ANALYTIC MODEL FOR 0-3 CONNECTIVITY PIEZOELECTRIC COMPOSITES

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1. Introduction

Theoretical modelling of 0-3 connectivity composites involves a model of piezoelectric spheres randomly dispersed in a dielectric continuum and describing the dielectric, elastic and piezoelectric parameters of the composite in terms of the parameters of its constituents and their volume content in the composite. Available analytic predictions based on the spherical particle model for the dielectric and piezoelectric constants of composites agree with experimental data for ceramic volume fractions up to about 0.2. However, at high volume fractions the analytic predictions differ when compared with experimental data.

In this paper the results of a theoretical model for the dielectric and piezoelectric parameters of a binary 0-3 composite are presented which give predictions that compare very favourably with experimental data at high volume fractions of ceramic. The model is then used to predict additional factors observed in real composites, such as porosity and the effect of ceramic particle size. The model is also used to investigate the optimum hydrostatic performance of composites.

2. Theoretical Considerations and Comparison with Experimental Data

2.1. Dielectric Constant

Consider a binary 0-3 composite model comprising piezoelectric spheres of dielectric constant ε_2 randomly dispersed in a dielectric continuum (matrix) of dielectric constant ε_1 where $\varepsilon_2 \gg \varepsilon_1$. The volume fraction of spheres and the continuous medium are v_2 and v_1 respectively and $v_1 + v_2 = 1$. The composite is subject to an externally applied electric field E_0 in the z direction. Of the several analytic formula quoted in the literature, the formula of Landauer [1] and Kerner [2] are claimed to be valid for large

ANALYTIC MODEL FOR 0-3 CONNECTIVITY PIEZOELECTRIC COMPOSITES

volume fractions of spheres. The Landauer and Kerner analytic model predictions are compared with the experimental data of Yamada et.al.[3] in Fig 1, for a PZT/PVDF composite.

The theory of Kerner, though it underestimates it does give much better agreement with experimental data than that of Landauer, so the Kerner theory has been adapted for high volume fractions of ceramic.

With the composite dielectric constant denoted by ε, the Kerner formula for a 2-phase composite is given by,

$$\varepsilon = \varepsilon_1 v_1 \frac{E_1}{E} + \varepsilon_2 v_2 \frac{E_2}{E} \qquad (1)$$

where E_1 and E_2 are the average electric fields in material 1 and material 2 respectively in the z direction and $E = v_1E_1 + v_2E_2$. In the Kerner model the average electric fields are determined for the case of an isolated dielectric sphere of material 2 surrounded by a dielectric medium of material 1 and given by [4],

$$E_1 = E_0$$
$$E_2 = \frac{3\varepsilon_1}{2\varepsilon_1 + \varepsilon_2} E_0 \qquad (2)$$

Since the Kerner model is based on an isolated dielectric sphere in a dielectric continuum, the predictions by Eqs (1) and (2) give agreement with experimental data for low volume fractions of spheres when the spheres are far apart. However, at high volume fractions when the spheres are closer together, the prediction by the Kerner model underestimates the experimental data because the interaction between the spheres has not been included in the formula.

The Kerner formula has been modified by modifying the electric field inside the sphere to include interactions. The modified fields have been shown to be given by [5],

$$E_1 \simeq E_0 \quad \text{for } \varepsilon_2 \gg \varepsilon_1$$
$$E_2 = \frac{3\varepsilon_1}{2\varepsilon_1 + \varepsilon_2} \left[1 + 3v_2 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} \right] E_0 \tag{3}$$

In Eq (3), the second term within the brackets for E_2 represents the interaction term. The predictions by Eqs (1) and (3) for ε are compared with two sets of experimental data of Yamada et.al.[3] for a PZT/PVDF composite and Garner et.al.[6] for a Modified Lead Titanate (MPT)/Epoxy composite in Figs 2 and 3, where the composite dielectric constant normalized w.r.t. the dielectric constant of the polymer matrix is plotted as a function of the volume fraction of ceramic in the composite.

Excellent agreement is shown with experimental data when the interactions between spheres are included in the Kerner formula.

2.2. Piezoelectric Constant

By considering the same spherical particle model as described above the composite piezoelectric constant d can be shown to be given by [7],

$$d = v_2 d_2 \frac{T_2}{T} \frac{\varepsilon}{\varepsilon_2} \left[1 + 3v_2 \frac{\varepsilon_2}{2\varepsilon_1 + \varepsilon_2} \right] \tag{4}$$

where d_2 is the piezoelectric constant of the spheres, T the applied stress to the composite and T_2 the average stress in the piezoelectric spheres.

