THE EFFECT OF ELECTRODE MATERIALS ON MEASURED PIEZOELECTRIC PROPERTIES OF CERAMICS AND CERAMIC-POLYMER COMPOSITES

S. Sherrit, N. Gauthier, H.D. Wiederick and B.K. Mukherjee
Royal Military College of Canada
Kingston, Ontario, Canada, K7K 5L0

and

S.E. Prasad
B.M. Hi-Tech Inc.
P.O. Box 97, Collingwood, Ontario, Canada

Abstract

We have investigated the effect of electrodes on the measurement of dielectric, piezoelectric and mechanical properties of PZT ceramics and of 1-3 connectivity ceramic-polymer composites. While fired silver and evaporated silver electrodes were found to have little effect on the measurements, silver epoxy electrodes resulted in a significant reduction in the measured values of the dielectric and piezoelectric constants. In the 1-3 composites the effect is independent of the ceramic content. Our observations can be understood on the basis of a model which takes account of the capacitance at the ceramic-electrode interface due to the presence of pores and binder material. It is clearly important to consider the effect of the electrodes when characterising new materials, such as 1-3 composites, using air dried electrodes. We have found that the effect of the electrodes can be nullified by the deposition of a thin metal film on the specimen before the electrode is applied.

I. Introduction

A variety of new piezoelectric materials such as ceramic-polymer composites [1,2] and piezoelectric polymers [3] have material characteristics that make them attractive for use in sonar hydrophones. A particularly desirable feature of these materials is their flexibility which makes them suitable for use in hull-mounted or towed sonar arrays. It is therefore important to use flexible electrodes on these materials.

The requirements for a good electrode on a rigid piezoelectric material are discussed in the IEEE standard on piezoelectricity [4] and they ensure the proper determination of the material constants from measurements of the impedance as a function of frequency. It is necessary that the impedance of the electrode be much less than that of the specimen and that acoustic resonances in the electrode occur at frequencies that are much higher than the measurement frequency. The more commonly used electrodes include neoprene, silver epoxy and various silver prints and paints. These electrodes are a mixture of a conducting material (carbon, silver) and a dielectric binder (polymer). The conducting properties of the electrode are due to the contact from grain to grain of the conducting phase. In the case of paints and prints, the electrode is meant to be fired so that the binder is driven out; however, if the firing temperature is below the sintering temperature, small pores may be left in the electrode and these pores affect the measurement of the material characteristics of the specimen.

As an example of the effect of electrodes on the measurement of material characteristics, Figure 1 shows the measured dielectric constant of a set of 1-3 connectivity PZT-polymer composites with silver epoxy [9] electrodes plotted as a function of volume % PZT in the specimen. The PZT used in these
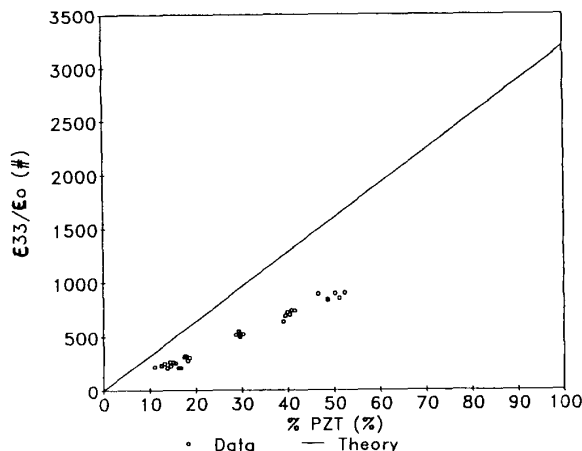

Figure 1. The dielectric constant of 1-3 PZT-polymer composites with silver epoxy electrodes. The solid line represents the predictions of a model based on parallel elements.

