

# Pore anisotropy in 3–3 piezoelectric composites

C.R. Bowen\*, H. Kara

Department of Engineering and Applied Science, Materials Research Centre, University of Bath, Bath BA2 7AY, UK

## Abstract

A piezoelectric composite of the ‘3–3’ type consists of an active piezoceramic phase and passive polymer phase that are interpenetrating. Previous research on analytical modelling 3–3 material has considered equiaxed open pores in a piezoelectric ceramic and has assumed complete stress transfer of an applied load into the stiffer ceramic matrix. This research examines the influence of pore anisotropy on the hydrostatic properties. The model developed and results are a useful aid to fabricate and optimise piezocomposite 3–3 structures for specific applications. © 2002 Published by Elsevier Science B.V.

*Keywords:* Piezoelectric composite; Piezoceramic phase; Polymer phase

## 1. Introduction

Piezoelectric composites have been developed in an attempt to improve on the properties of monolithic piezoelectric materials, such as lead zirconate titanate (PZT). They are of interest for applications such as acoustic transducers, SONAR applications, medical imaging and non-destructive evaluation [1]. Generally, these materials consist of an active piezoelectric phase and a passive phase, usually a polymer or air. A two-figure number describes the architecture of a piezoelectric composite [2], which designates the connectivity of the piezoelectric material and the polymer phase, respectively. A ‘0–3’ piezocomposite consists of individual piezoelectric particles distributed in a continuous polymer matrix and a ‘1–3’ represents single pillars of piezoelectric phase in a continuous polymer matrix. The composites investigated in this paper are the ‘3–3’ variety where both the piezoelectric and polymer are connected in three dimensions. In simple terms, this can be regarded as an open porosity piezoelectric material that has been impregnated with a polymer phase [3,4].

To examine the properties of 3–3 piezocomposites, the figures of merit that describe the performance of the material must be described. If the material is to be used as a hydrophone to detect a low frequency signal (<100 kHz), the acoustic wavelength dimension is greater than that of the hydrophone and the stress on the device/composite due to the acoustic wave is hydrostatic [5]. Under these conditions, *passive* hydrophone sensitivity is characterised by the *hydrostatic piezoelectric voltage constant* ( $g_h$ ), defined as

the electric field generated per unit hydrostatic stress [6], which is calculated from Eq. (1).

$$g_h = \frac{d_h}{\epsilon_{33}^T} \quad (\text{V m}^{-1} \text{Pa}^{-1}) \quad (1)$$

where  $\epsilon_{33}^T$  is the permittivity at constant stress of the composite ( $\text{F m}^{-1}$ ) and  $d_h$  the hydrostatic strain constant ( $\text{m V}^{-1}$ ).

The *hydrostatic strain constant* ( $d_h$ ) describes the performance of the material as an active transducer and is defined as the hydrostatic strain per unit electric field [6] or charge developed per unit hydrostatic force

$$d_h = d_{33} + 2d_{31} \quad (\text{m V}^{-1} \text{ or } \text{C N}^{-1}) \quad (2)$$

where  $d_{33}$  is the charge per unit force parallel applied parallel to the poling direction (3-direction), and  $d_{31}$  the charge per unit force applied perpendicular to the poling direction.

Both  $d_h$  and  $g_h$  values are used to calculate the *hydrostatic figure of merit* ( $d_h g_h$ ), which describes the device both as a hydrophone and an actuator (active–passive transducer) and is reported to indicate the signal to noise ratio [6,7].