Eq (4) is in the same form as that developed by Furukawa et.al.[8], but with the electric field interaction between spheres included by the second term within the brackets.

The stress ratio T / T has been shown to be given by [8],

$$\frac{T_2}{T} = \frac{1}{v_2} \frac{c_2}{c} \frac{c - c_1}{c_2 - c_1} \tag{5}$$

where c, c_1 and c_2 are the elastic stiffness constants for the composite, matrix and ceramic phases respectively. As a first approximation at high volume fractions of ceramic v_2, assuming $c, c_2 \gg c_1$,

ANALYTIC MODEL FOR 0-3 CONNECTIVITY PIEZOELECTRIC COMPOSITES

$$\frac{T_2}{T} \simeq \frac{1}{v_2} \qquad (6)$$

Substituting Eq (6) in Eq (4) gives,

$$d \simeq d_2 \frac{\varepsilon}{\varepsilon_2} \left[1 + 3v_2 \frac{\varepsilon_2}{2\varepsilon_1 + \varepsilon_2} \right] \qquad (7)$$

Using the analytic formula for the dielectric constant ε given by Eq (1) and (3), the prediction by Eq (7) is compared with the experimental data of Yamada et.al.[3] for the d_{31} constant of a PZT/PVDF composite as a function of volume fraction of ceramic in Fig 4. The agreement is good.

2.3. Piezoelectric Hydrostatic Constants

The hydrostatic constant g_h can be calculated from the relation $g_h = d_h / (\varepsilon\varepsilon_0)$ where $d_h = d_{33} + 2d_{31}$ is the hydrostatic d constant, ε the dielectric constant and ε_0 the permittivity of free space. The predictions for g_h are compared with the experimental data of Garner et.al.[6] for a modified Lead Titanate (MPT)/Epoxy composite in Fig 5. The experimental data shown are for the maximum polarizing field in Ref [6]. The agreement is encouraging.

Hydrostatic sensitivity measurements on MPT/Epoxy composite samples with dimensions 29.5mm x 29.5mm x 0.3mm were carried out in the laboratory by using an acoustic chamber of dimensions 125mm x 125mm x 82mm, which was mounted with a moving coil loudspeaker used as a transmitter operating at 75 Hz. The test chamber was calibrated with a B & K Pistonphone Type 4220 of known sensitivity. The sensitivity of the samples were then measured by comparing the output of the samples with a B & K Hydrophone Type 4145. The dielectric constants of the samples were calculated from capacitance measurements.
The measured values for ε, g_h and d_h were 31.2, 87.85 $mVmN^{-1}$ and 26.6 pCN^{-1}respectively compared to the predicted values from the analytic model of 36.4, 80.48 $mVmN^{-1}$ and 25.9 pCN^{-1} respectively for a volume fraction of ceramic $v_2 = 0.62$.

ANALYTIC MODEL FOR 0-3 CONNECTIVITY PIEZOELECTRIC COMPOSITES

3. Additional Factors

3.1. Effect of Porosity on the Dielectric Constant

When there are air inclusions in the ceramic/matrix composite, it has to be considered as a 3-phase system, and consequently Eq (1) for a 2-phase composite is modified to

$$\varepsilon = \varepsilon_1 v'_1 \frac{E_1}{E} + \varepsilon_2 v'_2 \frac{E_2}{E} + \varepsilon_3 v_3 E_3 \qquad (8)$$

where v'_1 and v'_2 are the modified volume fractions of phase 1 and 2 due to the presence of phase 3 of volume fraction v_3, E_3 is the average field in phase 3 and the average field in the composite $E = v'_1E_1 + v'_2E_2 + v_3E_3$. The modified volume fractions v'_1 and v'_2 can be shown to be given by [9],
$v'_1 = v_1(1 - v_3)$ and $v'_2 = v_2(1 - v_3)$.