specimens is Navy type V material and has a dielectric constant of 3200 and the polymer has a dielectric constant of 5. Hence a simple parallel path model [1] predicts a linear variation of the dielectric constant as a function of PZT percentage according to

$$K_{measured} = 3200x + 5(1-x) \qquad (1)$$

where x is the volume fraction of PZT. Although the data in Figure 1 is linear in accord with the above expression, an extrapolation to 100% PZT gives a dielectric constant of the order of 2000, which is well below the expected value of 3200. Initially the decrease in the dielectric constant was thought to be due to degradation of the ceramic material during processing of the composite specimens. However, the decrease in the dielectric constant disappeared when measurements were made using evaporated silver electrodes, as shown in Figure 2. Clearly the electrodes significantly influence measurements of the material characteristics. In this paper we compare the effect of different electrodes on the measurement of various material characteristics and we present a simple model to understand the effect of the electrodes.
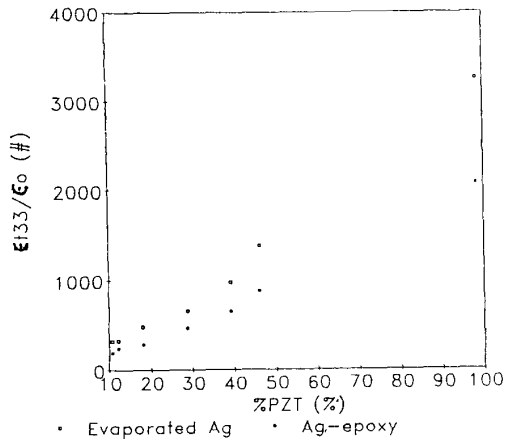
Figure 2. The dielectric constant of 1-3 PZT-polymer composites with silver epoxy and evaporated silver electrodes.

II. A simple model

A scanning electron micrograph of the surface of a silver epoxy electrode shows two distinct (conducting and binder) phases. A model of a two phase electrode on 1-3 PZT-polymer composite is represented by a schematic diagram in Figure 3; this simplified two-dimensional diagram is not drawn to scale nor does it show the 3-3 connectivities of the dielectric binder and the conducting phase. Figure 3 shows that the dielectric binder (and/or pores) partially covers the surfaces of the PZT ceramic pillars in the composite. The binder is in series with the PZT and the addition of this series capacitance reduces the measured dielectric constant since the capacitance of the binder is considerably lower than that of PZT. The magnitude of the reduction is clearly dependent on the binder thickness, the dielectric constant of the binder and the percentage of PZT surface covered by the binder. The presence of the binder on the surfaces of the polymer in the 1-3 composites does not have much influence on the measured dielectric constants because the dielectric constants of the binder and of the polymer are of the same order and because the thickness of the binder is much less than the thickness of the composites.

Figure 4 shows an equivalent electric circuit model for a 1-3 composite with a two phase electrode system. The model circuit has three branches: the first branch (Z_1) represents the polymer in the
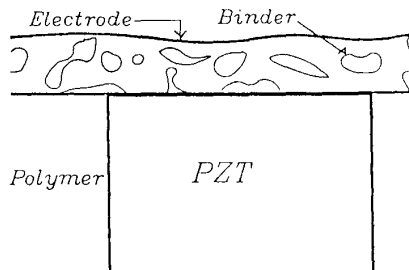

Figure 3. Simple model of a two phase electrode on a 1-3 PZT-polymer composite.
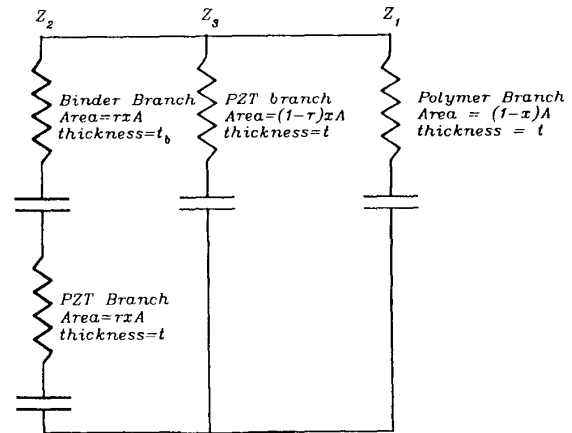

