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THE FABRICATION AND CHARACTERISATION OF 0-3 COMPOSITES

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1.INTRODUCTION

Piezoelectric ceramic - polymer composites have been the subject of a considerable research effort over recent years [1,2,3]. 1-3 composites in which the ceramic rods are aligned within a polymer matrix are of interest for both medical and sonar applications [4,5]. Whilst such transducers offer good performance, their fabrication is both time consuming and expensive. 0-3 composites consisting of a piezoelectric ceramic powder dispersed in a polymer matrix offer the potential for lower cost, larger area devices compared with 1-3 types. However, polarisation of the ceramic grains within the polymer is not easily accomplished. Using a simple model, this paper discusses the effect of the electrical properties of the ceramic and the polymer on the field distribution within the composite. The model is then tested experimentally and the results compared with the theoretical predictions.

2.COMPOSITE THEORY

2.1 Introduction

The aim of much composite research has been to fabricate new piezoelectric materials with improved d and g coefficients.

The d coefficient relates the strain, X, generated by an applied electric field, E, by the equation

$$X = dE \qquad (1)$$

Transmitting transducer applications require high d coefficients.

The g coefficient relates the electric field, E, resulting from applied stress, T, by the equation

$$E = gT \qquad (2)$$

Receiving transducer applications require high g coefficients.

For applications where the same transducer is used for both transmit and receive functions, a useful figure of merit is the product, dg.

Both d and g are related to the compliance, s, the permittivity, ϵ, and the coupling coefficient, k, of the material by the relationships

$$d = k(\epsilon s)^{\frac{1}{2}} \qquad (3)$$

$$g = k(s/\epsilon)^{\frac{1}{2}} \qquad (4)$$

$$dg = k^2 s \qquad (5)$$

Piezoelectric polymers such as PVDF have low ϵ and high s making them useful as receiving transducers, but have rather low coupling coefficients. Piezoelectric ceramics have high coupling and permittivity making them useful as transmitting transducers, but have only low compliance. One of the driving forces for composite research has been the prospect of producing high coupling, high compliance materials with higher d and g coefficients than are obtainable from either the best piezoelectric ceramics or the best polymers.
The microstructure of 0-3 composites is such that each ceramic particle is isolated from its neighbours by a continuous polymer matrix. To obtain a high degree of polarisation of the ceramic grains, large applied fields may be required which can cause electrical breakdown. An analysis of the field distribution within the material as a function of the electrical properties of the component phases is necessary. This is discussed below.

2.2 Field Distribution in a Two Phase Dielectric

Consider a simple two phase dielectric in which a slab of dielectric, permittivity ϵ_1, resistivity ρ_1, is sandwiched between two slabs of a different dielectric, permittivity ϵ_2, resistivity ρ_2 (Fig.1).
If an electric field, E, is applied normal to the boundary, then time at t=0.

$$E_1\epsilon_1 = E_2\epsilon_2 \qquad (6)$$

i.e. the field is concentrated in the low permittivity phase. If this field is maintained such that conduction can take place, then at time t = infinity.

$$\frac{E_1}{\rho_1} = \frac{E_2}{\rho_2} \qquad (7)$$

i.e. the field is concentrated in the high resistivity phase.
For the two phases, relative permittivites between 200 and 5000 for ceramics and between 1 and 10 for most polymers are typical.
Thus, at best the field in the ceramic would only be 1/20 of that in the polymer. In contrast, resistivities in the range 10^{10} to $10^{13}\Omega$m for ceramics and 10^{9} and $10^{15}\Omega$mfor polymers can be obtained.
This wide range of polymer resistivities suggests that the best way to improve the field in the ceramic is to carefully select a polymer of comparable or lower resistivity. However, a simple series model of dielectric slabs is inappropriate for the situation of isolated ceramic grains in a polymer matrix. A more realistic model is considered in the next section.

2.3 Simple Model of 0-3 Composite

In this model, cubic ceramic grains of side G, resistivity ρ_c are embedded in a polymer matrix, resistivity ρ_p. Each grain is arranged in a perfect three dimensional pattern being separated from its nearest neighbour by a film of polymer of thickness δ. This idealised arrangement can then be reduced to a single grain surrounded by polymer (Fig.2).

