

Piezoelectric polymer composite materials

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Diphasic composites of piezoelectric and polymer materials have outstanding properties from device application point of view. These materials offer a possibility of design and fabrication of the materials with definite properties for specific application. Hence these are called smart materials. In this paper we present an outline of this field of research. The mixture rules of dielectric properties of these composites with 0-3 or 3-0 connectivity are presented. The modified equation takes into account the local field interactions. Impedance and electromechanical coupling coefficients of these composites with 2-2 connectivity for circular and rectangular geometry can be estimated. The piezoelectric constants of these materials exhibit Debye-type relaxations. Cole-Cole plots can be drawn. A stress field applied to this material can produce an overall piezoelectricity. Piezoelectric constant of these materials can be related to the elastic and dielectric properties of the component phases.

MATERIALS engineering in the past three decades appears to have entered a new era, the age of carefully patterned inhomogeneous solids designed to perform specific functions. Instead of single phase materials, many investigators now search for the best combination of materials and ways to process them. An electromechanical transducer requires a combination of properties such as large piezoelectric coefficient, low density and high mechanical flexibility. Large piezoelectric effects are found in poled piezoelectric ceramics, but ceramics are brittle and stiff, lacking the required flexibility, while polymers with the desired mechanical properties are at best very weak piezoelectrics. Thus for such an application, a composite material combining the desirable properties of two different phases might be vastly superior. The main problem is to effect the combination in such a manner as to exploit the desirable features of the components and hence maximize figure of merit.

During the past few years, materials scientists have been experimenting with the composites of piezoelectric polymer composite materials, hoping to improve on some of the properties of the homogeneous materials¹⁻⁵. There is capability of tailoring material properties, such as acoustic impedance and piezoelectric response. These materials have been successfully used as advanced transducers⁶ including medical imaging transducers and under-water transducers⁷. There is a possibility of using these materials as transducers involving applications such as automatic vehicle guidance, manufacturing assembly,

nondestructive testing and vibration control⁸. In this paper we present dielectric and piezoelectric properties of polymer piezoelectric composite materials. Here we present an outline of this developing and interesting field. We also recapitulate the work done by our group.

Design of composite materials

Basic steps involved in the fabrication of tailor-made piezoelectric polymer composites are shown in Figure 1. Component phases with the right properties are selected and coupled in the best possible way to yield optimum results. Porosity, density, grain size and required poling procedures decide the properties of the individual phases. Proper processing technology should be adopted to establish the desired connectivity of one phase with the other phase. Connectivity is important because it controls the electrical flux pattern and mechanical properties of

