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## MODIFIED-LEAD-TITANATE/POLYMER COMPOSITES FOR HYDROPHONE APPLICATIONS

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Composite piezoelectrics made from Calcium-modified lead titanate rods embedded in a polymer matrix have been evaluated for hydrophone applications. These composites behave quite differently from the conventional 1-3 composites made with lead zirconate titanate ceramics. Specifically, in the modified lead-titanate case the magnitude of the  $d_{31}$  coefficient is enhanced in the composite structure, and consequently the hydrostatic  $d_h$  coefficient is suppressed. Nevertheless, these composites exhibit a large  $g_h$  coefficient and a remarkable pressure stability. An analysis shows that a substantial contribution to the composite's  $d_{31}$  coefficient arises from internal stresses which develop along the ceramic rods and produce a piezoelectric charge through the  $d_{33}$  coefficient of the ceramic. This effect is particularly pronounced in the composite structure of the modified lead-titanate ceramic since the ratio  $d_{33}/d_{31}$  in this ceramic is exceptionally large.

### INTRODUCTION

Designs of advanced sonar transducers call for operation in a hydrostatic mode, and require a flexible and low-density piezoelectric material with large hydrostatic coefficients,  $d_h$  and  $g_h$ . Recent developments in piezoelectric composites of different connectivity patterns have demonstrated that this new class of materials is promising in meeting the new requirement.<sup>1,2</sup> Previous efforts have been focused on "1-3" type PZT/polymer composites in which PZT rods are aligned in the poling direction and held together by a polymer matrix.<sup>3,4</sup> In this composite structure, the negative contribution of the  $d_{31}$  coefficient to the  $d_h$  coefficient is suppressed, while the positive contribution of the  $d_{33}$  coefficient remains substantially unchanged. As a result, the hydrostatic coefficient,  $d_h = d_{33} + 2d_{31}$ , increases. The hydrostatic voltage sensitivity,  $g_h = d_h / \epsilon_{33}^T$ , increases even more because of the reduction in  $\epsilon_{33}^T$  due to the dilution of the high permittivity of the piezoceramic by the low permittivity of the polymer phase. Further reduction in the  $d_{31}$  coefficient, resulting in a dramatic enhancement in the hydrostatic coefficients, has been achieved in these composites by foaming the polymer phase and bracing it with fibers in the lateral direction.<sup>5,6</sup> However this technology is complex and introduces unwanted pressure dependence into the hydrostatic sensitivity.

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The new modified lead titanate ceramics have negligible  $d_{31}$  coefficient and low permittivity.<sup>7,8</sup> This work assesses whether composites made from these ceramics possess advantages over the PZT composites. Samples of 1-3 Calcium-modified-lead-titanate/polymer composites with different spatial scales were fabricated and characterized as a function of pressure. These measurements reveal properties of the lead-titanate composites quite different from those of the conventional PZT/polymer composites. In this paper, we present the experimental data and an analysis based on the parallel-series connectivity model of Haun and Newnham.<sup>9</sup>

## EXPERIMENTS

The 1-3 composites reported in this paper were made from a Calcium modified lead titanate ceramic (Toshiba C-24) and either of two polymers: a moderately stiff (Spurr) and a stiffer one (Stycast). Figure 1 illustrates the composite structure and the fabrication technique. An array of square rods was formed by cutting grooves into a solid block of the piezoceramic. Casting a polymer into the grooves produced the desired composite structure. Using this dice-and-fill technique,<sup>10</sup> square plates (19x19x1 mm) of 1-3 composites were made with a rod size of 0.1 mm, and ceramic volume percentages ranging from 10% to 35%.