While many papers are concerned with modelling the behaviour and manufacture of 0–3 and 1–3 composites, there has been less research in the area 3–3 composites. Levasort et al. [8] developed models to determine the effective properties of composites with both a 0–3 and 3–3 structure and Dunn and Taya [9] have presented models based on the effective medium approach (up to 50% porous). The most useful models developed by Rittenmyer et al. [10] and Banno [11] have equiaxed pores and assume that the polymer phase bears no load due to complete stress transfer of the load into the stiffer piezoelectric phase. Previous work by the authors

\* Corresponding author. Tel.: +44-1225-323660; fax: +44-1225-826098.  
E-mail address: c.r.bowen@bath.ac.uk (C.R. Bowen).

has extended the model to examine the influence of load transfer into the passive polymer phase. This becomes increasingly significant as the volume fraction of the polymer and polymer elastic modulus increases [12]. The aim of this paper is to use the analytical model to investigate anisotropic pores to examine how the hydrostatic properties of these piezocomposites are affected by elongation of pores parallel and perpendicular to the poling direction. Pore elongation has been readily achieved using polymer foams which are stretched in a particular direction [13]. It has been observed that 3–3 piezocomposites also have cracks elongated in a particular direction within their structure [10], which can be regarded as elongated pores.

## 2. Modelling of 3–3 piezocomposites

Rittenmyer et al. [10] reported an analytical model describing the physical properties of 3–3 piezocomposites. The model consists of three intersecting rectangular columns of piezoelectric embedded in a polymer matrix, as shown in Fig. 1. This model assumes that the piezoelectric material is fully poled parallel to the poling direction (3-direction).

### 2.1. Pore anisotropy

The pore height in the 3-direction ( $l_1$ ) is different to the pore width in the 1 and 2 directions ( $l_2$ ). By examining various  $l_1/l_2$  ratios, the effect of pore elongation on the hydrostatic parameters of the material is to be investigated.

### 2.2. Permittivity

The permittivity at constant stress in the 3-direction ( $\epsilon_{33}^T$ ) is of importance in calculating the hydrostatic voltage constant ( $g_h = d_h/\epsilon_{33}^T$ ) of the composite. As the permittivity

of the piezoelectric phase is significantly greater than that of the polymer it will dominate the effective permittivity of the composite. For example, for PZT-5H, a commercially available soft lead zirconate titanate (PZT),  $\epsilon_{33}^T = 3400\epsilon_0$  while for many polymers  $\epsilon_{33}^T \sim 10\epsilon_0$  (where  $\epsilon_0$  is permittivity of free space). By examination of Fig. 1b, the vertical column parallel to the poling direction can be considered to contribute to  $\epsilon_{33}^T$  of the composite. The other volumes contribute little to the effective permittivity of the composite as they consist of either purely polymer or a piezoelectric phase in series with the low permittivity polymer phase. For the model cube, the dielectric constant can be approximated to Eq. (3) [10].

$$\epsilon_{33}^{T, \text{Composite}} = \epsilon_{33}^{T, \text{PZT}} v^{\epsilon_{33}^{\text{PZT}}} \quad (3)$$

where  $\epsilon_{33}^{T, \text{Composite}}$  is the effective permittivity at constant stress of the composite;  $\epsilon_{33}^{T, \text{PZT}}$  the permittivity at constant stress of the piezoelectric phase;  $v^{\epsilon_{33}^{\text{PZT}}}$  the volume fraction of piezoelectric phase contributing to the composite permittivity.

### 2.3. Piezoelectric strain constant ( $d_{33}$ )

In order to calculate the  $d_{33}$  piezoelectric charge coefficient of the composite material, the fraction of force experienced by both the active piezoelectric material and the passive polymer must be calculated. If a force,  $F_3$  is applied in the 3-direction, the total force is distributed through volumes indicated in Fig. 1b. The polymer phase will experience less force, being of significantly higher compliance than the piezoceramic phase (elastic modulus of PZT is  $\sim 50$  GPa and for polymers is less than 10 GPa). This has led to the assumption in some models of complete stress transfer into the active ceramic phase [10]. However, the actual distribution of the force will depend on the respective