The field E_3 can be estimated for the two limiting cases of the air inclusion being completely surrounded by the ceramic phase and the matrix phase respectively using the expression given in Eq (2) and Eq (3). The field E_3 calculated for when the air inclusion is completely surrounded by the ceramic phase is much smaller than that calculated for the air inclusion being completely surrounded by the matrix phase, and therefore only the case for the air inclusion surrounded by the matrix phase need be considered. For this case $E_3 = 1.29\ E_0$. The volume fraction of air inclusions has been empirically determined to give reasonable agreement with experimental data. It is found that using a polynomial expression for v_3 given by,

$$v_3 = 2.56 \times 10^{-4} - 4.23 \times 10^{-2} v_2 + 1.24\ v_2^2 \qquad (9)$$

for $v_2 > 0.4$ in Eq (8) and $E_3 = 1.29\ E_0$ give reasonable agreement with experimental data as shown in Fig 6, where the prediction by the 2-phase composite model is also shown for comparison. The spread in the experimental data is due to several measurements being made on batches of composites [10]. The porosity in one of the samples of these composites were estimated by SEM photographs and the measured porosity data is compared with the prediction by Eq (9) in Fig 7.

ANALYTIC MODEL FOR 0-3 CONNECTIVITY PIEZOELECTRIC COMPOSITE

3.2. Effect of Particle Size

The analytic expressions given previously for the dielectric and piezoelectric constants assume a true 0-3 connectivity model for the composite. This is indeed likely to be the case in a composite where the ceramic particle size is small compared to the thickness of the composite. However, when the average ceramic particle size is comparable to the thickness of the composite and at high volume fractions of ceramic it is possible that there is some 1-3 connectivity associated with the ceramic phase. For such composites a 0-3/1-3 mixed connectivity model is considered.

Recent experimental work has used Quenched Modified Lead Titanate (QMPT) ceramic powder in an epoxy matrix. The QMPT particle size distribution is compared to the thickness of the composite in Fig 8, where the calcined MPT particle sizes considered previously are also shown for comparison [11]. As shown in Table 1, columns 2,3 and 5,6 the predictions by the pure 0-3 connectivity model for the QMPT/Epoxy composite underestimate the measured dielectric constant and piezoelectric constant respectively.

The 0-3/1-3 mixed connectivity model assumes that part of the ceramic phase in the composite is in 1-3 connectivity and that the remainder mixes with the matrix phase in 0-3 connectivity. This results in the ceramic 1-3 connectivity phase and the 0-3 connectivity phase being in 1-3 parallel connectivity [12,13]. By empirically determining that part of of the ceramic phase in 1-3 connectivity and using available analytic models for parallel 1-3 connectivity composites [12,13], the prediction by the 0-3/1-3 mixed connectivity model are given in columns 4 and 7 of Table 1, with the empirically determined 1-3 connectivity ceramic phase as a percentage of the total ceramic in the composite given in column 8,[7]. It is to be noted that the same 1-3 connectivity percentages are used in calculating both the dielectric and piezoelectric constants.

4. Hydrophone Material Hydrostatic Figure of Merit, dg

The hydrophone material constant dg under hydrostatic conditions is defined as the product of the hydrostatic constants d_h and g_h where

$d_h = d_{33}+2d_{31}$ and $g_h = g_{33}+2g_{31} = d_h /(\varepsilon\varepsilon_0)$. The prediction for the dg product by the 0-3 connectivity model is compared with three sets of published experimental data [6,14,15] for different volume fractions and materials in Fig 9, where the dg product of the composite normalized w.r.t. the dg product of the ceramic is plotted as a function of the matrix dielectric constant ε_1. It is observed that good agreement is found with the limited experimental data.

The prediction from the 0-3/1-3 mixed connectivity model for the dg product of the composite normalized w.r.t. the dg product of the ceramic is compared with the measured data for the QMPT/Epoxy composite [10] in Table 2, where again reasonable agreement is found between predicted and measured data.

5. Conclusions

The predictions by the analytic model for 0-3 connectivity composites which include interactions between spheres give excellent agreement with experimental data for the composite dielectric and piezoelectric constants. The analytic expressions have also been used to predict additional factors observed in real composites such as porosity and particle size, and the predictions compare favourably with experimental data. The analytic expressions have also been used to predict the optimum hydrostatic performance of composites.

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ANALYTIC MODEL FOR 0-3 CONNECTIVITY PIEZOELECTRIC COMPOSITES

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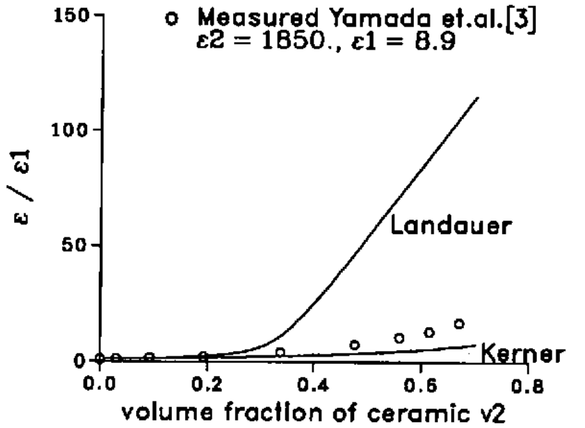

