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High Piezoelectric Sensitivity Composites Based on Ferroelectric Ceramics

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This paper describes the modelling and comparison of 0-3 and 3-3 piezocomposites, including three-component structures such as 0-0-3 systems. The piezoelectric properties are calculated for $PbTiO_3$ based piezocomposites where the anisotropy factor $(-d_{33}/d_{31})$ of the piezoelectric can be varied from small to infinitely large values. Maxima of these parameters are determined and factors influencing piezoelectric sensitivity are analysed.

Keywords: Composites; modelling; piezoelectric

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Significant improvements in the materials for electromechanical transducers are attained using the composite route and utilising existing piezoelectric materials combined with another phase, such as a polymer or air. Piezoelectric sensitivity is characterised by parameters [1–3], such as the piezoelectric voltage coefficients (g_{33} and g_{31}), piezoelectric figure of merit ($d_{33} \cdot g_{33}$) and hydrostatic figure of merit (HFOM) $d_h \cdot g_h$, where the hydrostatic piezoelectric charge coefficient $d_h = d_{33} + 2d_{31}$, the hydrostatic piezoelectric voltage coefficient $g_h = d_h/\varepsilon_{33}^T$ and ε_{33}^T is permittivity along the poling axis (OX_3) at constant stress.

A two-figure number describes the piezocomposite [1], which designates the connectivity of the active and inactive phases. '0-3' represents individual piezoelectric particles distributed in a continuous polymer and '3-3' represents interconnected piezoelectric and polymer phases. The aim of this paper is to compare sensitivity parameters of 0-3 and 3-3 $PbTiO_3$-based composites. The advantage of using $PbTiO_3$ is that, in addition to varying the connectivity, the anisotropy factor $(-d_{33}/d_{31})$ can be varied [4] from small values, where d_{31} is large compared to d_{33}, to infinitely large values, where d_{31} is small compared to d_{33}. This has not been examined, which is surprising since the principal benefit of using piezocomposites is to develop a structure with a reduced d_{31}, higher $-d_{33}/d_{31}$ and higher d_h compared to the monolith.

The 0-3 composite is represented by a cubic *Banno unit cell* [5] containing a piezoceramic inclusion surrounded by a matrix. The inclusion is a rectangular parallelepiped and its length, width and height make up the *t*th, *n*th and *h*th parts of the unit-cell edge. The composite is poled along the OX_3 axis of a rectangular $(X_1X_2X_3)$ system. Calculations are carried out using room-temperature elastic, piezoelectric and dielectric constants of $PbTiO_3$, $(Pb_{0.76}Ca_{0.24})TiO_3$ and $Pb(Zr_{1-x}Ti_x)O_3$ ceramics. The constants were taken from experimental data [6, 7] or evaluated in accordance with an algorithm [4]. The elastic and dielectric constants of the elastomer matrix were from Ref. [2]. The electromechanical constants of the piezoceramic and polymer components are averaged by a matrix method that has been applied to other systems [8]. The averaging procedure determines of the effective constants of a laminated piezoceramic–polymer structure by taking into account the electrical and mechanical boundary conditions at (i) $x_1 =$ constant, (ii) $x_2 =$ constant and (iii) $x_3 =$ constant separately.

The first calculations considers the variation of the composite concentration parameters $0 < (t, n, h) < 1$. By variation of n and t, maxima of g_h, $d_{33} \cdot g_{33}$ and $d_h \cdot g_h$ are established. The values of these maxima increase with increasing h_0 (ceramic particle height) and when $h = 1$ the composite has 1–3 connectivity, where absolute maxima are achieved. Concentration dependences with $h = 0.95$ and variable (t, n) are in Fig. 1. These composites display high $g_h \approx 4\ g_h^m$ (Fig. 1a) and $d_{33} \cdot g_{33} \approx 15\ d_{33}^m \cdot g_{33}^m$ (Fig. 1b). The 'm' superscript relates to the monolithic piezoceramic. The location of the g_h and $d_{33} \cdot g_{33}$ maxima are at $t \ll 1$, $n \to 1$ or $n \ll 1$, $t \to 1$, which correspond to 'plate-like' piezoceramic inclusions along the OX_1 or OX_2 axes. The HFOM $(d_h \cdot g_h)$ shows a monotonous concentration dependence on both t and n as they vary from 0.01 to 0.99 (Fig. 1c). The composite HFOM remains two orders of magnitude lower than bulk $PbTiO_3$ due to a discontinuous distribution of the piezoceramic along the poling axis.

The second calculations incorporates disk-like porosity into the polymer matrix. Air inclusions are described by an equation $(x_1^2/a_1^2) + (x_2^2/a_1^2) + (x_3^2/a_3^2) = 1$ where $\alpha_{sa} = a_3/a_1$ is the ratio of semiaxes. The porous polymer structure achieves large increases in sensitivity for the 0-0-3 connectivity composite. Even at low polymer porosity $m_p = 0.10$ and ratio $\alpha_{sa} = 0.1$, g_h and $d_h \cdot g_h$ are 3-4 times larger than those measured on similar 0-3 composites [9] and data in Fig. 1a, c. The improved figures of merit are due to the increased compliances s_{11}^p and s_{12}^p and reduced permittivity ε_{33}^p of the porous polymer.

