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EVALUATION OF THE PROPERTIES OF 1-3 PIEZOCOMPOSITES OF A NEW LEAD TITANATE IN EPOXY RESINS

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By using a new calcium-modified lead titanate ceramic with a near-zero planar coupling coefficient, a series of 1-3 piezocomposite samples was fabricated with a dice-and-fill technique. The ceramic rods were approximately 0.10 mm in size, and the percent of ceramic loading varied from 10 to 30%. Two epoxy resins with different glass transition temperatures and moduli were used. The dielectric properties and the piezoelectric d_{31} and g_{31} coefficients of the composites were measured as a function of pressure and temperature and were found to exhibit little variation, but 10–25% lower than theoretical predictions. A prototype hydrophone made from one of the piezocomposite samples was tested to show a constant free-field voltage sensitivity of -201 dB re V/ μ Pa from 100 Hz to 6 kHz.

INTRODUCTION

The development of future submarines is expected to emphasize a greater speed and depth capability, in addition to an increased acoustic aperture for their sonars. One may therefore envision that these new sonar arrays will become very large in size and be totally under the influence of flow noise. A potential solution to abate this noise problem is to use large-area hydrophones in such arrays. This requirement for hull-mounted hydrophone arrays calls for piezoelectric materials that exhibit high sensitivities in a hydrostatic mode far exceeding what the conventional PZT ceramics can offer. Piezoelectric PVDF polymers were investigated earlier for this application,¹ but were found to be limited by the temperature dependence of their piezoelectric properties and the inherently low dielectric constant of this polymer.² New piezoelectric composite materials with different connectivity patterns³ were therefore considered as potential alternatives to PVDF in the design of future large-area hydrophones for hydrostatic-mode sensing.⁴

Among many types of piezocomposites that have been investigated, the 1-3 type, consisting of thin parallel rods of ceramic imbedded in a polymeric matrix, was successfully developed for use in pulse-echo ultrasonic transducer arrays.⁵ This success in the medical field has led to the interest in considering the 1-3 piezocomposites for hydrophone applications. In this paper, the dielectric and the piezoelectric properties of a series of 1-3 composite were investigated. These samples were made by using a new calcium-modified lead titanate ceramic.⁶ This material, having a negligible d_{31} coefficient and near-zero planar coupling coefficient, is itself very sensitive in hydrostatic mode. Furthermore, the permittivity of this ceramic is much lower than that of conventional PZT ceramics, resulting in a higher pi-



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piezoelectric voltage coefficient for increased hydrophone sensitivity.⁷ Composite samples were fabricated by using this lead titanate and two different types of epoxy resins. Their dielectric constant and dissipation, and their piezoelectric d_h and g_h coefficients were evaluated as a function of pressure and temperature. A prototype hydrophone was also assembled by using one of the composite sample for evaluating its acoustic response in water. These experimental results are presented and discussed here.

EXPERIMENTAL

The 1-3 piezocomposite samples investigated were fabricated by using a calcium-modified lead titanate ceramic, designated as the C-24 type by Toshiba. Two epoxy polymers of different stiffnesses were used as the matrix material in order to assess the effect of polymer phase on the properties of the composite. One epoxy resin with the trade name of Stycast was stiffer than the second one called Spurr, when both were cured at 70°C overnight. Composite samples were made by using the dice-and-fill technique⁸ to form 40-mm diameter disks that were 1 mm thick. Square ceramic rods were 0.10 mm in size, and ceramic volume fraction varied from 10 to 30%. Figure 1 illustrates this fabrication technique. Deep grooves were cut into a solid ceramic disk that was previously poled. The epoxy resin was then back filled into the grooves, followed by heat cure and slow cool to room temperature before grinding off the remaining ceramic base to form the required experimental samples for evaluation. Metallized chromium-gold electrodes were added to either side of the disk sample, but no additional poling was necessary since the starting ceramic disk was already poled.

The hydrostatic d_h and g_h coefficients of each sample were determined from measurements in an acoustic coupler. Direct measurements of the dielectric constant and voltage sensitivity were obtained by using an acoustic reciprocity technique⁹ at 1 kHz. This measurement frequency was well below any potential resonance of the composite disks, so that a hydrostatic response of the sample was ensured. The experiments covered the pressure range from ambient to 20 MPa, and a temperature range of 0 to 50°C. The d_{33} coefficient of each composite sample was also measured at 100 Hz by using a Berlincourt meter. At least twenty measurements were made over the surface of the sample in order to obtain an acceptable average d_{33} value for the composite.