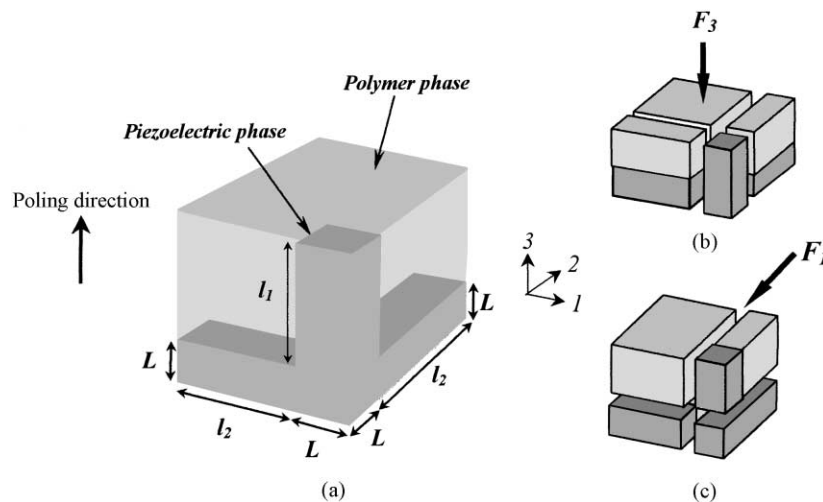


Fig. 1. (a) Model representing an interpenetrating 3–3 piezocomposite structure. (b) The force ( $F_3$ ) is distributed through the volumes shown. (c) The force ( $F_1$ ) is distributed through the volumes shown.

compliances of the volumes and the cross-sectional area of each volume, very much similar to that of composite fibre reinforced systems. The  $d_{33}$  of the 3–3 piezocomposites structure can therefore be calculated from [12],

$$d_{33}^{\text{Composite}} = d_{33}^{\text{PZT}} \times \text{fraction of load experienced active volumes} \\ = d_{33}^{\text{PZT}} \frac{L^2}{s_{33}^{\text{PZT}}} \left[ \frac{L^2}{s_{33}^{\text{PZT}}} + \frac{l_2 l_2}{s_{33}^{\text{Poly}}} + \frac{2Ll_2(L+l_1)}{Ls_{33}^{\text{PZT}} + l_1 s_{33}^{\text{Poly}}} \right]^{-1} \quad (4)$$

where  $s_{33}^{\text{PZT}}$  is the compliance of the piezoelectric in the 3-direction and  $s_{33}^{\text{Poly}}$  the compliance of the polymer in the 3-direction.

#### 2.4. Piezoelectric strain constant ( $d_{31}$ )

The same procedure is undertaken to calculate the  $d_{31}$  piezoelectric charge coefficient of the composite. If a force,  $F_1$  is applied in the 1-direction; the total force is distributed through the volumes indicated in Fig. 1c.

The  $d_{31}$  of the unit cell is [12]

$$d_{31}^{\text{Composite}} = d_{31}^{\text{PZT}} \frac{L}{(L+l_2)} \times \text{fraction of force experienced active volumes} \\ = d_{31}^{\text{PZT}} \frac{L}{(L+l_2)} \left[ \frac{Ll_1(L+l_2)}{Ls_{11}^{\text{PZT}} + l_2 s_{11}^{\text{Poly}}} + \frac{L^2}{s_{11}^{\text{PZT}}} \right] \\ \times \left[ \frac{l_1 l_2}{s_{11}^{\text{Poly}}} + \frac{L(l_1+l_2)(L+l_2)}{Ls_{11}^{\text{PZT}} + l_2 s_{11}^{\text{Poly}}} + \frac{L^2}{s_{11}^{\text{PZT}}} \right]^{-1} \quad (5)$$

where  $s_{11}^{\text{PZT}}$  is the compliance of the piezoelectric in the 1-direction and  $s_{11}^{\text{Poly}}$  the compliance of the polymer in the 1-direction.

