ENHANCED LATERAL ELECTROMECHANICAL COUPLING IN LEAD-TITANATE-ROD/POLYMER PIEZOELECTRIC COMPOSITES

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While modified lead titanate ceramics exhibit negligible d_{31} piezoelectric coefficient, piezoceramic-rod/polymer-matrix composites made from them exhibit a substantial d_{31}. A theoretical analysis shows that the composite's enhanced d_{31} coefficient 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, thus producing a charge through the ceramic's d_{33}. For hydrophone applications, this enhanced d_{31} suppresses the hydrostatic response so that the composite's hydrophone figure-of-merit, $d_h g_h$, is less than that of the constituent ceramic. Nevertheless, the composite's still substantial $d_h g_h$, high g_h coefficient, remarkable pressure stability, low density, formability, and availability in thick sheets provide advantages for naval applications. In ultrasonic transducer applications, the composite structure provides no enhancement in electromechanical coupling since the modified-lead-titanate's k_{33} is nearly the same as its k_t. These expectations are in good agreement with measurements on 1-3 modified-lead-titanate/polymer composites made by the dice-and-fill technique.

INTRODUCTION

Vanishingly small lateral electromechanical coupling has been achieved in modified lead titanate ceramics.[1,2] This property commends these materials for certain pulse-echo ultrasonic transducer arrays[3-5] and naval hydrophones.[6] Namely, the low lateral coupling inhibits the excitation of unwanted lateral modes in the ultrasonic arrays and eliminates the need for lateral shielding in the naval hydrophones.

1-3 composite piezoelectrics, consisting of thin rods of PZT held parallel to each other by a polymer matrix, also provide benefits in naval hydrophones,[7-10] and medical ultrasonic transducers.[11-17] Enhanced hydrophone figure-of-merit, $d_h g_h$, are the PZT-composite's advantage in naval applications, while their higher electromechanical coupling, k_t, describes their key benefit for ultrasonic transducers.

This paper explores the properties of 1-3 composite piezoelectrics made using the modified lead titanate ceramics. We first use simple physical models to sketch in broad brush the range of properties achievable. We then compare these predictions to the results of our measurements and measurements of others.[18] We conclude with an assessment of the utility of 1-3 modified-lead-titanate/polymer composite for ultrasonic and hydrophone applications.

MODELING

In ultrasonic applications, thin plates of the piezoelectric are excited near their thickness-mode resonance both during the transmission of the probe pulse and the reception of its echos. The frequencies involved are so high that lateral motion of the plate as a whole is inertially clamped; only the uniaxial stress perpendicular to the face of the plate plays a role. A simple physical model for the properties of 1-3 piezocomposites relevant to describing these thickness mode oscillations has already been presented.[19] We shall use the results of that analysis without further exposition. In particular, Figure 1 plots the thickness-mode electromechanical coupling coefficient, k_t, versus ceramic volume fraction for composites made from both a calcium-modified lead titanate and a conventional lead zirconate-titanate, PZT5. The material parameters used in these calculations are listed in Table I.
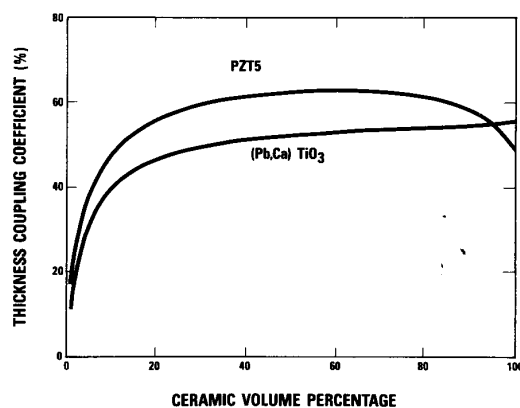

FIGURE 1 For *PZT5/STYCAST* and *(Pb,Ca)TiO₃/STYCAST* composites, the composite's thickness-mode electromechanical coupling coefficient, k_t, as a function of the ceramic volume percentage.