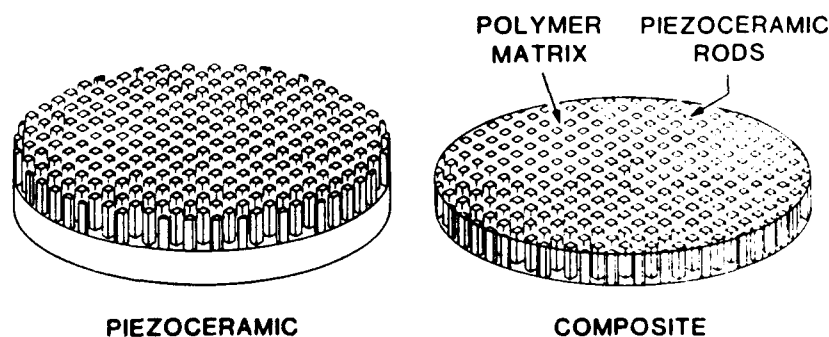


FIGURE 1 A schematic for the dice-and-fill technique of sample fabrication.

A 1-3 composite sample containing 0.10-mm square rods spaced at a distance of 0.14 mm in Stycast epoxy was used for hydrophone fabrication. It had a density of 2.5, giving an estimated ceramic volume fraction of 17%. The composite sample was bonded to a 5-cm thick stainless steel base plate by using Shell Epon 828 epoxy. The assembly was then water-proofed by encapsulation with a medium hardness Eccobond resin. The prototype hydrophone was tested at the Naval Research Laboratory's Lake Facility at a water depth of 4 m over the frequency range of 100 Hz to 100 kHz.

RESULTS AND DISCUSSION

Figure 2 shows the measured d_{33} and d_h coefficients for the composite samples of different lead titanate (PT) volume fractions. The data points represent the experimental result obtained at room temperature and ambient pressure. As indicated earlier, the d_h coefficients were measured at 1 kHz, and d_{33} at 100 Hz. Ceramic volume fraction was calculated from the measured density of each sample, using a simple mixture law. The data points at the extreme right of Figure 2 are the measured d_{33} and d_h values of a solid lead titanate ceramic disk. In general, it is noted that the d coefficients increase rapidly with increasing ceramic loading in the composites for ceramic volume fractions in the range of 10 to 30%. The two curves in Figure 2 represent the result from a theoretical calculation¹⁰ based on the simple parallel-series connectivity model of Haun and Newnham¹¹ for PT/Stycast samples. The analysis predicted a trend similar to the experimental observation, but the calculated values of the d coefficients were approximately 10 to 25% too large.

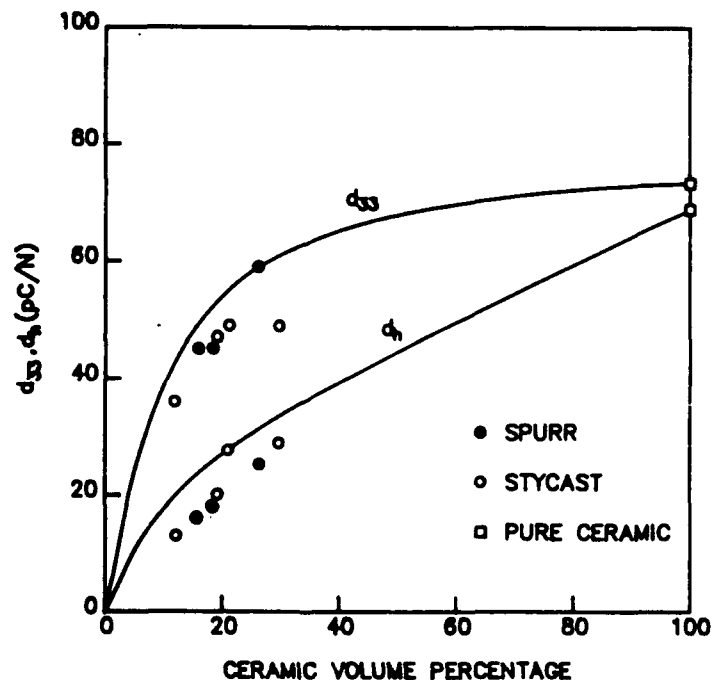


FIGURE 2 Piezoelectric d_{33} and d_h coefficients of 1-3 composites as a function of ceramic volume fraction.