Fig 1. Landauer and Kerner Models compared with experimental data of Yamada et.al.[3]

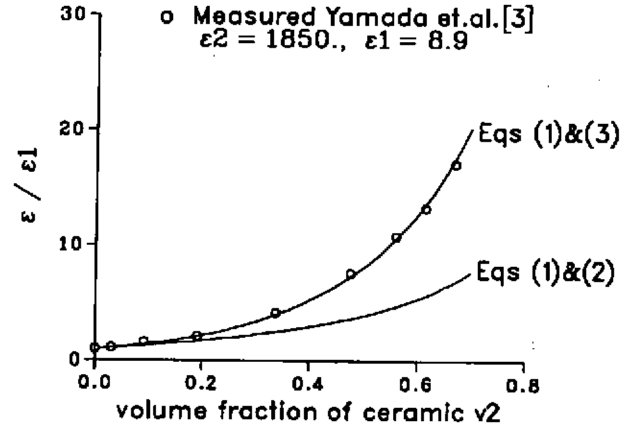

Fig 2. Prediction by Eqs (1) and (3) compared with experimental data of Yamada et.al.[3]

ANALYTIC MODEL FOR 0-3 CONNECTIVITY PIEZOELECTRIC COMPOSITES

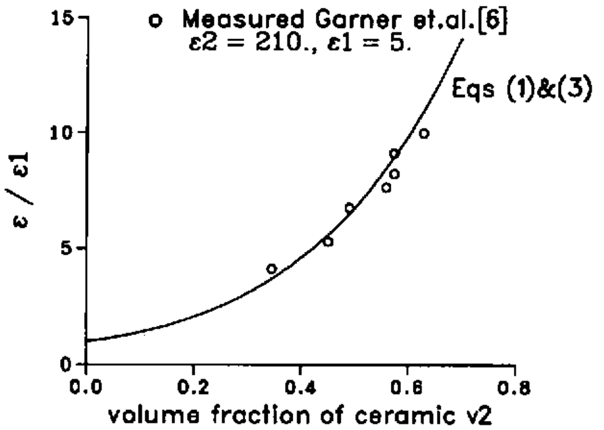

Fig 3. Prediction by Eqs (1) and (3) compared with experimental data of Garner et.al.[6]

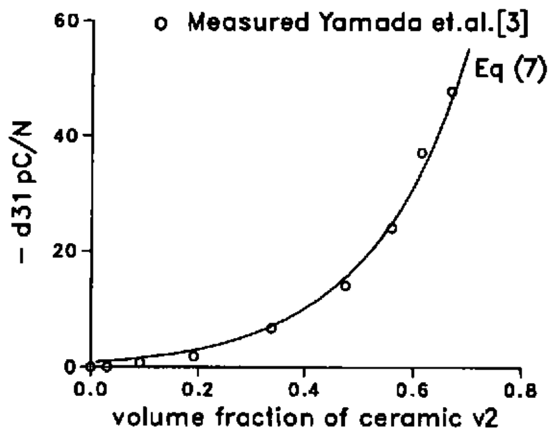

Fig 4. Prediction by Eq (7) compared with experimental data of Yamada et. al.[3]

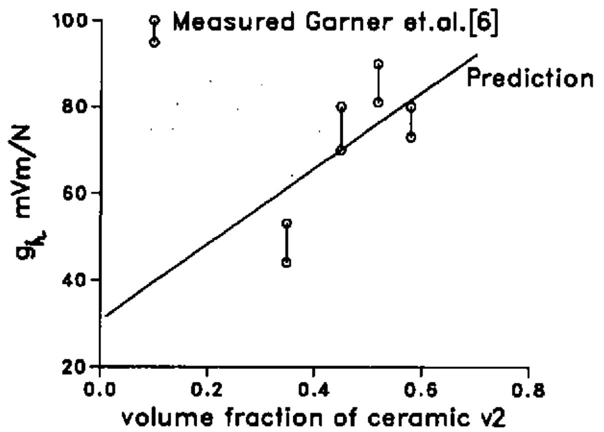

Fig 5. Prediction compared with the experimental data of Garner et.al.[6] for the g_h constant

