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PIEZOELECTRIC PROPERTIES OF 1-3 COMPOSITES  
OF A CALCIUM-MODIFIED LEAD TITANATE IN EPOXY RESINS

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A series of 1-3 piezocomposite samples were fabricated by using lead titanate ceramic with a dice-and-fill technique. The ceramic rods were approximately 0.10 mm in size, and the ceramic volume fraction varied from 10 to 30%. Two different epoxy resins were used. The piezoelectric  $d_h$  and  $g_h$  coefficients of the composites were found to be stable with pressure from ambient to 20 MPa. The temperature dependence of the composite properties was similar to that of the solid ceramic. The free-field voltage sensitivity of a prototype hydrophone made from the composite was calibrated and shown to be constant up to 6 kHz.

## INTRODUCTION

The development of future hull-mounted hydrophone arrays requires piezoelectric materials that exhibit high sensitivities in a hydrostatic mode far exceeding what the conventional PZT ceramics can offer. New piezoelectric composite materials with different connectivity patterns [1] were considered as potential candidates for hydrostatic-mode sensing [2]. Among different types of piezocomposites, the 1-3 type, consisting of thin parallel rods of ceramic imbedded in a polymer, was successfully developed for use in pulse-echo ultrasonic transducer arrays [3]. This success has led to an interest in considering this composite for hydrophone applications. In this paper, the piezoelectric properties of a series of 1-3 composites were investigated. Samples were fabricated by using lead titanate and two different types of epoxy resins. Their piezoelectric  $d_h$  and  $g_h$  coefficients were evaluated as a function of pressure and temperature, and a prototype

hydrophone was also assembled for evaluating the acoustic response of the composite in water. These experimental results are presented and discussed here.

## EXPERIMENTAL

The ceramic used for composite fabrication was a calcium-modified lead titanate, designated as the C-24 type by Toshiba. Two epoxy polymers were used to assess the effect of polymer phase on the properties of the composite. The Stycast epoxy 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 technique [4] to form 40-mm diameter and 1-mm thick disks. Square ceramic rods were 0.10 mm in size, and ceramic volume fraction varied from 10 to 30%.

The hydrostatic  $d_h$  and  $g_h$  coefficients of each sample were determined from measurements in an acoustic coupler by using an acoustic reciprocity technique [5] at 1 kHz. This measurement frequency was selected to ensure a true hydrostatic response from the sample. The experiments covered the pressure range from ambient to 20 MPa and a temperature range of 0 - 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.

A 1-3 composite sample containing approximately 17% ceramic rods in Stycast epoxy was used for hydrophone fabrication. The composite sample was bonded to a 5-cm thick stainless-steel base

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plate, and the assembly was then water-proofed by encapsulation with an Eccobond resin. The prototype hydrophone was tested at a water depth of 4 m over the frequency range of 100 Hz through 100 kHz.

## RESULTS AND DISCUSSION

Figure 1 shows the  $d_{33}$  and  $d_h$  coefficients for the composites as a function of lead titanate (PT) volume fraction. The data represent the experimental result obtained at room temperature and ambient pressure. Ceramic volume fraction was calculated from density measurement. The data points at the extreme right are those measured for a solid lead titanate ceramic disk. The two curves in Fig. 1 represent the result from a theoretical calculation [6] based on the simple parallel-series connectivity model of Haun and Newnham [7]. The analysis predicted a trend similar to the experimental observation, but the calculated values were approximately 10 to 20% too large.

The pressure dependence of the piezoelectric  $d_h$  and  $g_h$  coefficients for composite samples is shown in Fig. 2. The samples contained approximately 20% of lead titanate ceramic. This result suggests that these composites are remarkably stable with pressure. The property degradation for the 1-3 composites at 20 MPa is less than 0.2 dB.

In Fig. 3, 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 sample [8] are also included for comparison. The composite  $d_h$  coefficients are reduced from that of lead titanate, but their temperature dependence is similar to that of the pure ceramic. The material is very stable over the temperature range tested. With the softer Spurr epoxy, there is a further reduction in  $d_h$ . But, the  $d_h$  property of this composite is still comparable to that of a solid PZT5 ceramic.