TABLE I
Material Parameters Used in Calculations

	s_{11}^E s_{13}^E s_{33}^E (10^{-12} m^2/N)			d_{33} d_{31} (pC/N)		ρ (g/cm^3)	ε_{33}^T
PZT5	16.4	-7.2	18.8	374	-171	7.75	1700
$(Pb,Ca)TiO_3$	7.3	-1.4	8.5	70	-2.4	6.94	207
Stycast	108	-32	108	0	0	1.59	4

PIEZOCERAMIC INTERNAL POISSON'S
RODS   RATIO STRESS

EXTERNAL
STRESS

POLYMER

FIGURE 2 Schematic representation of the Poisson-ratio effect giving contributions to the composite's $\bar{d}_{31}$ from the ceramic's d_{33}.

In hydrophone applications, the piezoelectric responds to hydrostatic pressure waves. While thickness oscillations are excited here also, the frequency range of interest is far below the thickness-mode resonance. The plates are laterally free and respond to the stresses both on their faces and on their sides. Our model for the ultrasonic properties can be modified for the hydrostatic regime, by replacing the laterally clamped restriction with laterally free boundary conditions and including external lateral stresses. Such an analysis leads to results essentially the same as those embodied in the series-parallel connectivity model of Haun and Newnham.[20]

Let us summarize the results of the Haun-Newnham analysis. The composite's $\bar{d}_{33}$ coefficient is calculated by assuming parallel connection along the piezoceramic rods and neglecting transverse effects, yielding

$$\bar{d}_{33} = d_{33}/\{1 + (1/v - 1)(s_{33}^E/s_{33})\} , \qquad (1)$$

where v denotes the volume fraction of the piezoceramic, and the superscript E distinguishes the elastic compliances of the piezoceramic from those of the polymer phase.

In calculating the $\bar{d}_{31}$ coefficient of the 1-3 composite, contributions arise from both the d_{31} and d_{33} coefficients of the ceramic phase, that is,

$$\bar{d}_{31} = \alpha d_{31} + \beta d_{33}, \qquad (2)$$

where the coefficients α and β are determined by the elastic compliances and volume fractions of the constituent phases. For 1-3 composites with square rods, α and β are

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

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

The first term in Equation (2) describes the direct response of the piezoceramic rods to the lateral stress on the composite.
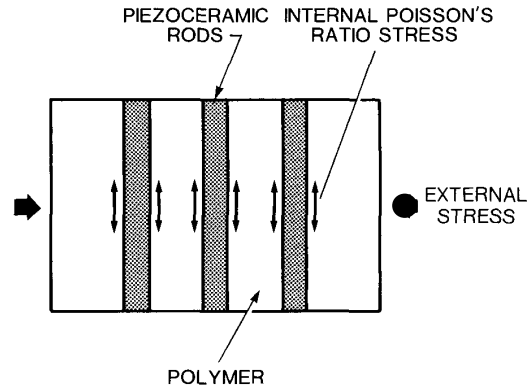
This contribution is essentially determined by the ceramic volume fraction and d_{31} coefficient, since generally ceramic compliances are much less than those of polymers. The second term in Equation (2) describes an indirect response. This contribution arises from lateral stress on the polymer phase being transferred to a longitudinal stress along the ceramic rods by the Poisson effect in the polymer, as is illustrated in Figure 2. This internal stress, which is due to the mismatch in the elastic compliances s_{13} of the two phases, produces a charge through the d_{33} coefficient of the ceramic.

Figures 3 depicts the variation with ceramic volume percentage of the composite's $\bar{d}_{31}$ and its components αd_{33} and βd_{31}; two ceramics are plotted as examples, a calcium-modified lead titanate and a conventional PZT5. Table I lists the material parameters used in these calculations. In the modified lead titanate composites, the indirect term βd_{33} dominates the composite's $\bar{d}_{31}$ because the ceramic's d_{31} is essentially negligible compared to its d_{33} (i.e., ~ 3 %). Moreover, this contribution exceeds the ceramic's d_{31} over most of the ceramic volume fraction range. Thus, for most volume fractions of ceramic, the composite's $|\bar{d}_{31}|$ is enhanced over that of the ceramic. In contrast, in PZT-rod composites, the direct term αd_{31} dominates over most of the range, and the $|\bar{d}_{31}|$ in the composite structure is always less than that of the constituent ceramic.