This geometry can be represented by a resistor network (Fig.3) in which R_G is the resistance of the grain, R_{ps} is the resistance of the polymer slabs in series with the grain and R_{pp} the resistance of the polymer surrounding the sides of the grain. In this way R_{pp} shunts R_G.

The objective of the model is to predict the ratio of the field in the ceramic grain, E_G, to the applied field E, as a function of ρ_c and ρ_p.

Clearly

$$\frac{E_G}{E} = \frac{V_G/G}{V/(G+\delta)} \tag{8}$$

where V_G is the voltage across the ceramic grain

V is the applied voltage

$$\frac{V_G}{V} = \frac{R}{2R_{ps} + R} \tag{9}$$

where

$$\frac{1}{R} = \frac{1}{R_g} + \frac{1}{R_{pp}} \tag{10}$$

Now

$$R_G = \frac{\rho_c}{G} \tag{11}$$

$$R_{pp} = \frac{\rho_p G}{\delta(2G + \delta)} \tag{12}$$

and

$$R_{ps} = \frac{\rho_p(\delta/2)}{(G + \delta)^2} \tag{13}$$

Subs (11), (12) and (13) in (10), (10) in (9) and (9) in (8) gives

$$\frac{E_G}{E} = \frac{1}{1 + \frac{G^2\delta}{(G + \delta)^3}\left(\frac{\rho_p}{\rho_c} - 1\right)} \tag{14}$$

The volume fraction, V_f, of ceramic in the composite is given by

$$V_f = \frac{G^3}{(G + \delta)^3} \tag{15}$$

Subs (15) into (14)

$$\frac{E_a}{E} = \frac{1}{1 + V_f \left(\frac{1}{V_f^{1/3}} - 1\right)\left(\frac{\rho_p}{\rho_c} - 1\right)} \qquad (16)$$

A plot of the field ratio $\frac{E_a}{E}$ vs.the resistivity ratio, $\frac{\rho_p}{\rho_c}$, (Fig.4) reveals the folowing:-

1) For a resistivity ratio >1, E_a/E falls off sharply as the ratio increases.

2) For a resistivity ratio <1, E_a/E only increases slowly as the ratio decreases.

3) For the ranges of V_f of interest (0.3 to 0.7), V_f has little effect on the E_a/E values.

This model demonstrates the importance of selecting a polymer with a resistivity similar to or less than that of the ceramic. Little benefit is to be gained from using too low a resistivity polymer, however, because of

(a) the risk of thermal breakdown of the composite during poling increases with decreasing resistivity.

(b) low resistivity gives the composite a high loss tangent (high self noise).

In the next section the fabrication of composites and testing of the model are described.

3.FABRICATION OF 0-3 COMPOSITES

3.1 Selection of Ceramic

For hydrophone applications it has been proposed that the appropriate figure of merit, (FOM), is the product $d_h g_h$. Lead zirconate titanate ceramics often have a poor FOM because of their low d_h value. The lead titanate family of piezoelectric ceramics have near zero d_{31} giving good d_h and high FOM. On this basis, a modified lead titanate (MPT) powder was selected to be the piezoelectric phase with composition $Pb_{0.76}Ca_{0.24}TiO_3$ plus additives designed to promote liquid phase sintering and maximise the electrical resistivity. This material can be sintered into dense components whose piezoelectric characteristics are assumed to be identical to those of the powder. The electrical resistances of electroded MPT discs were measured in a silicone oil bath over the temperature range 20-110°C using an EIL twenty million megohmmeter. From the disc dimensions the resistivities were calculated (Fig.5). A room temperature resistivity of $10^9\Omega m$ was found for MPT.

3.2 Selection of Polymer.

From the model described above, a suitable polymer for the composite is one with a resistivity similar to or lower than that of the MPT.

Whilst many polymers have resistivities of as high as $10^{15}\Omega m$, epoxy resins have resistivities in the range $10^{9}-10^{10}\Omega m$. Epoxies also have the advantage of low uncured viscosities (0.2-3.0 Pas) which permit the incorporation of volume fractions of ceramic powder greater than 50% with relatively simple processing techniques. For this work a cold curing epoxy (Araldite CY1311, plus hardener HY1300, Ciba Geigy) was chosen. Discs of this resin were cast and electroded prior to resistance measurements which were conducted as for the MPT samples. The results (Fig.5) show the room temperature resistivity of the epoxy to be 5 x $10^{9}\Omega m$. The resistivity of the epoxy and the MPT were equal at 30°C.