Figure 4. The equivalent circuit model used to calculate the effect of a two phase electrode on the measured dielectric constants of 1-3 PZT-polymer ocmposites.

composite, the second branch (Z_2) represents that portion of the PZT pillars which is in contact with the binder in the electrode and the third branch (Z_3) represents the remaining portion of the PZT pillars which is in contact with the conducting phase of the electrode. For frequencies above and below resonance, the impedances of the three branches are

$$Z1 = \frac{D_p t - ti}{\omega \epsilon_p A (1-x)} \qquad (2)$$

$$Z2 = \frac{2D_b t_b - 2t_b i}{\omega \epsilon_b A x r} + \frac{D_{PZT} t - ti}{\omega \epsilon_{PZT} A x r} \qquad (3)$$

$$Z3 = \frac{D_{PZT} t - ti}{\omega \epsilon_{PZT} A x (1-r)} \qquad (4)$$

where the symbols used are: i for $\sqrt{-1}$, t for the specimen thickness, A for the surface area of the specimen, D for the dissipation, ϵ for the permittivity, r for the fraction of PZT surface covered by the binder, t_b for the average binder thickness and x for the volume fraction of PZT in the composite. The subscripts PZT, p and b refer to the PZT, polymer and binder respectivley. The measured impedance can be found as the parallel sum of Z_1, Z_2 and Z_3 and the dielectric constant and the dissipation can then be derived knowing the frequency of measurement and the sample geometry. Figure 5 shows results derived from this model for a 1-3 composite using Navy type V PZT and Hysol polymer with the following assumptions: $\epsilon_p = \epsilon_b = 5\epsilon_0$, $t_b = 3\mu m$ and $D_p = D_b = 0.06$; these values are reasonable but it should be noted that the dielectric properties of the binder used in the electrode is not known. It can be seen that the dielectric constant decreases as the PZT-binder interface area, r, increases. The experimental data on the dielectric constant which is shown in Figure 1 is in reasonable agreement with our theoretical model for r = 0.5 and this value of r is not inconsistent with the SEM micrograph of the electrode. It should also be noted that the dielectric constant of 1-3 PZT-polymer composites

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is known to decrease with an increase in the size of the PZT elements [5].

Interface thickness   3 microns

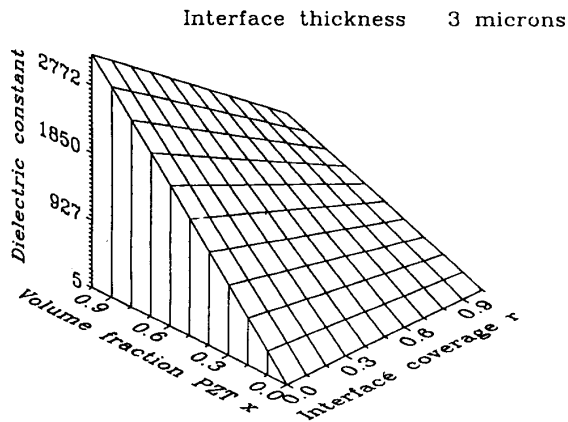
Figure 5.   Theoretical values of the dielectric constant as a function of PZT-binder interface area, r, and as a function of the PZT percentage, x, in the composite. (See text for values assumed in the calculations).

III.   Experimental Results/Discussion

In Table 1 we present measurements of the electromechanical coupling constant k_{33}, the dielectric constant ϵ_{33}, the elastic stiffness constant c_{33}, and the piezoelectric constant e_{33} for two types of PZT ceramic with three different kinds of electrodes: fired silver, silver print and silver epoxy.   The two types of PZT ceramic discs, BM532 (Navy Type V) and BM500 (Navy type IV), were obtained from B.M. Hi-Tech Inc.   All measurements were made using standard IEEE methods [4].