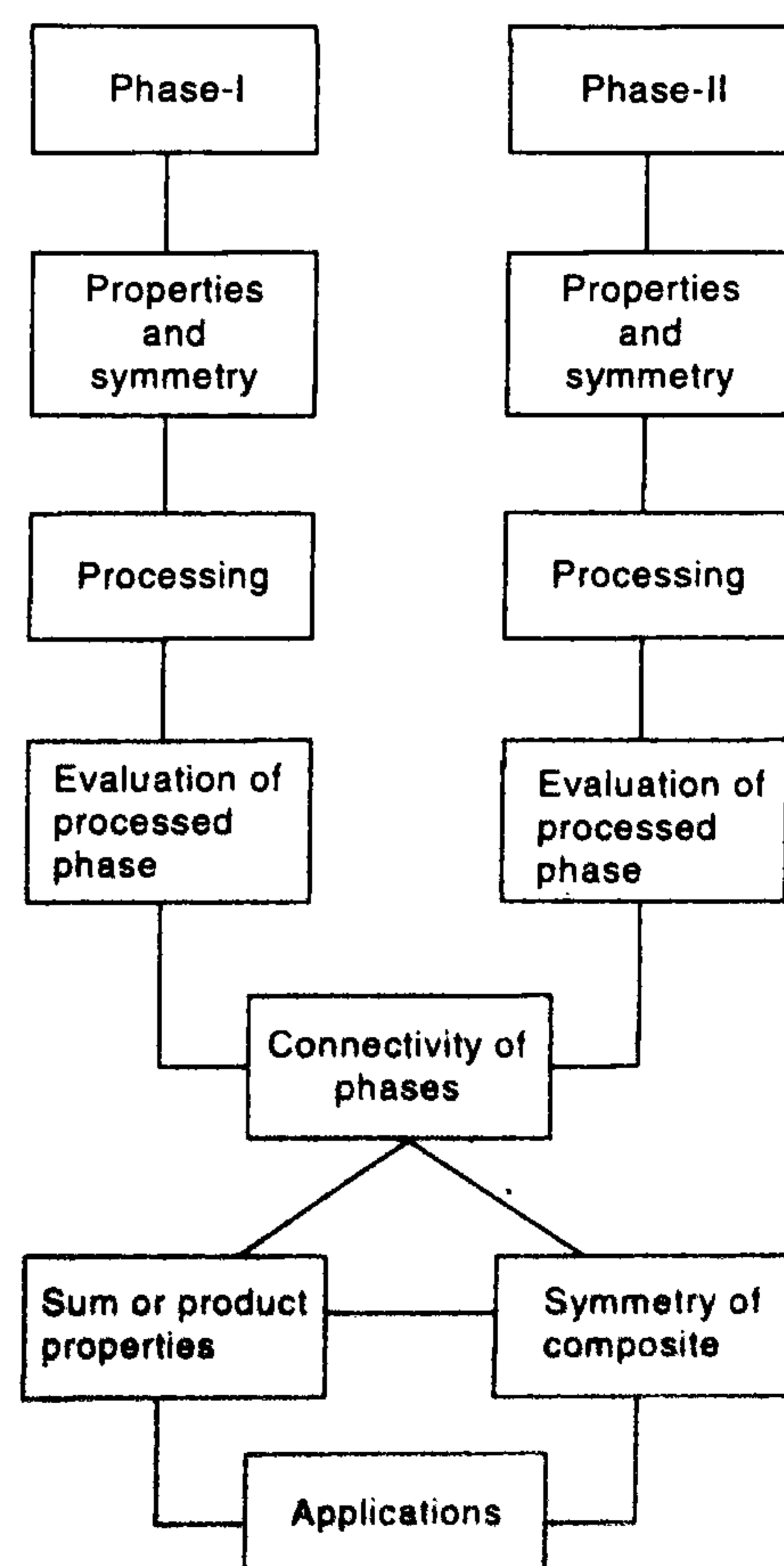


Figure 1. Flow chart of polymer piezo-electric composites.

individual phases, and of composite, are related to their properties through tensor coefficients and hence symmetry considerations are of importance.

Each phase in a composite may be self-connected in zero, one, two or three dimensions. In biphasic composites, there can be ten different connectivities as shown in Figure 2. A 2-1 connectivity pattern has phase 1 connected in two directions and phase 2 is connected in one direction. There are two variations in this connectivity. The chains of phase 2 can be either parallel or perpendicular to the planes of phase 1. If the number of component phases in a composite is increased, then the number of ways in which different component phases can be connected increases. For a n phase composite this number is $(n+3)!/3!n!$. Hence there can be 20 three-phase composites and so on. Different experimental methods have been used to make biphasic ceramic composites of different connectivity patterns. Extrusion,