Figure 4 shows the temperature dependence of the  $g_h$  coefficients of the composites. As the temperature increases, the  $g_h$  coefficients decrease gradually. When compared with the property of solid lead titanate, the slopes in this plot are approximately the same. It is believed that the

reduction in  $g_h$  is related to the increase in the permittivity  $\epsilon_h$  of the sample with temperature through the relationship  $g = (d/\epsilon)$ .

It is also noted from Fig. 4 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 [6], 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 discrepancy suggests a need to improve the predictive capability of the simple parallel-series connectivity model. When compared with the pure lead titanate, the  $g_h$  coefficients are seen to have been increased by a factor of 2 or greater in the composite samples. For conventional PZT5 ceramics, the  $g_h$  values are typically in the range of 2-3 mV-m/N, as is also shown in Fig. 4. 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.

A prototype hydrophone was fabricated as described above by using one of the PT/Stycast 1-3 composite samples. The hydrophone was calibrated in water for its free-field voltage sensitivity over the frequency range of 100 Hz through 100 kHz. The calibration result is shown in Fig. 5. At the end of a 0.3-m cable, a constant sensitivity of about -201 dB re 1 V/ $\mu$ 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 4-5 dB increase in sensitivity seemed to be present. To take advantage of this 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. 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, together with the advantages of low density and high  $g_h$  values they offer, suggest that the 1-3 piezocomposites represent a class of promising new materials for underwater acoustic applications.

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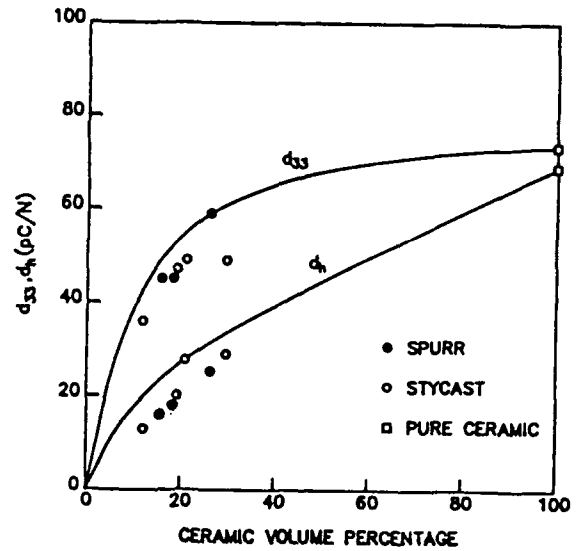


Fig. 1: Piezoelectric  $d_{33}$  and  $d_h$  coefficients of 1-3 composites as a function of ceramic volume fraction.

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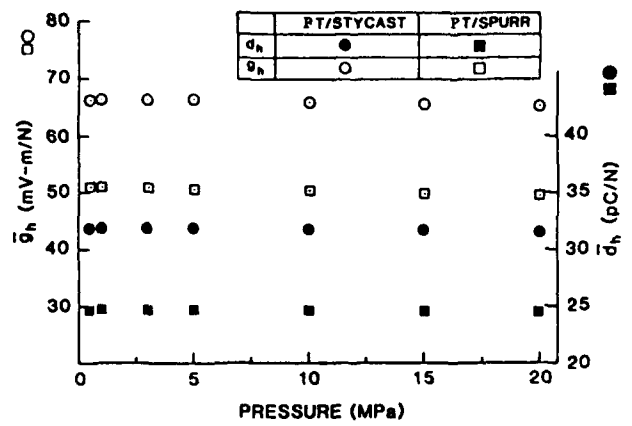


Fig. 2: Pressure dependence of the  $d_h$  and  $g_h$  coefficients of 1-3 composites.