As can be seen in Table 1, the elastic stiffness is more or less independent of the electrode material.   However, the measured values of the other constants decrease a little when silver print electrodes are used and they decrease much more with

Piezoelectric	Electrode	k_{33}	$\epsilon_{33}^T/\epsilon_0$	c_{33}^D $(10^{11}N/m^2)$	e_{33} (C/m^2)
PZT 532 Navy V	fired Silver	.49	3254	1.35	26.4
PZT 532 Navy V	Silver print	.48	2640	1.39	23.7
PZT 532 Navy V	Silver epoxy	.44	2070	1.41	19.7
PZT 500 Navy IV	fired Silver	.62	1990	1.42	13.3
PZT 500 Navy IV	Silver print	.61	1790	1.43	11.9
PZT 500 Navy IV	Silver epoxy	.60	1530	1.37	11.2

Table 1.   Material constants of two types of PZT discs measured using different electrodes.

silver epoxy electrodes, with the effect being largest for the dielectric constant.   We also note that the effect of the electrodes is more significant for PZT 532 which has the larger dielectric constant.   This is consistent with our model since a larger effect would correspond to a larger difference between the dielectric constants of the ceramic and of the dielectric binder in the electrode.   We have also tried to measure the effect in low dielectric constant material: NTK piezocomposite [6] with a dielectric constant of $=34$; in this case there was no appreciable difference in the measured dielectric constant between samples with conducting neoprene electrodes and those with silver print electrodes.   Clearly the electrodes have little effect in the case of measurements on materials with a low dielectric constant.   This would suggest that the effect of the electrodes on dielectric measurements should be investigated on high dielectric constant materials such as bulk PZT.

Figures 6, 7 and 8 show the variation of the piezoelectric constant, the elastic stiffness and the piezoelectric charge coefficient d_{33} as a function of PZT content in a series of 1-3 PZT-polymer composites with silver epoxy and evaporated silver electrodes.   Once again we find that whereas the measurements of elastic stiffness are more or less independent of the electrode used, all the other constants show smaller values when the two phase silver epoxy electrodes are used which is consistent with the model presented in the previous section.
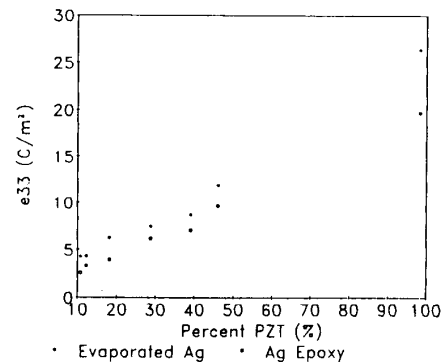

Figure 6.   The piezoelectric constant, e_{33}, of 1-3 PZT-polymer composites with silver epoxy and evaporated silver electrodes.
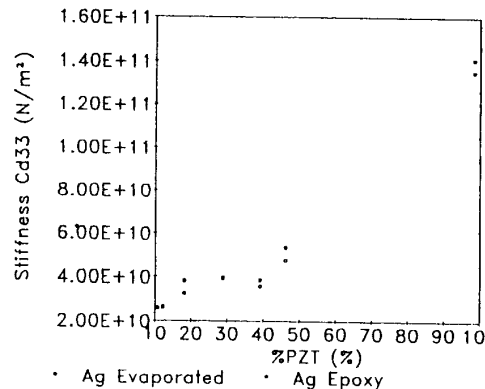

Figure 7.   The elastic stiffness, c_{33}, of 1-3 PZT-polymer composites with silver epoxy and evaporated silver electrodes.