For examination of model results of the properties of 3–3 piezocomposites, the piezoelectric phase was chosen to be PZT-5H, with  $d_{33} = 593 \text{ pC N}^{-1}$ ,  $d_{31} = -274 \text{ pC N}^{-1}$ ,  $\epsilon_{33}^T = 3400\epsilon_0$ ,  $s_{33}^{\text{PZT}} = 20.8$  and  $s_{11}^{\text{PZT}} = 16.4 \text{ pPa}^{-1}$ . The polymer was considered to be isotropic ( $s_{11}^{\text{Poly}} = s_{33}^{\text{Poly}}$ ) and a polymer elastic modulus ( $1/s_{11}^{\text{Poly}}$ ) of 6 GPa.

## 3. Results

### 3.1. Porosity anisotropy

The results presented here are for a polymer infiltrated 3–3 piezocomposite with a variety of different pores shapes (shown in Fig. 2), namely:

- (i) equiaxed pores ( $l_2 = l_1$ ) as shown in Fig. 2a,
- (ii) pores aligned parallel to the direction of poling ( $l_2 = 0.5l_1$  and  $l_2 = 0.25l_1$ ) as shown in Fig. 2b,

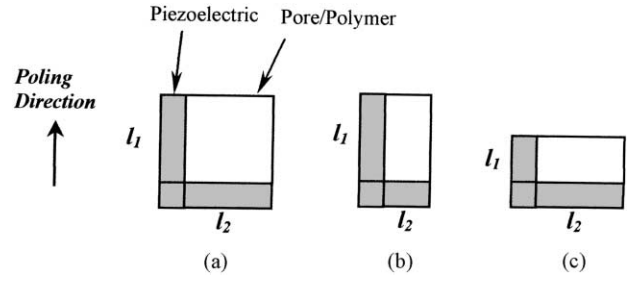


Fig. 2. Typical pore geometry analysed. (a) Equiaxed pores ( $l_1 = l_2$ ). (b) Pores aligned parallel to the direction of poling ( $l_2 = 0.5l_1$ ). (c) Pores aligned perpendicular to the direction of poling ( $l_2 = 2l_1$ ).

- (iii) pores aligned perpendicular to the direction of poling ( $l_2 = 2l_1$  and  $l_2 = 4l_1$ ) as shown in Fig. 2c.

Fig. 3 shows that the permittivity in the 3-direction of the composite is increased at a specific polymer volume fraction by having the pores aligned in the direction of poling. This is as would be expected due to the increased volume fraction of piezoelectric contributing to the permittivity of the composite, i.e. the vertical column of piezoelectric in Fig. 1b is effectively increased.

Fig. 4 shows that the hydrostatic strain constant,  $d_h$ , reaches a maximum at approximately 50–70% polymer volume fraction and it can be seen that the maximum is a function of pore anisotropy. As pores are elongated in the direction of poling the volume fraction of material contributing to  $d_{33}$  increases, which leads to an increase in  $d_h$  (again this is effectively due to the increase in the vertical column in Fig. 1b). This has been examined by Creedon and Schulze [13] who produced polymer foams with elongated pores which were coated with a PZT slurry and sintered. It was found that by producing a distorted

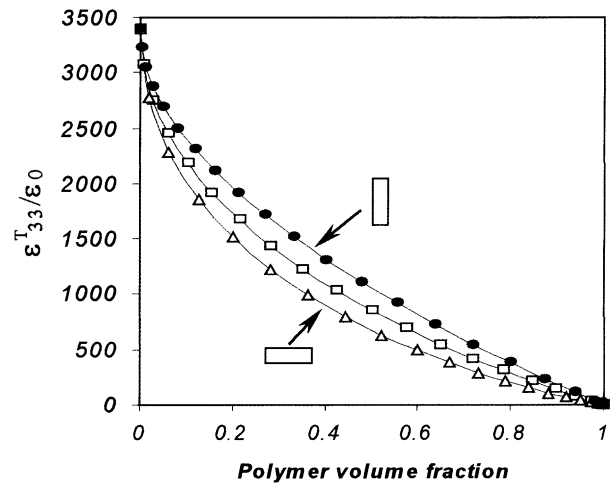


Fig. 3. Relative permittivity at constant stress as a function of polymer volume fraction for pore geometries of different morphology. (□)  $l_2 = l_1$ , (Δ)  $l_2 = 2l_1$ , (●)  $l_2 = 0.5l_1$ .