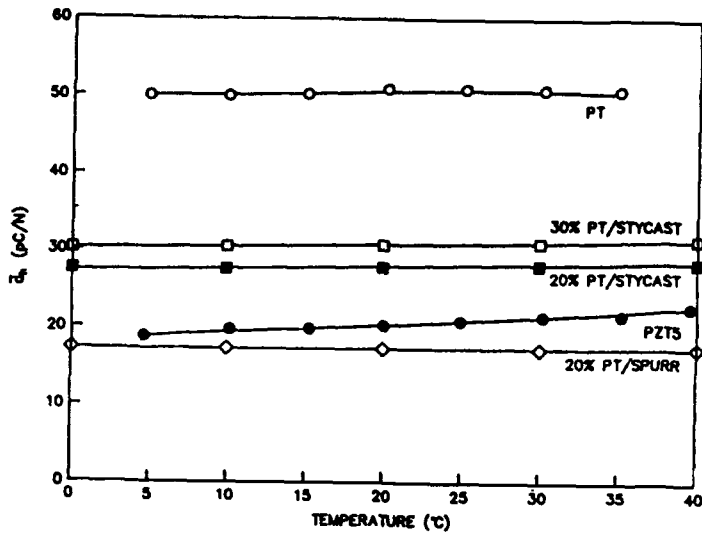


Fig. 3: Temperature dependence of the  $d_h$  coefficients of 1-3 composites.

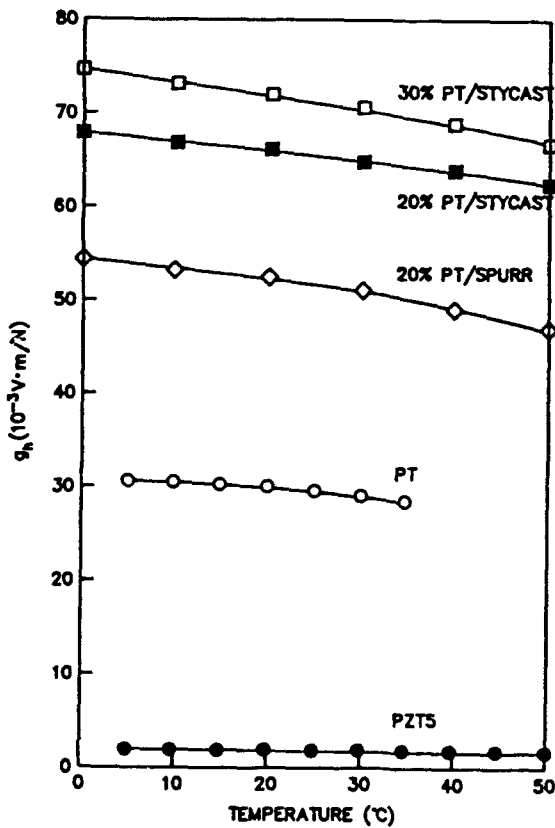


Fig. 4: Temperature dependence of the  $g_h$  coefficients of 1-3 composites.

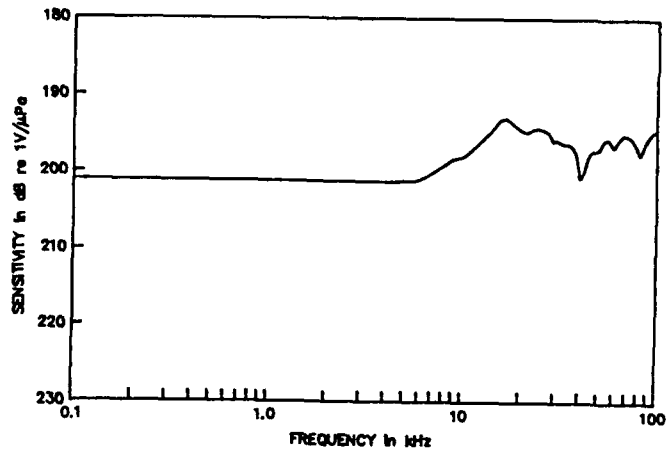


Fig. 5: Free-field voltage sensitivity of a 1-3 composite hydrophone.