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600.0

500.0

400.0

d33 (pC/N)

300.0

200.0

100.0

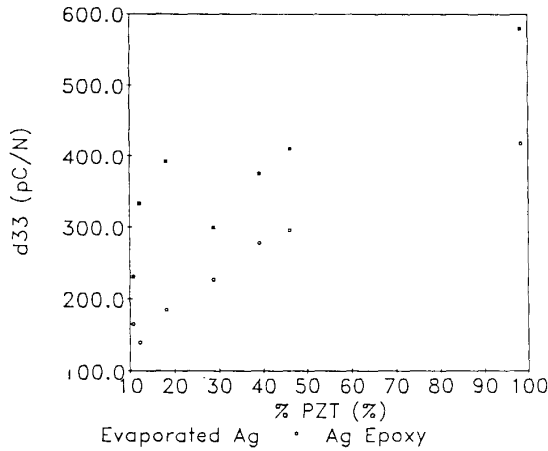0 10 20 30 40 50 60 70 80 90 100

% PZT (%)

Evaporated Ag • Ag Epoxy

Figure 8. The hydrostatic charge coefficient, d_{33}, of 1-3 PZT-polymer composites with silver epoxy and evaporated silver electrodes.

In order to understand our result on the elastic stiffness, we consider the composite as a homogeneous piezoelectric resonator in the thickness mode (see, for example, [7,8]. In this approximation, the equivalent circuit only contains two branches: piezoelectric and dielectric binder in electrode (Z_1) and piezoelectric and conductor in electrode (Z_2). The impedances of these branches are

$$Z(\omega) = [t/\varepsilon_{33}^{s} i\omega wl]$$

$$\left[1 - 2h_{33}^{2}\varepsilon_{33}^{s}/\omega t \sqrt{c_{33}^{D}\rho} \tan[\omega t/2\sqrt{c_{33}^{D}/\rho}] \right] \quad (5)$$

where

$$Z1 = \frac{2D_{b}t_{b} - 2t_{b}i}{\omega \varepsilon_{b}Ar} + Z(\omega)/r \quad (6)$$

$$Z2 = Z(\omega)/(1-r) \quad (7)$$

is the impedance of the piezoelectric resonator near resonance with ideal electrodes [4]. Our approximation does not take account of additional resonances caused by coupling between the vibrations of nearest neighbour PZT pillars. The above equations allow us to calculate the variation of the resistance R, the admittance G and the reactance X of the resonator as a function of frequency for the case of a two phase electrode and compare these results with similar curves for the case of a single phase electrode such as evaporated silver. We have carried out these calculations for the case of the PZT 500 specimen for x = 0.5 and r = 0.5. The peak in the resistance scan corresponds to the parallel resonance frequency, f_p, and our calculations show that the value of f_p is the same for both electrodes. Since the elastic stiffness is only a function of f_p [4], it follows that measurements of elastic stiffness should be independent of the electrode used in accord with our experimental data. The peak in the admittance scan corresponds to the series resonance frequency, f_s, which allows us to calculate the thickness mode electromechanical coupling constant k_t. We obtain $k_t = 0.69$ for the ideal electrode and $k_t = 0.67$ for the two phase electrode, which corresponds to an error of 2.7% when the latter electrode is used. Similarly the reactance scan allows us to look at the error in the measurement of the dielectric

constant; in this case the error caused by using a two phase electode can be as much as 20%. The piezoelectric constant is given by [4]

$$e_{33} = (k_{t}^{2}c_{33}^{D}\varepsilon_{33}^{s})^{1/2} \quad (8)$$

and our results show that the use of a two phase electrode would cause an error of the order of 13% in the measurement of the piezoelectric constant. (Note that the percentage values given refer to the PZT 500 specimen). A comparison of Figure 2 and Figure 6 confirms that the error in the dielectric constant is indeed larger than the error in the piezoelectric constant when measurements are made with a two phase electrode.

We have found that silver print [10] electrodes give only a small decrease in measured values of dielectric and piezoelectric constants when compared with evaporated silver electrodes. If silver epoxy is then applied on top of the silver print, there is no further decrease in the values measured. These results indicate clearly that it is indeed the dielectric properties of the two phase electrode and not its mechanical properties which degrade the measured values. Our results also suggest that two phase electrodes with dielectric binders may be used without degrading the material characteristics if a conducting metal film is inserted between the electrode and the specimen.

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