Measurements of the hydrostatic  $d_h$  and  $g_h$  coefficients, as a function of pressure, were performed in an acoustic coupler using the reciprocity technique.<sup>11</sup> The  $d_{33}$  coefficient was measured at a frequency of 100 Hz using a Berlincourt meter; twenty measurements of  $d_{33}$  at different locations across the composite plate were averaged to yield the  $\bar{d}_{33}$  of the composite. Capacitance measurements at 1 kHz provided the dielectric constant  $\epsilon_{33}^T$ . For some samples, direct measurements of  $k_{31}$  and  $d_{31}$  were made using narrow composite strips cut from the composite plates; these parameters were determined in the vicinity of length expander mode resonance (about 50 kHz) using the impedance circle technique.

Table I shows the properties of our composites along with those of the solid ceramic. These measurements were performed on a poled ceramic and poled composite samples with a lateral spatial scale of 0.1 mm in both the ceramic and polymer phases. The data of Table I reveal peculiar phenomena, namely, in the composite structure the  $d_{31}$  and  $k_{31}$  coefficients are enhanced, and the hydrostatic  $d_h$  coefficient is suppressed compared to the values in the ceramic. Moreover, these phenomena are more pronounced in the composite structure with the softer polymer matrix. This is in sharp contrast to the behavior of the PZT rod composites. With PZT, the  $d_{31}$  and  $k_{31}$  are suppressed and the  $d_h$  coefficient is enhanced in the composite structure. This unusual behavior of the modified lead titanate composites is a direct result of the anomalous piezoelectric anisotropy (large  $d_{33}/d_{31}$ ) of the ceramic.

Although the  $d_h$  coefficient of these composites is less than that of the solid ceramic, the composite offers a larger  $g_h$  coefficient and comparable  $d_h g_h$  product. In addition, these composites exhibit remarkable pressure stability. Figure 2 shows that the degradation in  $d_h$  and  $\bar{g}_h$  is less than 0.2 dB at pressures ranging up to 20 MPa.

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## ANALYSIS

The behavior of the lead-titanate/polymer composites can be interpreted on the basis of the parallel-series connectivity model of Haun and Newnham.<sup>9</sup> According to this model, the  $\bar{d}_{31}$  coefficient of a 1-3 composite has contributions from both the  $d_{31}$  and  $d_{33}$  coefficients of the ceramic phase, namely,

$$\bar{d}_{31} = \alpha d_{31} + \beta d_{33}, \quad (1)$$

where  $\alpha$  and  $\beta$  are functions of the elastic compliances and volume fractions of the constituent phases. For 1-3 composites with square rods,  $\alpha$  and  $\beta$  are given by,

$$\alpha = \nu / \{1 + (\nu - \sqrt{\nu})(1 - s_{11}^E / s_{11})\}$$

$$\beta = \nu(1-\nu)(s_{13} - s_{13}^E) / \{(1-\nu)s_{33}^E + \nu s_{33}\},$$

where the elastic compliances of the piezoceramic are distinguished from those of the polymer phase by the superscript E, and  $\nu$  is the volume fraction of the piezoceramic. The first term in Equation (1) represents the direct contribution to the piezoelectric charge from the lateral stress on the piezoceramic rods. This term is essentially determined by the ceramic volume fraction and  $d_{31}$  coefficient, since in general  $s_{11}^E \ll s_{11}$ . The second term in Equation (1) arises from lateral stress on the polymer phase being transferred to a longitudinal stress along the ceramic rods by the Poisson effect in the polymer. This internal stress develops as a result of the mismatch in the transverse elastic compliances  $s_{13}$  of the two phases and it produces a charge through the  $d_{33}$  coefficient of the ceramic. The relative contribution of this term to the composite's  $\bar{d}_{31}$  coefficient is more pronounced as the ratio  $d_{33}/d_{31}$  increases. In calculating the composite's  $\bar{d}_{33}$  coefficient, the model assumes parallel connection along the piezoceramic rods, and neglects transverse effects normal to the rods, yielding,