Some of this discrepancy may be attributed to the uncertainty in the values for the material parameters used in the calculation.

The pressure dependence of the piezoelectric d_h and g_h coefficients for composite samples with either Stycast or Spurr epoxy is shown in Figure 3. The samples contained approximately 20% of lead titanate ceramic. This result suggests that these composites are remarkably stable with pressure. At the maximum test pressure of 20 MPa, the degradation of either the d_h or the g_h coefficient for the 1-3 composites is less than 0.2 dB.

In Figure 4, the measured d_h coefficients of three composite samples are shown as a function of temperature. The d_h properties of a solid lead titanate and a PZT5 sample⁷ are also included for comparison. As shown in Figure 2, the d_h property of the PT/epoxy 1-3 composites increases monotonically with increasing ceramic volume fraction. This relationship is different from that found earlier in the 1-3 composites of PZT5/polymer,¹² which exhibited a maximum in the composite d_h coefficients that exceeded the value for the pure PZT5 ceramic. The peculiar behavior of the PT/epoxy composites was investigated earlier,¹⁰ and found to be caused by the combined effect of the Poisson stress in the polymer and the high d_{33} coefficient of lead titanate. Figure 4 shows that the composite d_h coefficients are reduced from that of lead titanate, but their temperature dependence is similar to that of the pure ceramic. Over the temperature range tested, the material was very stable. With the softer Spurr epoxy, there was a further reduction in d_h from that of the composite containing the stiffer Stycast polymer. However, even in that case, the d_h property of the PT/epoxy 1-3 composite is still comparable to that of a solid PZT5 ceramic.

Although the d_h properties of the composite samples are stable with temperature, the temperature dependence of their g_h coefficients is slightly more pronounced. This result is shown in Figure 5. As the temperature increases, the g_h coefficients decrease gradually. The g_h values of the composites at 50°C are approximately one dB less than those at 0°C. When compared with the temperature dependence of

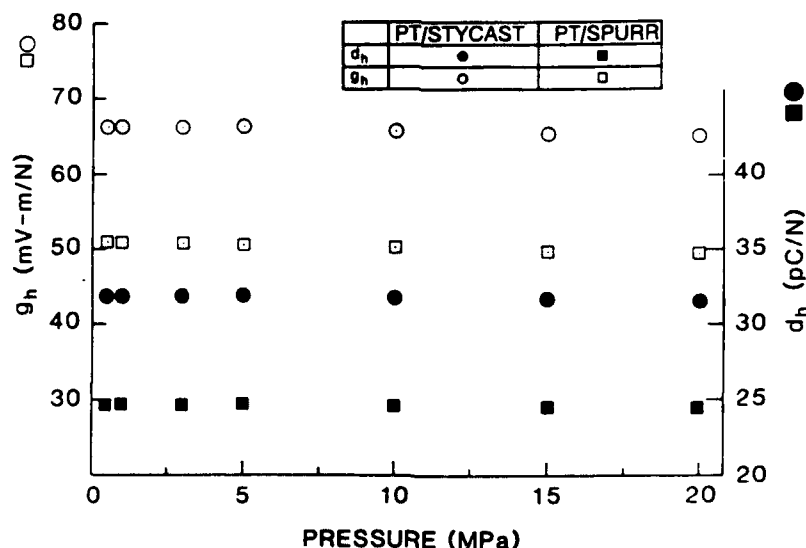


FIGURE 3 Pressure dependence of the d_h and g_h coefficients of 1-3 composites.

