielectric constant
A = area of one panel (in²)
S = spacing between panels (in)

and: $C = \frac{0.225 \times 4.96 \times 9.62}{0.008} = 1268 \mu F$

This capacitance represents the value of one of two capacitors in series, added across the disc. Two series capacitors, each with a capacitance of 1268 pF combine to form a capacitance of 634 pF as shown by the following equation:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2}$$

If this value is added to 316.2 pF, the measured capacitance in air, the total capacitance is 950.2 pF. The actual measured capacitance in seawater was 934.2 pF. To reduce this capacitance effect a thicker coating or a thin coating with a lower dielectric constant would have to be used.

Thickness of EN-2 waterproof coatings on deliverable 3.5 inch diameter piezocomposites was increased to an average of 0.080 inches. The method of coating application was changed from multilayer dip and brush coating to casting a single layer in place in one operation. Typical test results obtained on the piezocomposites coated at this thickness are as follows:

PN 16927 LCR Testing @ 1KHz

<u>Test Condition</u>	<u>Capacitance</u>	<u>Dissipation Factor</u>	<u>Resistance</u>	<u>Impedance</u>
Dry	1.687 nF	0.032	$\infty K\Omega$	94.3 K Ω
After 20 hrs in seawater	1.730 nF	0.034	$\infty K\Omega$	97.6 K Ω

All of the disc shaped piezocomposite deliverables were treated in this manner and shipped to Robert Gallant of Vector Research Center.

POLING

A continuous corona discharge poling system, shown schematically in Figure 13, has been designed, fabricated and

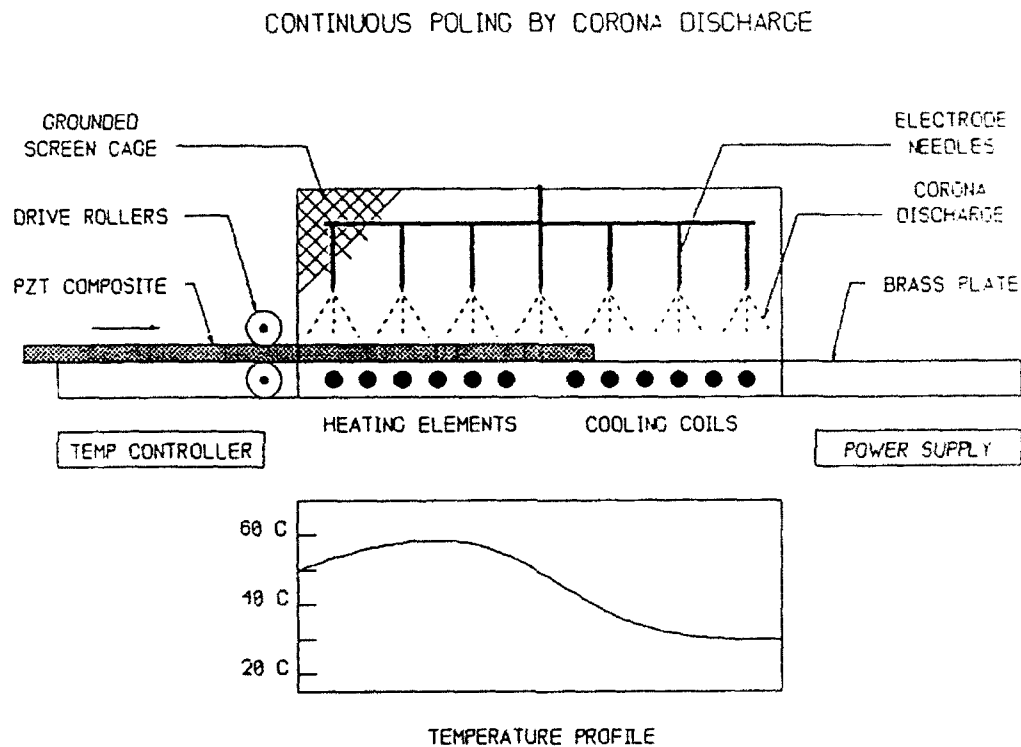


Figure 13

assembled. The corona discharge chamber has been designed to accommodate 10" x 20" panels. Initial temperature profile tests were run as shown in Figure 14.

CORONA POLING CHAMBER
BASE PLATE TEMP PROFILE

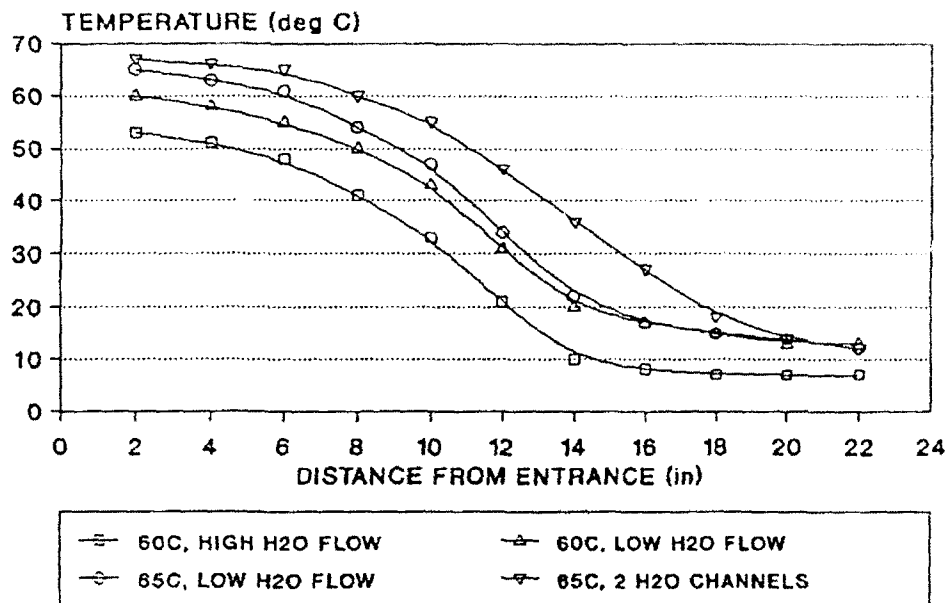


Figure 14

A roller drive system has been designed, built and installed at the entrance end of the poling chamber to precisely control the feed rate of the piezocomposite panels as they are transported through the chamber. This design is based on characterization tests run on a batch type corona discharge system currently used at FMI. Electrode configuration, temperature, voltage and time were some of the parameters optimized and incorporated into this new design. The system design allows a piezocomposite panel to be fed through the poling chamber at an optimized speed rate, heated to 60°C and subjected to a 25 KV electric field. This process poles the PZT rods within the panel. The panel will then pass through a cooled zone to reduce the temperature while maintaining the electric field thus assuring that depoling will not occur during cool down. The d_{33} of the rods within the panel will be measured with a Berlincourt meter to ensure sufficient poling has occurred. Tests will be run during the next few weeks to optimize the poling parameters and to qualify the system for poling panels.