Increasing piezoelectric sensitivity is associated with increasing the connectivity of the piezoactive component. In a 3-3 composite the connectivity is increased to three dimensions to create interpenetrating piezoceramic and polymer. The effective parameters ε_{33}^T, d_h and g_h are calculated as a function of ceramic volume fraction and materials properties using model concepts [10]. The most important results (Fig. 2) show d_h, g_h and $d_h \cdot g_h$ as a function of ceramic volume fraction for $PbTiO_3$-based composites, where the

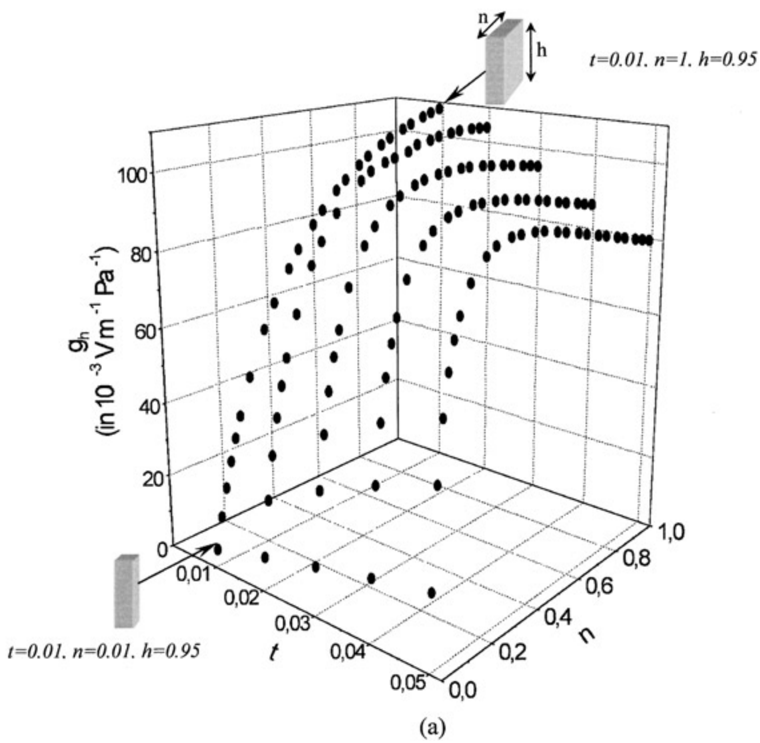
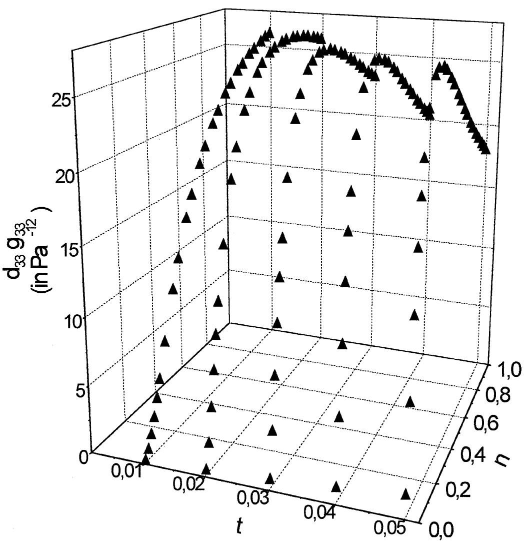
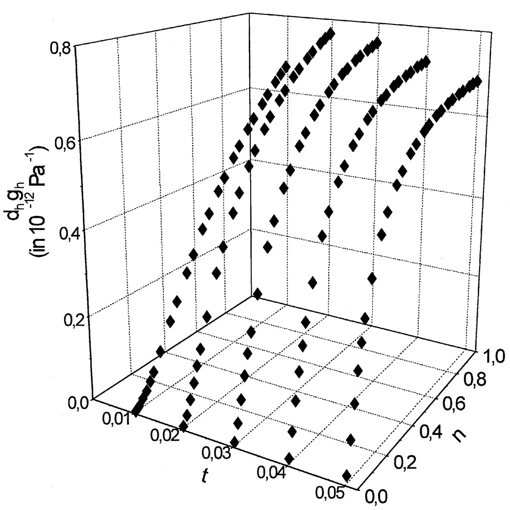


FIGURE 1 Parameters g_h (a), $d_{33} \cdot g_{33}$ (b) and $d_h \cdot g_h$ (c) that characterise piezoelectric sensitivity of the 0-3 composite "modified $PbTiO_3$ piezoceramic-elastomer" with inclusions in the form of a rectangular parallelepiped. h, the particle height along poling direction (OX_3), is 0.95. *(Continued)*