$$\bar{d}_{33} = d_{33} / \{1 + (1/\nu - 1)(s_{33}^E / s_{33})\}. \quad (2)$$

Figure 3 shows the behavior of  $\bar{d}_{31}$  and its components  $\alpha d_{31}$  and  $\beta d_{31}$  for Modified-Lead-Titanate/Stycast and PZT5/Stycast 1-3 composites. Table II lists the material parameters used in these calculations. In the modified lead titanate composites the relative contribution of the term  $\beta d_{31}$  to the composite's  $\bar{d}_{31}$  is substantial because the ratio  $d_{33}/d_{31}$  in the ceramic is very large (about 33). This contribution increases beyond the  $d_{31}$  of the solid ceramic over most of the ceramic volume percentage range. Consequently, over most of the range, the  $|\bar{d}_{31}|$  of the composite is larger than that of the ceramic. In contrast, in the PZT/Stycast composites, the term  $\alpha d_{31}$  makes the dominant contribution over most of the range. In this case, the magnitude of  $\bar{d}_{31}$  of the composite structure is always less than that of the ceramic.

Figure 4 shows the behavior of the  $\bar{d}_{33}$  coefficient and the hydrostatic  $\bar{d}_h = \bar{d}_{33} + 2\bar{d}_{31}$  and  $\bar{g}_h = \bar{d}_h / \bar{\epsilon}_{33}^T$  coefficients for composites made from Stycast and either PZT5 or Calcium modified lead titanate. In the PZT5 composite,  $\bar{d}_h$  has a maximum at a ceramic volume percentage of about 20%. In contrast, in the lead titanate composite,  $\bar{d}_h$  increases monotonically with the ceramic volume fraction; the maximum value is obtained for the solid ceramic.

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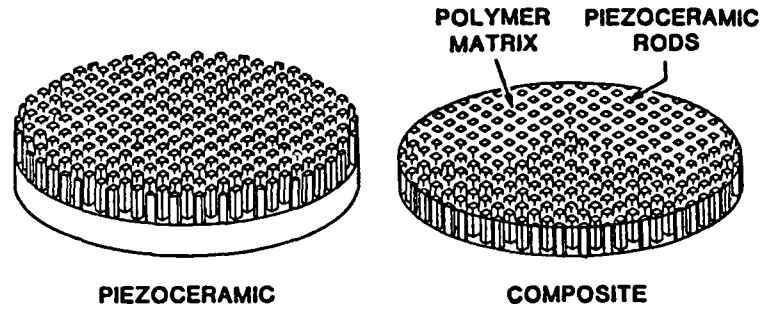


FIGURE 1 Fabrication of 1-3 composites from solid ceramic by the dice-and-fill technique.

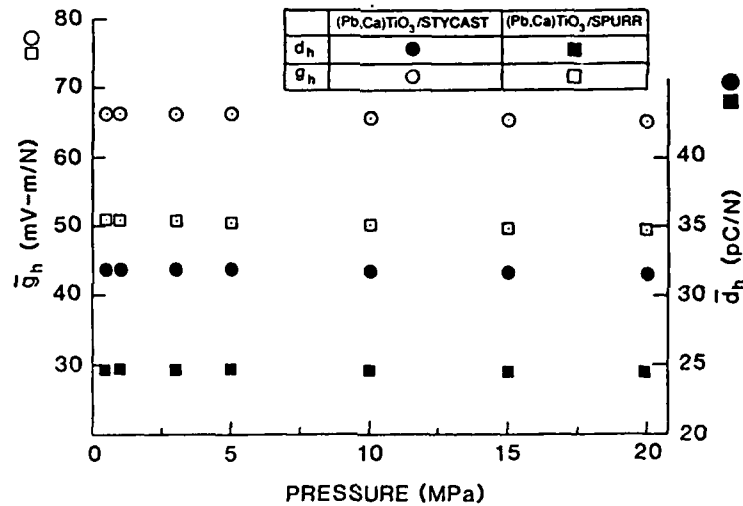


FIGURE 2 Pressure dependence of piezoelectric  $\bar{d}_h$  (solid) and  $\bar{g}_h$  (hollow) coefficients in 1-3 (Pb,Ca)TiO<sub>3</sub> composites made from Stycast (circles) and Spurr (squares).