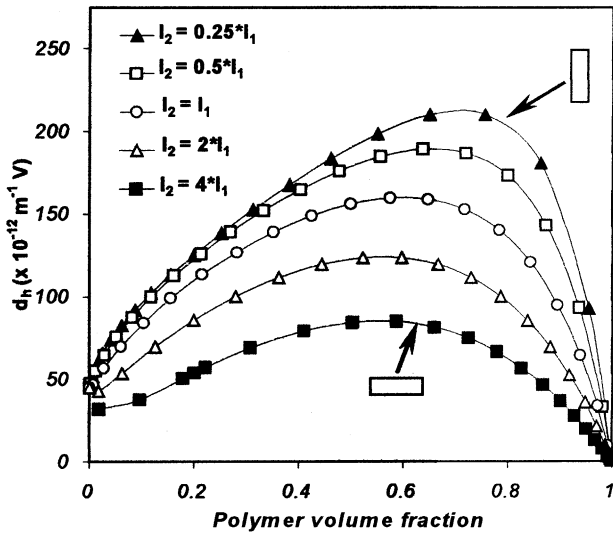


Fig. 4. Graph of hydrostatic strain constant ( $d_h$ ) versus polymer volume fraction for a 3–3 piezocomposite. Results are shown for equiaxed and elongated pores.

structure and aligning porosity in the poling direction, the hydrostatic properties ( $d_h$  and  $d_{hg_h}$ ) could be improved [14].

From Fig. 5, it is interesting to note that the value of  $g_h$  is not sensitive to pore shape. In this case, while alignment of pores parallel to the direction of poling leads to an increase in  $d_h$ , there is also a similar increase in the value of  $\epsilon_{33}^T$ . As  $g_h = d_h/\epsilon_{33}^T$ , there is no overall change in the hydrostatic voltage constant for elongated porosity. Finally Fig. 6, the hydrostatic figure of merit  $d_{hg_h}$  reaches a maximum at  $\sim 80\%$  polymer volume fraction and is increased by elongating pores in the direction of poling due to the increase in  $d_h$ .

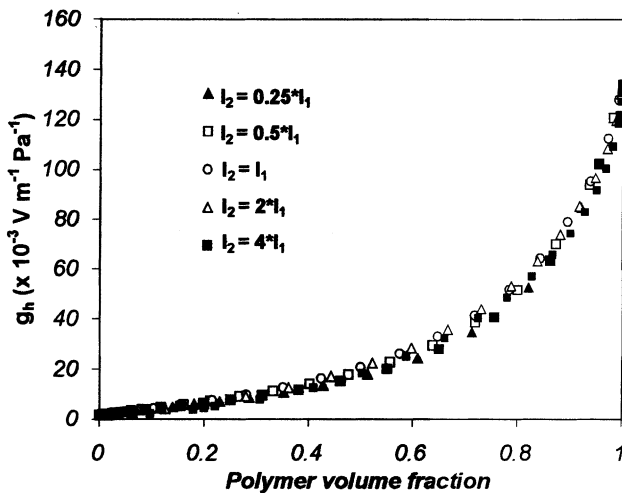


Fig. 5. Graph of hydrostatic voltage constant ( $g_h$ ) versus polymer volume fraction for a 3–3 piezocomposite with equiaxed and elongated pores.