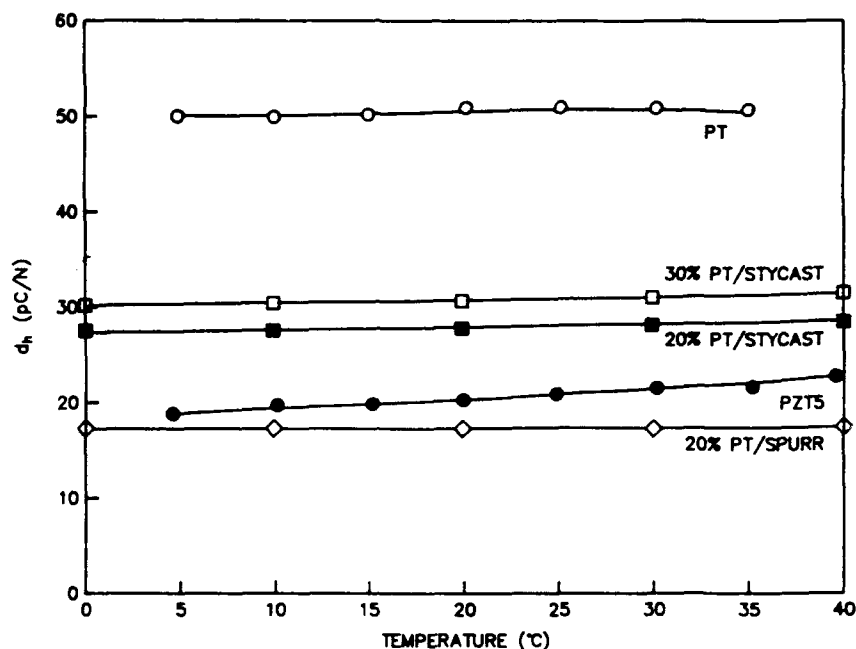


FIGURE 4 Temperature dependence of the d_h coefficients of 1-3 composites in comparison with those of solid lead titanate (PT) and PZT5 ceramics.

the g_h for solid lead titanate, the slopes in this plot are approximately the same. One may therefore conclude that the reduction in g_h is mainly due to the increase in the permittivity ϵ of the sample with temperature. While the d_h values are stable with temperature, a slight increase in ϵ leads to the gradual reduction of g_h with increasing temperature because of the relationship $g = (d/\epsilon)$.

It is also noted from Figure 5 that the g_h coefficients increase with an increase in the ceramic volume fraction from 20 to 30%. This result is different from the prediction of an early calculation,¹⁰ which suggested that the g_h coefficients of the PT/epoxy 1-3 composite would show a maximum value at about 8% ceramic loading. This additional discrepancy indicates that there is a need to improve the predictive capability of the simple parallel-series connectivity model. Nevertheless, the g_h coefficients are seen to have been increased by a factor of 2 or greater in the composite samples, when compared with that of the pure lead titanate. For conventional PZT5 ceramics, the g_h values are typically in the range of 2 to 3 mV-m/N, as is also shown in Figure 5. Thus, the improvement obtained in the PT/epoxy 1-3 composites is even more impressive in comparison. Since the hydrostatic sensitivity of a hydrophone is equal to the product of g_h and the thickness of the sensing element, the 1-3 composite provides a viable means to the design of sensitive new transducers for passive detection.

Experimental results presented in both Figures 4 and 5 show that the use of a stiffer epoxy leads to higher d_h and g_h values in the 1-3 composites. Table I also summarizes the measured data for a number of composite samples containing different epoxies. The selection of the Stycast and Spurr epoxies was based on their elastic properties for resins cured at 70°C. It was therefore considered instructive to examine if that was the optimum cure condition for either resin. Pure polymer samples were prepared and their dynamic mechanical properties characterized by