(b)



(c)

FIGURE 1 (Continued)

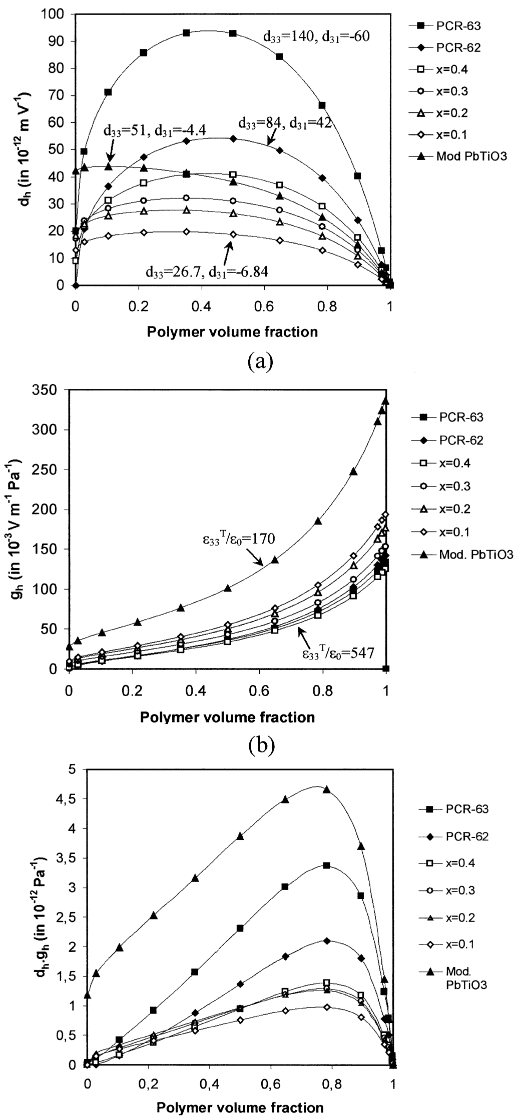


FIGURE 2 Parameters d_h (a), g_h (b) and $d_h \cdot g_h$ (c) calculated for the 3-3 composite "$PbTiO_3$-based piezoceramic-polymer." Ceramics presented include modified $PbTiO_3$, PCR-62, PCR-63 and $Pb(Zr_{1-x}Ti_x)O_3$ where $x = 0.1$, 0.2, 0.3 and 0.4 and the abbreviation "PCR" means "piezoelectric ceramic from Rostov-on-Don" ($Pb(Zr_{1-x}Ti_x)O_3$ type). Selected d_{33} and d_{31} values indicated in pCN^{-1}.

polymer component is ten times more compliant than the ceramic. For example, d_h reaches a maximum at polymer volume fractions ~0.4–0.5 for PCR-63, PCR-62 and different solid solutions of $Pb(Zr_{1-x}Ti_x)O_3$ (Fig. 2a). The highest composite d_h values are achieved using piezoceramics with high d_{33} (PCR-62 and PCR-63). The mechanism by which d_h increases is similar to that for 1-3's [11]; whereby the structure leads to a large reduction in d_{31} relative to d_{33}. Therefore, the ceramics which experience the greatest d_h enhancement are those with a small anisotropy factor $-d_{33}/d_{31}$ (i.e. a high $-d_{31}$), such as PCR-62 and PCR-63 (Fig. 2a). Incorporating polymer into modified $PbTiO_3$ merely decreases the d_{33} and d_h value (Fig. 2a).

The g_h parameter increases for all the 3-3 composites examined as polymer is introduced into the structure (Fig. 2b); due to the increased d_h and decreased permittivity. The highest g_h is for the modified $PbTiO_3$-based composite, mainly due to the low permittivity ($\varepsilon_{33}^{m,T}/\varepsilon_0 = 170$) [6]. The HFOM ($d_h \cdot g_h$) reaches a maximum at ceramic fractions of ~0.2 and, unlike 0-3 composites, large increases are observed compared to the bulk material (Fig. 2c).

CONCLUSIONS

Our study of 0-3, 0-0-3 and 3-3 piezocomposites based on $PbTiO_3$ enables the prediction of concentration dependences of the effective parameters and establish important extreme points of these parameters. Due to the lack of connectivity in 0-3's, piezoelectric strain constants such as d_{33} and d_h are low, but the reduced permittivity provides enhanced piezoelectric voltage constants such as g_{33} and g_h. High piezoelectric sensitivity depends on ceramic particle microgeometry, ceramic volume fraction and the presence of elongated porosity in the polymer, an area that has not been studied in detail.

The 3-3 materials are more sensitive to the anisotropy factor $-d_{33}/d_{31}$. The greatest benefits in d_h are at high ceramic volume fractions using materials with high d_{33} and small $-d_{33}/d_{31}$ ratios, although in all cases the reduced permittivity leads to increased g_h. The models enable 0-3 and 3-3 composites to be optimised depending on the application and the relevant figure of merit.

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