3.3 Composite Fabrication.

MPT powder was produced using the mixed oxide route. This was dry ball milled for 3 hrs to give a particle size distribution of 100%<5µm. Gas pycnometry was used to determine the powder density of $7.272 gcm^{-3}$.

Quantities of ceramic powder, resin and hardener were prepared to give $V_f=0.55$, loaded into a sigma blade shear mixer and mixed for 30 minutes. The resulting compound was placed between two flat aluminium plates lined with release paper and loaded into a press. A high pressure was applied to form a sheet of the required thickness, the pressure was reduced and the sheet left to cure for 16 hours. The sheet was then removed from the press and left at room temperature for a further 32 hours to complete the curing schedule. Test pieces 35mm square x 0.3-2.0mm thick were cut from the sheets and furnished with 100nm thick evaporated aluminium electrodes. These test pieces were then used for the poling experiments.

3.4 Polarisation of Composites

Polarisation was carried out in a stirred silicone oil bath at temperatures of between 45 and -15°C using a 30kV stabilized d.c. high voltage supply (Brandenburg). The temperature was controlled to ±1°C and the voltage measured using an ultra high impedance voltmeter (Brandenburg, model 139D) to ±10V. A polarisation time of 20 minutes was used. For the composite test pieces, a field of $10kVmm^{-1}$ was applied. As the temperature was expected to significantly affect the degree of polarisation of the ceramic grains, a control experiment was conducted using dense sintered discs of MPT. These were subjected to a field of $4kVmm^{-1}$ for 20 mins over the same temperature range. The d_{33} of all samples were measured immediately after poling (Berlincourt d_{33} meter). Using this method the MPT discs represented the maximum degree of polarisation achievable at any temperature.

4. RESULTS AND DISCUSSION

The results of the polarisation experiments (Table 1) can best be assessed by examining the ratio d_{33} (MPT)/d_{33} (Composite) as a function of temperature. This ratio (Fig.6) is constant at 0.45 for temperatures greater than 20°C, whilst below this temperature the ratio rapidly declines to zero at -15°C. These findings are consistent with the predictions of the model. According to the model and the resistivity measurements (Fig.5) at temperatures of less than 30°C the resistivity ratio is greater than one and the ratio E_a/E falls quickly.

At -15°C the field distribution is so adverse as to prevent any polarisation of the ceramic grains.

5.CONCLUSIONS

A model has been presented which proposes that the resistivities of the ceramic and polymer phases control the field distribution within a 0-3 composite. This model predicts that the resistivity ratio ρ_p/ρ_c should be equal to or greater than 1 to obtain a favourable polarising field within the ceramic. The good agreement between the theory and the experimental results supports the model and suggests that such an approach can be usefully employed in the optimisation of the 0-3 composites.

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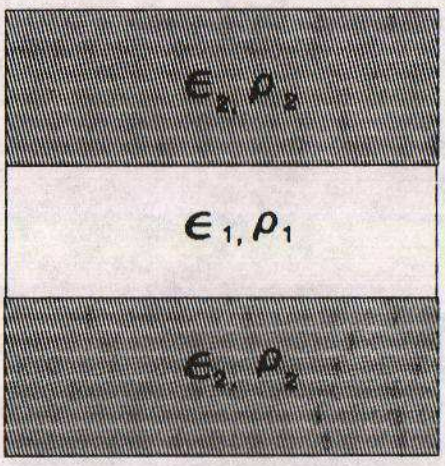