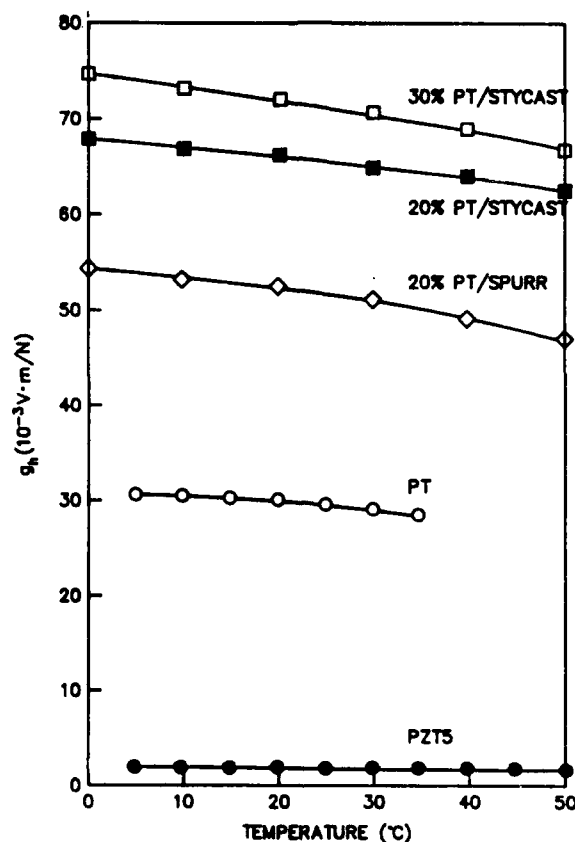


FIGURE 5 Temperature dependence of the g_h coefficients of 1-3 coefficients in comparison with those of solid lead titanate (PT) and PZT5 ceramics.

using a Polymer Laboratory's Dynamic Mechanical and Thermal Analyzer (DMTA). Dynamic Young's modulus and loss tangent were measured at 1 Hz as a function of temperature. The sample was heated at a heating rate of 4°C per minute over the temperature range of 0 to 150°C for the experiment. When cured at 70°C overnight as one would have cured a polymer-filled composite sample, the result of a DMTA scan for the Stycast sample showed a glass transition temperature of about 62°C, as indicated by the peak position of the loss tangent curve labelled "1" for Run 1 in Figure 6. This low glass transition temperature indicated that the polymer was not fully cured. When the sample was scanned in the DMTA for a second run, the heating cycle in the instrument alone caused the glass transition temperature to increase to about 82°C. At the same time, the peak value of mechanical loss tangent has decreased from 1.04 to 0.62. These are clear indications that additional cure has taken place in the polymer. This glass transition temperature continued to increase until about 95°C after the fourth run, as shown in Figure 6. During these repeated scans, the dynamic Young's modulus of the Stycast polymer at the temperature corresponding to the loss peak location increased from 63.1 to 158.5 MPa. On the other hand, the 70°C overnight cure was sufficient for the Spurr polymer, because such a cured sample gave a glass transition temperature of 70°C, which remained unchanged in repeated DMTA scans. This fully cured Spurr epoxy sample had a dynamic Young's modulus of only 11.2 MPa at 70°C.

TABLE I
Dielectric and piezoelectric properties of 1-3 lead titanate composites at 1 kHz

Epoxy Type	Ceramic Percentage	ϵ'' ^T	D [*] (%)	d_{33}^0 (pC/N)	d_h (pC/N)	ϵ_h (mV-m/N)
Stycast	29.4	54	1.1	49	31	66
"	20.7	43	1.7	44	23	72
"	19.0	40	1.1	47	20	56
"	12.1	27	1.4	36	13	50
Spurr	26.4	53	1.6	59	25	52
"	18.2	34	1.4	50	18	52
"	15.6	31	1.2	44	16	59

* Dielectric dissipation.