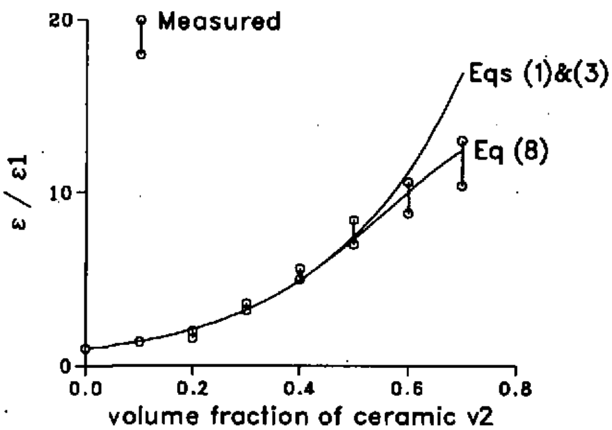

Fig 6. Prediction by Eq (8) showing the effect of porosity on the composite dielectric constant

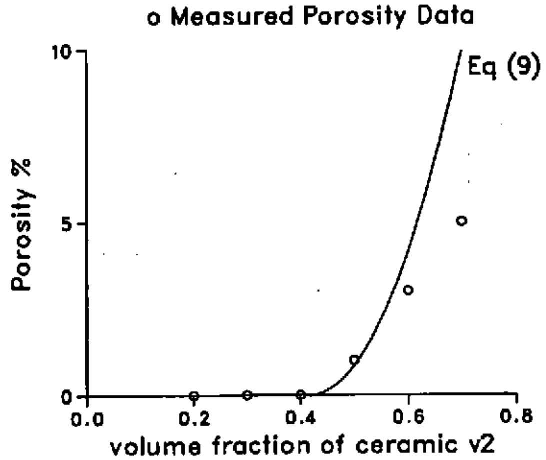

Fig 7. Eq (9) compared with measured porosity data

ANALYTIC MODEL FOR 0-3 CONNECTIVITY PIEZOELECTRIC COMPOSITES

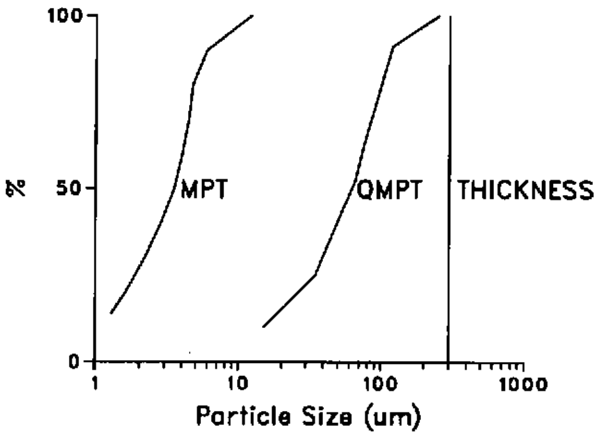

Fig 8. Particle size data for calcined and Quenched MPT

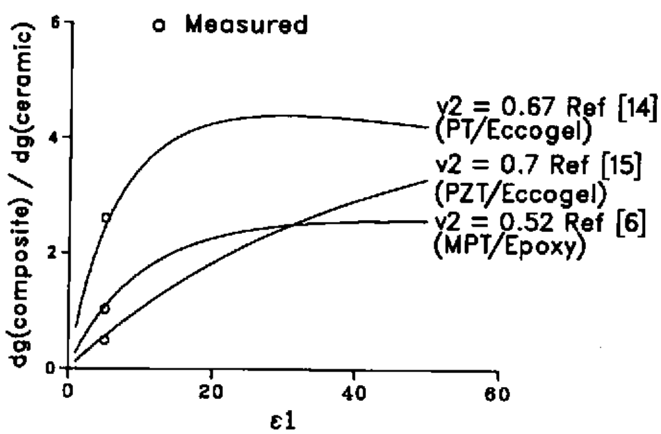

Fig 9. Prediction for the dg product compared with published experimental data [6,14,15]

TABLE 1

QMPT/EPOXY COMPOSITE

ceramic %	ε			d_{33} pC/N			1-3 %
	measured	prediction 0-3	prediction 0-3/1-3	measured	prediction 0-3	prediction 0-3/1-3	
50	35	22.3	35.1	31	14.5	29.7	8
60	53	33.5	52.9	40	25.1	38.7	13.5
70	71	50.8	71	46	42.8	46.6	17

TABLE 2

Normalized dg product for QMPT/Epoxy Composite

ceramic %	measured	predicted	1-3 %
50	1.12	1.38	8
60	1.58	1.54	13.5
70	1.49	1.65	17