Figure 4 plots the corresponding volume fraction dependence of the $\bar{d}_{33}$ coefficient and the hydrostatic $\bar{d}_h = \bar{d}_{33} + 2\bar{d}_{31}$ and $\bar{g}_h = \bar{d}_h / \varepsilon_{33}^T$ coefficients for composites made from calcium-modified lead titanate and PZT5. In the PZT5 composite, $\bar{d}_h$ reaches a maximum for about 20% ceramic. In the lead titanate composite, however, $\bar{d}_h$ increases monotonically with the ceramic volume fraction; the maximum value is obtained for 100% ceramic.

(Pb, Ca) TiO₃ / STYCAST
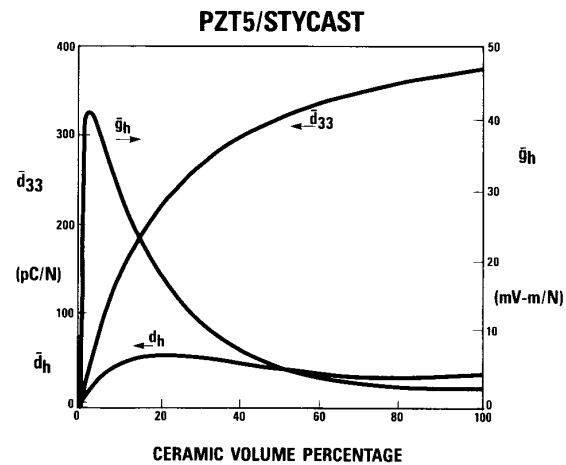

(Pb,Ca) TiO₃ / STYCAST
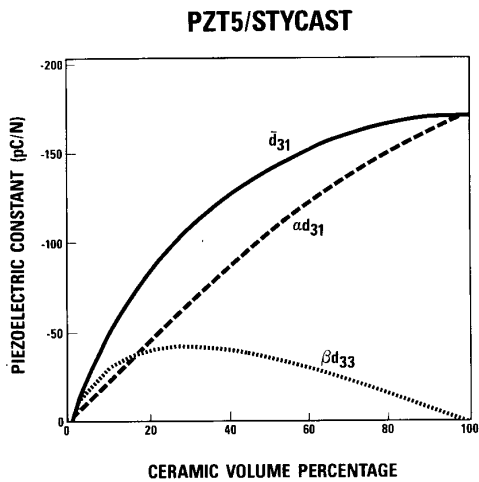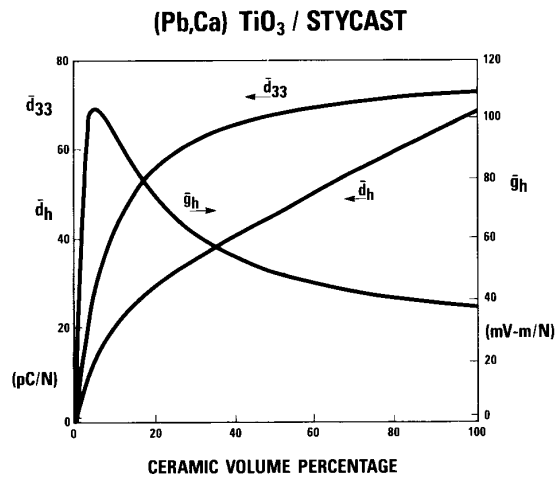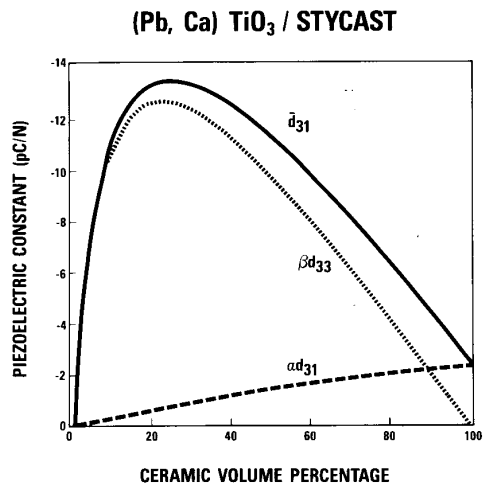

PZT5/STYCAST

PZT5/STYCAST

FIGURE 3 For $(Pb,Ca)TiO_3/STYCAST$ (above) and $PZT5/STYCAST$ (below) composites, the composite's total $\bar{d}_{31}$ piezoelectric coefficient (solid curves), the portion of $\bar{d}_{31}$ stemming from the ceramic's d_{31} (dashed curves), and the portion of $\bar{d}_{31}$ stemming from the ceramic's d_{33} (dotted curves), all as a function of the ceramic volume percentage. In the modified lead titanate composites, the contribution βd_{33} exceeds the d_{31} of the pure ceramic for most ceramic volume fractions, resulting in an enhancement of the composite's $\bar{d}_{31}$ over that of the pure ceramic. Quite the opposite occurs in the PZT composites; the direct term αd_{31} is the dominant contribution for most ceramic volume fractions, resulting in a $\bar{d}_{31}$ for the PZT composite that is always less than that of the pure ceramic.