0 Measured at 100 Hz.

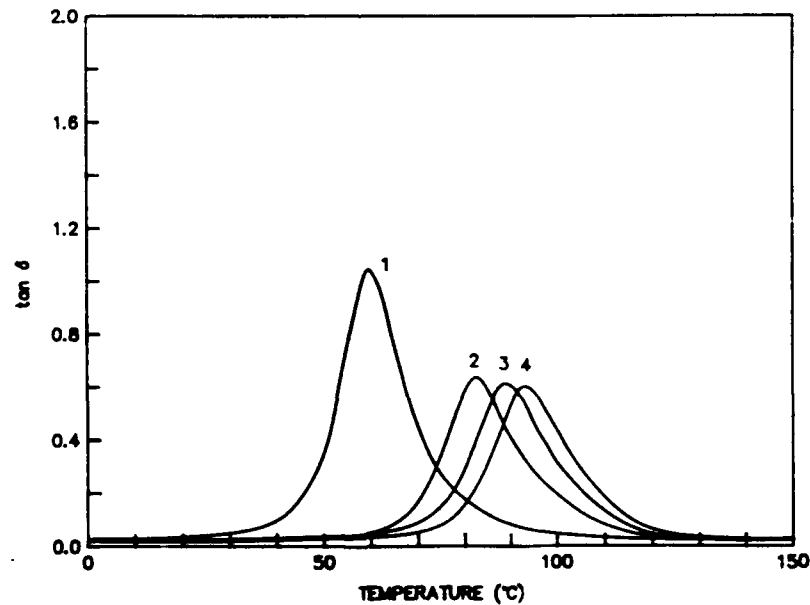


FIGURE 6 Dynamic mechanical loss tangent of the Stycast polymer measured at 1 Hz as a function of temperature under repeated runs at a heating rate of 4°C/min.

The result of this cure study suggests that the stiffer Stycast epoxy is a higher temperature resin, and an improved cure cycle for the PT/Stycast 1-3 composite samples may further stiffen the polymer phase. As a result, this modification may possibly further improve the composite piezoelectric properties, according to the

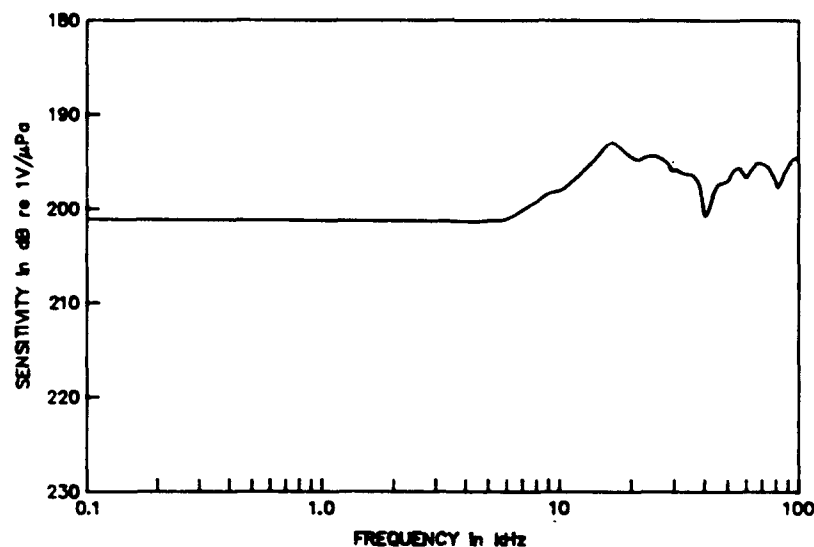


FIGURE 7 Free-field voltage sensitivity of a 1-3 composite hydrophone.

data given in Figures 4 and 5. Further studies on the design of the polymer phase for optimized 1-3 composite performance are warranted.

A prototype hydrophone was fabricated as described above by using one of the PT/Stycast 1-3 composite samples, which had a ceramic volume fraction of approximately 17%. The hydrophone was calibrated in 29°C water for its free-field voltage sensitivity over the frequency range of 100 Hz to 100 kHz at a water depth of 4 m. The calibration result is shown in Figure 7. At the end of a 0.3-m cable, a constant sensitivity of about -201 dB re 1 V/ μ Pa was measured from 100 Hz to 6 kHz, a response ideal for broadband acoustic detection. At higher frequencies, different modes of the motion of the base plate began to interfere with the acoustic response of the sensor, but on the average a 4 to 5 dB increase in sensitivity seemed to be present. To take advantage of his high frequency behavior, a different hydrophone design will be required for the 1-3 piezocomposites.

CONCLUSION

New 1-3 piezocomposites of lead titanate and epoxy were experimentally investigated to show their stable d_h and g_h properties with pressure up to 20 MPa. While the d_h coefficient was found to be stable with temperature, the g_h coefficient decreased slightly with temperature, which was believed to be related to the temperature behavior of the permittivity of the ceramic. A comparison of the experimental result with calculations from a simple parallel-series connectivity model indicated the need to improve the predictive capability for the performance of 1-3 composites. The role of the polymer phase was examined to show the benefit of using a stiff matrix. The result from a preliminary hydroacoustic evaluation suggests that the 1-3 piezocomposites represent a class of promising new materials for underwater acoustic applications.

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