TABLE I  
Measured and Calculated Properties of Calcium Modified Lead Titanate Ceramic and Stycast and Spurr Composites Containing 25% Ceramic by Volume. Underlined Quantities Are Measured Directly. Others Are Inferred.

	Ceramic Meas'd	Stycast Composite		Spurr Composite	
		Meas'd	Calc'd	Meas'd	Calc'd
$\epsilon_{33}^T$	<u>207</u>	55	55	<u>54</u>	55
$d_{33}$ (pC/N)	<u>70</u>	<u>49</u>	57	<u>59</u>	65
$d_{31}$ (pC/N)	<u>-2.4</u>	<u>-8.5</u>	-13	-17	-18.6
$d_h$ (pC/N)	<u>65</u>	<u>32</u>	31	<u>25</u>	28
$\bar{g}_h$ (mV-m/N)	35	66	64	52	57
$d_h \bar{g}_h$ ( $10^{-13} m^2/N$ )	2280	2100	1980	1300	1600
$k_{-1}$ (%)	<u>2.1</u>	<u>4.2</u>	6.8	5.2	5.6

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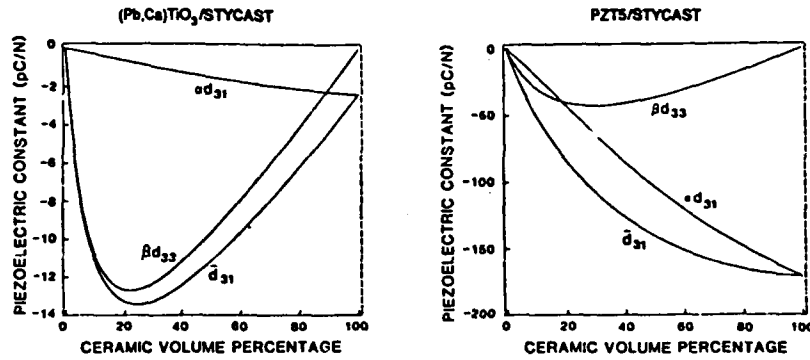


FIGURE 3 Theoretical  $\bar{d}_{31}$  coefficient and its components  $\alpha d_{31}$  and  $\beta d_{33}$  versus piezoelectric volume percentage for 1-3 composites made by combining Stycast polymer with (Pb,Ca)TiO<sub>3</sub> and PZTS piezoceramic.

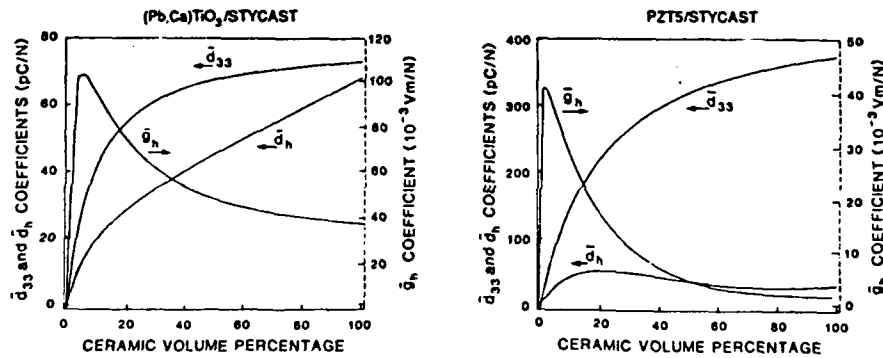


FIGURE 4 Theoretical  $\bar{d}_{33}$ ,  $\bar{d}_h$  and  $\bar{g}_h$  versus piezoelectric volume percentage for 1-3 composites made by combining Stycast polymer with (Pb,Ca)TiO<sub>3</sub> and PZTS piezoceramic.