Fig.1 Field Distribution in a Two Phase Dielectric

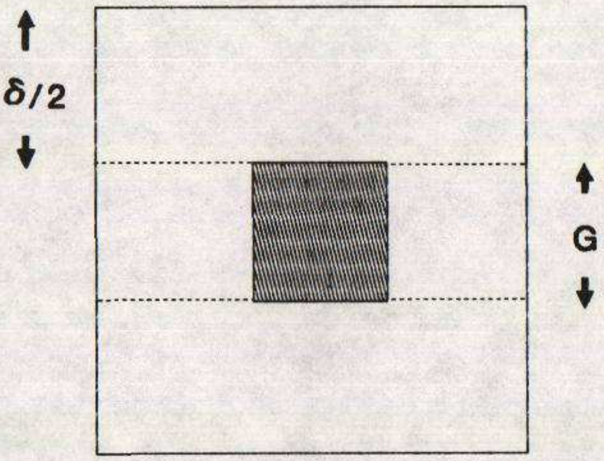

Fig.2 Simple Model of Ceramic Grain in Polymer Matrix

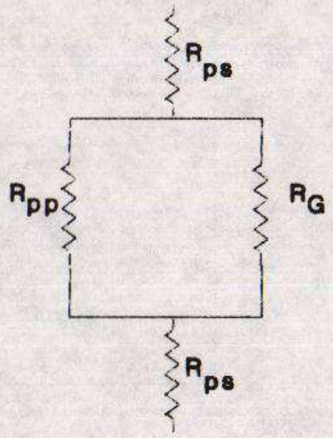

Fig.3 Resistor network model

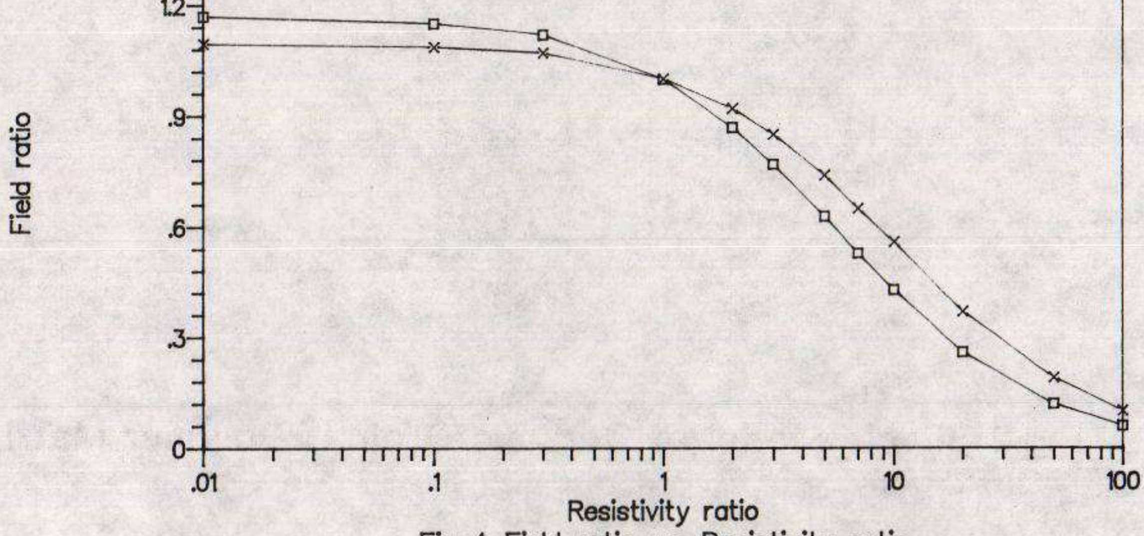

Fig 4 Field ratio vs. Resistivity ratio

0-3 COMPOSITES