FIGURE 4 For $(Pb,Ca)TiO_3/STYCAST$ (above) and $PZT5/STYCAST$ (below) composites, the composite's $\bar{d}_{33}$ piezoelectric coefficient, the hydrostatic current response, $\bar{d}_h$, and hydrostatic voltage response, $\bar{g}_h$, all as a function of the ceramic volume percentage. The PZT composites show a maximum in their $\bar{d}_h$ coefficient which exceeds the value for the pure ceramic. The situation is quite different for the modified lead titanate composites; the enhancement of $\bar{d}_{31}$ suppresses this maximum, resulting in a $\bar{d}_h$ for the composite which is always less than that of the pure ceramic.
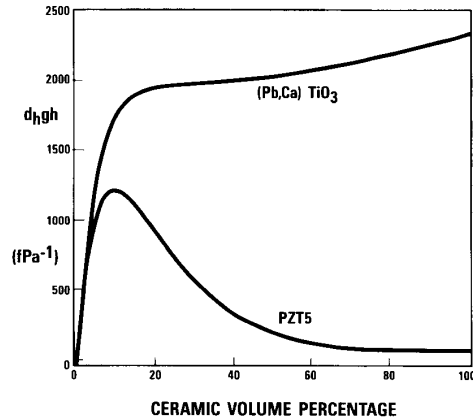
CERAMIC VOLUME PERCENTAGE

FIGURE 5 For *PZT5/STYCAST* and *(Pb,Ca)TiO₃/STYCAST* composites, the composite's hydrophone figure-of-merit, $\bar{d}_h \bar{g}_h$, as a function of the ceramic volume percentage.

In Figure 5, the model's predictions for the hydrophone figure-of-merit, $d_h g_h$, is plotted versus ceramic volume percentage. Here we see the most dramatic manifestation of the enhanced d_{31} in the $(Pb,Ca)TiO_3$ composite structures. The $d_h g_h$ product of the modified-lead-titanate composite is always less than that of the solid ceramic. This is in direct contrast to the situation for lead-zirconate-titanate composite where the composite structure provides a substantial enhancement in $d_h g_h$ over that of the solid ceramic.

EXPERIMENTS

To test the theoretical predictions, 1-3 composites were made from a calcium-modified lead titanate ceramic (Toshiba C-24) and a rather stiff polymer (Stycast). The measured properties of this ceramic and polymer are given in Tables I and II. The dice-and-fill technique[21] was used to make square plates (19 mm x 19 mm x 1 mm) of 1-3 composites with 100 micron rods and ceramic volume fraction from 10% to 35%. Figure 6 illustrates the the fabrication technique. Deep grooves are cut into a solid block of poled ceramic. A polymer is cast in these grooves and the remaining ceramic base ground off, yielding the desired composite structure.

Table II presents measured properties of the composites containing 25% ceramic, along with those of the solid ceramic. The dielectric constant, ε_{33}^T, was obtained from a capacitance measurement at 1 kHz. A Berlincourt d_{33}-meter was used to measure d_{33} at a frequency of 100 Hz; the $\bar{d}_{33}$ of the composite is the average of twenty measurements at different locations on the composite plate. Direct measurements of k_{31}
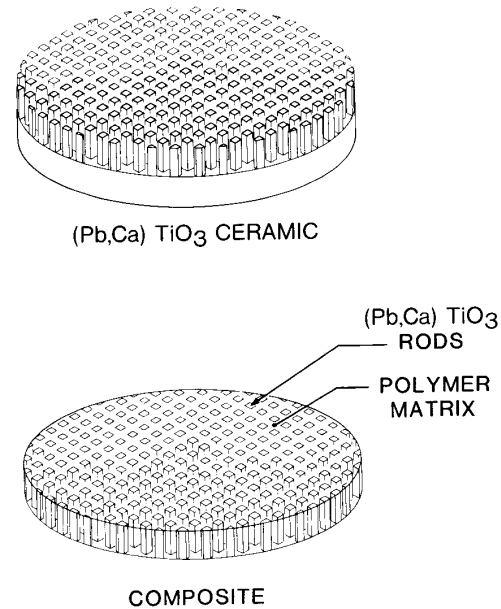
(Pb,Ca) TiO₃ CERAMIC