TABLE II  
Material Parameters Used in Calculations

	$s_{11}^E$	$s_{13}^E$ ( $10^{-12} m^2/N$ )	$s_{33}^E$	$d_{33}$	$d_{31}$	$\rho$ ( $g/cm^3$ )	$\epsilon_{33}^T$
PZTS	16.4	-7.2	18.8	374	-171	7.75	1700
(Pb,Ca)TiO <sub>3</sub>	7.3	-1.4	8.5	70	-2.4	6.94	207
Stycast	108	-32	108	0	0	1.59	4
Spurr	332	-123	332	0	0	1.10	4

A comparison between the calculated and measured properties of Calcium modified lead titanate composites with 25% ceramic is given in Table I. The measured  $\bar{d}_h$  and  $\bar{g}_h$  agree remarkably well with the theoretical calculations. However, the magnitudes of the experimental  $\bar{d}_{33}$  and  $\bar{d}_{31}$  coefficients are slightly lower than the theoretical

values. The agreement between the theory and experiment become less satisfactory as the volume fraction of piezoceramic drops below 15%.

## DISCUSSION

The combination of a modified lead titanate ceramic and a polymer in a 1-3 composite structure forms a unique system in that essentially the entire  $d_{31}$  coefficient arises from the internal Poisson's ratio stress. Although the  $d_h$  coefficient of such a composite is less than that of the solid ceramic, the composite offers a larger  $g_h$  coefficient and a comparable  $d_h g_h$  product. Additional benefits of the composite structure include lower density and formability. The  $g_h$  coefficient achievable with these composites is comparable to that of the PVDF polymers. However, the ability to produce these composites in thickness up to a centimeter is a marked advantage over the thicknesses achieved with PVDF. In addition, the modified lead titanate composites offer better pressure stability, higher dielectric constant and higher hydrostatic current sensitivity than PVDF. With present commercial modified lead titanates, the dielectric constant of these composites are already several times that of PVDF; moreover recent work at Pennsylvania State University showed that  $\epsilon_{33}$  can be more than doubled while retaining the same hydrophone sensitivity.<sup>12</sup> Continuing research can be expected to bring further enhancement in  $\epsilon_{33}$ .

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## REFERENCES

1. R. E. Newnham, L. J. Bowen, K. A. Klicker and L. E. Cross, *Materials in Engineering* 2, 93-106 (1980).
2. R. Y. Ting, *Ferroelectrics* 67, 143-157 (1986).
3. K. A. Klicker, J. V. Biggers, and R. E. Newnham, *J. Am. Ceram. Soc.* 64, 5 (1981).
4. K. A. Klicker, W. A. Schulze, and J. V. Biggers, *J. Am. Ceram. Soc.* 65, C208 (1982).
5. M. J. Haun, P. Moses, T. R. Gururaja, W. A. Schulze and R. E. Newnham, *Ferroelectrics* 49, 259-264 (1983).
6. S. Y. Lynn, R. E. Newnham, K. A. Klicker, K. Rittenmyer, A. Safari, and W. A. Schulze, *Ferroelectrics* 38, 955-958 (1981).
7. H. Takeuchi, S. Jyomura, E. Yamamoto, and Y. Ito, *J. Acoust. Soc. Am.* 72, 1114 (1982).
8. Y. Yamashita, S. Yoshida, and T. Takahashi, *Japanese Journal of Applied Physics* 22, 40 (1983).
9. M. J. Haun and R. E. Newnham, *Ferroelectrics* 68, 123-139 (1986).
10. H. P. Savakas, K. A. Klicker and R. E. Newnham, *Materials Research Bulletin* 16, 677-680 (1981).
11. C. C. Sims and T. A. Hendriquez, *J. Acoust. Soc. Am.* 36, 1704 (1964).
12. K. Takeuchi, D. Damjanovic, T. R. Gururaja, S. J. Jang, and L. E. Cross, *Proceeding of the 1986 IEEE International Symposium on Applications of Ferroelectrics* 402-405 (1986).