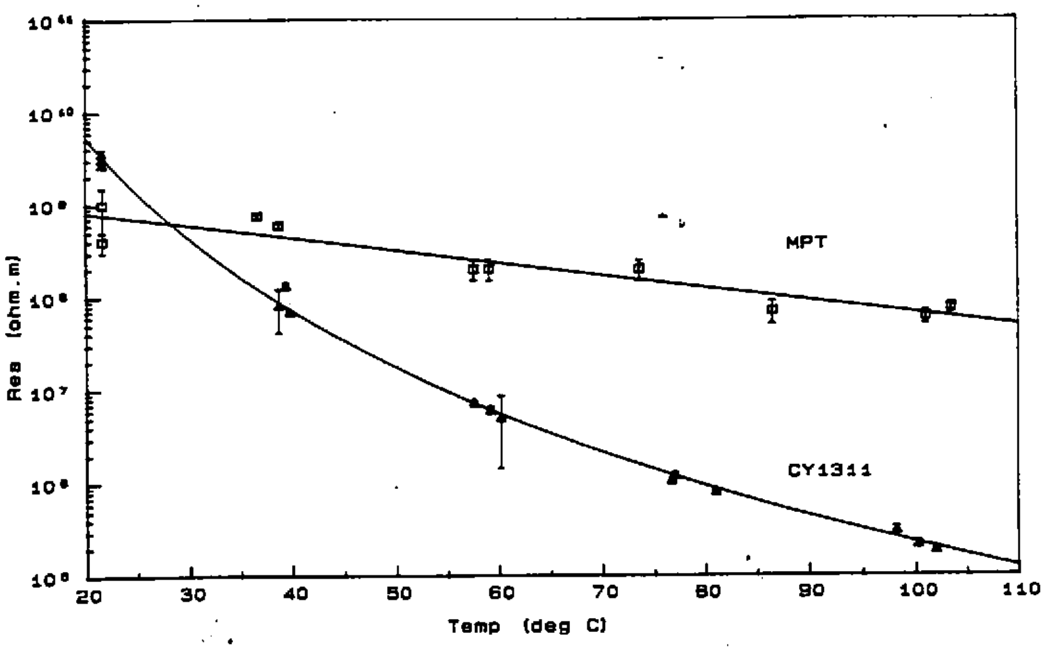

Fig 5 Resistivity vs. Temperature for MPT & CY1311

Table 1

T/°C	d_{33}/pCN^{-1}		d_{33} ratio
	MPT	Composite	
-15	18	0	0
-1	24	6	0.25
20	30	12	0.40
31	39	18	0.46
43	56	25	0.45

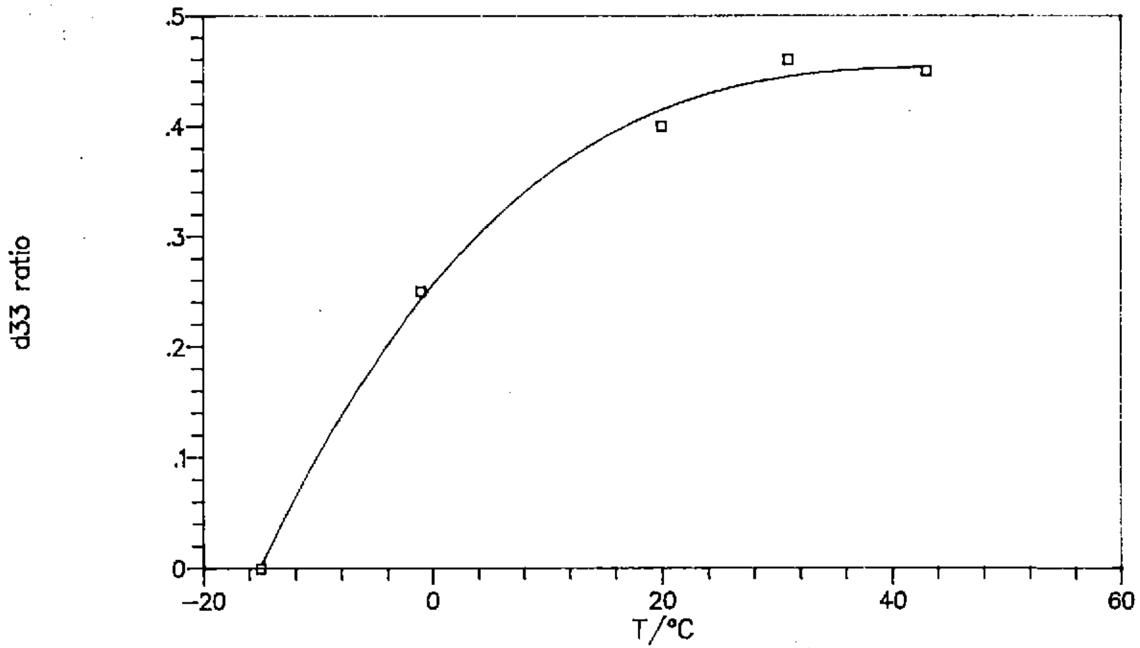

Fig 6 d33 ratio as a function of poling temperature