(Pb,Ca) TiO₃ RODS

POLYMER MATRIX

COMPOSITE

FIGURE 6 Schematic representation of the dice-and-fill technique for the fabrication of 1-3 $(Pb,Ca)TiO_3/polymer$ composites.

TABLE II
Measured and Calculated Properties of $(Pb,Ca)TiO_3$ Ceramic and Stycast Composites Containing 25% Ceramic by Volume. Underlined Quantities Are Measured Directly. Others Are Inferred.

	Ceramic Meas'd	Composite Meas'd	Composite Calc'd
ε_{33}^T	207	55	55
d_{33} (pC/N)	70	49	57
d_{31} (pC/N)	-2.4	-8.5	-13
k_{31} (%)	2.1	4.9	6.8
d_h (pC/N)	65	32	31
g_h (mV-m/N)	35	66	64
$d_h g_h$ ($10^{-15} m^2/N$)	2280	2100	1980

and d_{31} were made using the impedance circle technique[22] on the length expander resonance (near 50 kHz) of narrow composite strips cut from the composite plates. The hydrostatic d_h and g_h coefficients, were measured as a function of pressure in an acoustic coupler using the reciprocity technique.[23] These hydrostatic measurements are also shown in Figure 7, where we see an insensitivity to pressure up to 20 MPa.
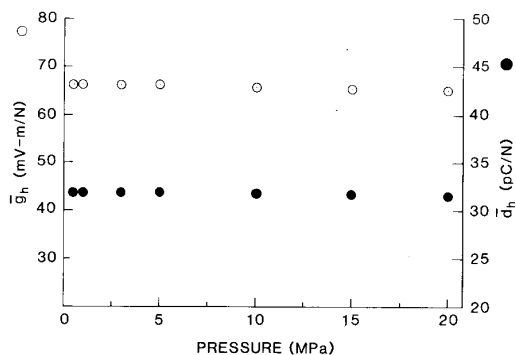
(Pb,Ca) TiO₃ / STYCAST

FIGURE 7 For $(Pb, Ca)TiO_3/STYCAST$ composites with 25 percent ceramic, the measured hydrostatic current response, $\bar{d}_h$, (solid circles) and hydrostatic voltage response, $\bar{g}_h$, (open circles), as a function of pressure.

DISCUSSION

Table II also compares the measured and calculated properties of calcium-modified lead titanate composites with 25% ceramic. The agreement is sufficiently good to provide confidence in drawing conclusions from the simple physical models used to project the composite's properties.

For ultrasonic applications, Figure 1 shows that we can expect no enhancement in the electromechanical coupling by using the $(Pb, Ca)TiO_3$ ceramics in a composite structure. This is in agreement with other experimental reports[18] and suggests little point in using 1-3 $(Pb, Ca)TiO_3$-rod composites for ultrasonic pulse-echo transducers. PZT-rod composites provide all the other benefits of the composite structure -- lower acoustic impedance, formability, suppression of spurious modes, etc. -- plus a much larger k_t.

For hydrophone applications, the absence of an enhancement in $d_h g_h$ for the composite structure is depicted in Figure 5. While disappointing, this is not fatal. In comparison to solid $(Pb, Ca)TiO_3$ ceramic, the composite provides a larger g_h coefficient, a comparable $d_h g_h$ product and the benefits of reduced density and formability. In comparison with PVDF, the $(Pb, Ca)TiO_3$ composites provide comparable g_h coefficient, coupled with the marked advantage of achievable thicknesses ranging up to a centimeter. 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 showed that ε_{33} can be more than doubled while retaining the same hydrophone sensitivity.[24] Thus, in the arena of naval hydrophone receivers, we can expect the $(Pb, Ca)TiO_3$-rod composites to find fruitful application.

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