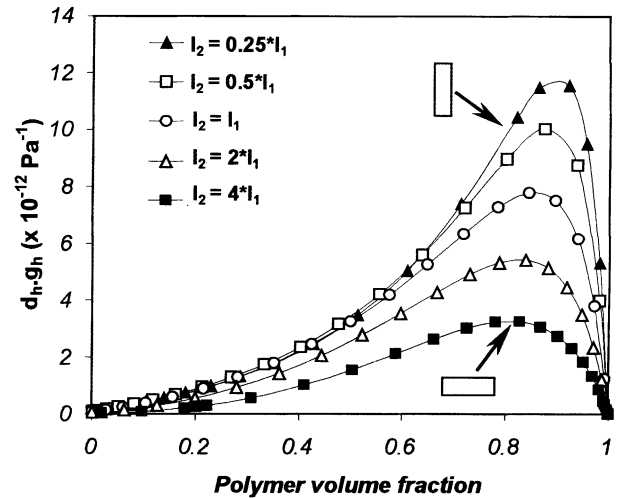


Fig. 6. Graph of hydrostatic figure of merit ( $d_{hg_h}$ ) versus polymer volume fraction for a 3–3 piezocomposite with equiaxed and elongated pores.

#### 4. Conclusions

Alignment of pores in the direction of poling results in an increase in  $\epsilon_{33}^T$ ,  $d_h$  and  $d_{hg_h}$ , due to an increase in the volume fraction of active material connected in the 3-direction. Pores shape did not greatly affect  $g_h$  as both  $\epsilon_{33}^T$  and  $d_h$  increased by similar amounts. The model is a useful tool for examination of microstructural and materials properties on the behaviour of 3–3 piezocomposites and can also be used to explain variations in hydrostatic behaviour due to the presence of directional cracking in these materials. The limitations of the model are the idealised structure of the model unit cell which may not fully represent manufactured 3–3 piezocomposites (the foams used to produce these composites are pentagonal dodecahedra [13]) and the assumption of the piezoelectric material being fully poled.

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#### References

- [1] V.F. Janas, A. Safari, J. Am. Ceram. Soc. 78 (1995) 2945.
- [2] R.E. Newnham, D.P. Skinner, L.E. Cross, Mater. Res. Bull. 13 (1978) 525.
- [3] T.R. Shrout, W.A. Schluz, J.V. Biggers, Mater. Res. Bull. 14 (1979) 1553.
- [4] D.P. Skinner, R.E. Newnham, L.E. Cross, Mater. Res. Bull. 13 (1978) 599.
- [5] P. Guillaussier, C.A. Boucher, Ferroelectrics 187 (1996) 121.
- [6] J. Bennett, G. Hayward, IEEE Trans. Ultra. Ferro. Freq. Contr. 44 (1997) 565.

- [7] H.R. Gallantree, *Br. Ceram. Proc.* 41 (1989) 161.
- [8] F. Levassort, M. Lethiecq, R. Desmare, L.P. Tran-Hue, *IEEE Trans. Ultra. Ferro. Freq. Contr.* 46 (1999) 102.
- [9] M.L. Dunn, M. Taya, *J. Am. Ceram. Soc.* 76 (1993) 1697.
- [10] K. Rittenmyer, T. Shrout, W.A. Schulze, R.E. Newnham, *Ferroelectrics* 4 (1982) 189.
- [11] H. Banno, *Jpn. J. Appl. Phys.* 32 (1993) 4214.
- [12] C.R. Bowen, H. Kara, S.W. Mahon, *J. Eur. Ceram. Soc.* 21 (2001) 1463.
- [13] M.J. Creedon, W.A. Schulze, *Ferroelectrics* 153 (1994) 333.
- [14] M.J. Creedon, S. Gopalakrishnan, W.A. Schulze, in: R.K. Pandey, M. Liu, A. Safari (Eds.), *Proceedings of the Ninth IEEE International Symposium on Applications of Ferroelectrics (ISAF'94)*, IEEE Press, New York, 1994, pp. 299–302.