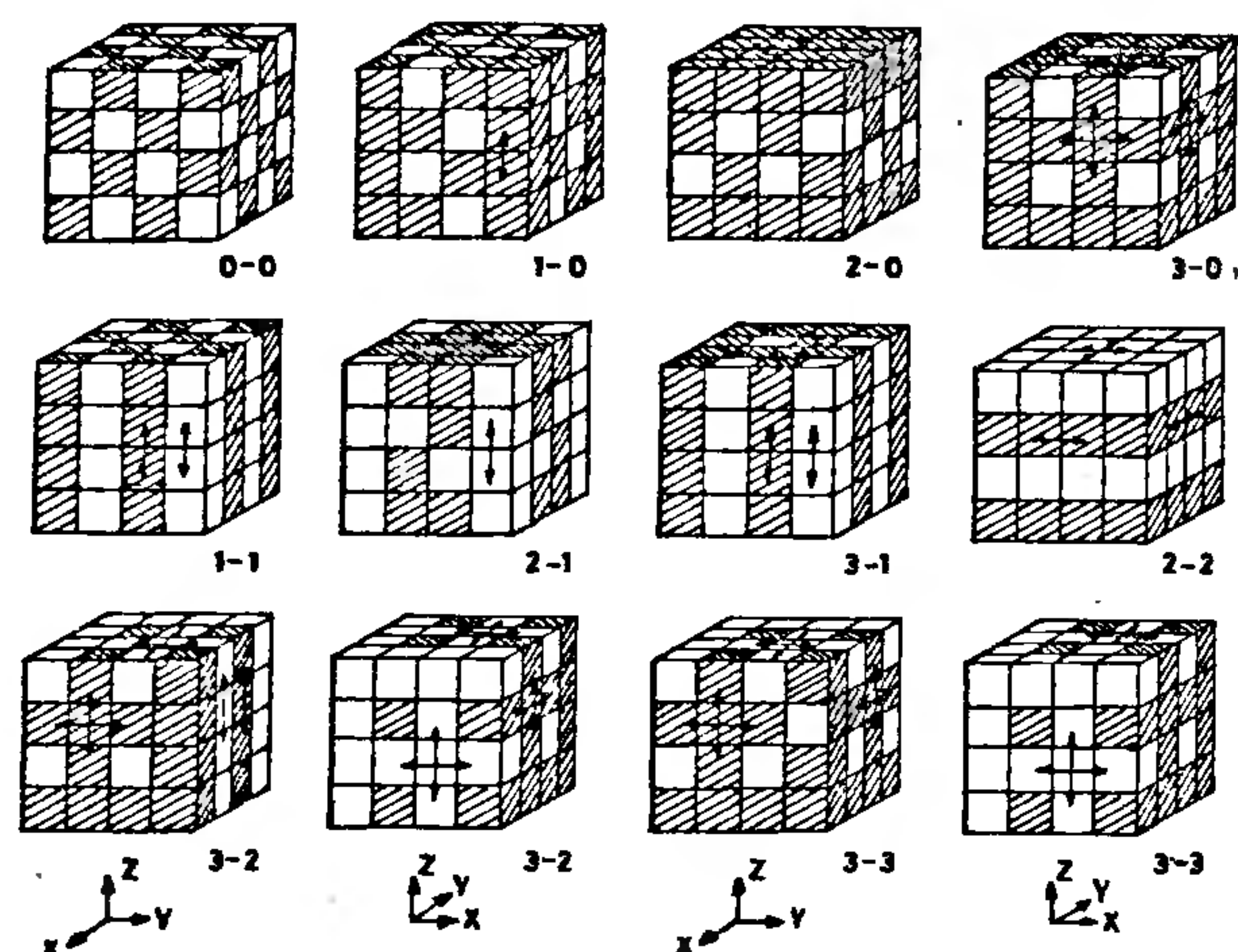


Figure 2. All the possible connectivities of a biphasic composite (after ref. 59).

Table 1. PbTiO_3 -copolymer composite characteristics with 3-0 connectivity¹⁵

PbTiO_3 vol. fraction	0	0.1	0.2	0.3	0.4	1.0
Dielectric constant	19	25.0	34.6	45.0	53.5	200.0
d_{33} (PC/N)	25	23.0	24.0	25.0	28.0	39.0
g_{33} (V-m/N)	0.15	0.1	0.08	0.06	0.06	0.02

Table 2. Piezoelectric-copolymer composite characteristics¹³

Piezoelectric	Polymer	Connectivity	K_{33}	d_h	g_h	$d_h g_h$
PZT	Nil	Nil	1600	50.0	4.0	200
PZT	Silicone rubber	0-3	100	28.3	32.0	900
PZT	Epoxy	1-3	200	77.6	40.4	3138
PZT	Polyurethane	1-3	83	176.2	239.0	42100
PZT	Epoxy	3-2	290	329.0	128.0	42000

tape-casting and replemine processes have been successfully used for the preparation of composites⁸⁻¹⁰.

Composite materials may show sum or product properties¹¹. Sum properties are those in which X-Y effect of the composite is determined by the X-Y effects of the phases 1 and 2. For example, dielectric and elastic properties of the composite are sum properties. Dielectric properties of the composite is approximately given by: $\epsilon_1\Phi + \epsilon_2(1 - \Phi)$, where ϵ_1, ϵ_2 are dielectric constants of the two phases and Φ is the volume fraction of the phase 1.

Product properties are less frequently encountered and are more complicated. An X-Y effect in the composite results from an X-Z effect in phase 1 and Z-Y effect in the phase 2. Magnetolectric composites are an example of this type. The piezoelectric and piezomagnetic biphasic composites, when electrically and magnetically poled, show magnetolectric effect. In strong magnetic fields, piezomagnetic grains of the composite get deformed and this causes strain in the piezoelectric grains, leading to the development of the electric fields¹⁰.

$$\begin{aligned} \text{Magnetolectric effect} &= \left(\frac{\text{Magnetic}}{\text{Mechanical}} \right) \left(\frac{\text{Mechanical}}{\text{Electrical}} \right) \\ &= \left(\frac{\text{Electrical}}{\text{Mechanical}} \right) \left(\frac{\text{Mechanical}}{\text{Magnetic}} \right) \end{aligned}$$

These are ME_H and ME_E effects respectively. In this paper we present some of the results of the dielectric, elastic and piezoelectric properties of piezoelectric polymer biphasic composites of different connectivities.

Several piezoelectric polymer composites have been fabricated to improve their piezoelectric properties. In all these composites dielectric constant of piezoelectric phase is lowered by the introduction of polymer phase and in all cases the hydrostatic piezoelectric coefficient d_h is enhanced. The hydrostatic piezoelectric voltage coefficient and the $d_h g_h$ product used as figure of merit are considerably enhanced¹²⁻²¹.

Klicker *et al.*¹⁶ have fabricated 1-3 composites of PZT rods embedded in an epoxy resin matrix. These composites have better piezoelectric properties than solid PZT. The hydrostatic coefficients d_h and g_h are a function of the dimension of PZT rods and thickness of the composite. The difference in the elastic compliance of

PZT and epoxy resin has a favourable influence on the piezoelectric properties by altering the stress pattern inside the composites.

Rittenmayer *et al.*¹⁷ have fabricated 3-3 composites of PZT rods and PMMA composite with PZT powder in an organic binder and firing the mixture to give a ceramic skeleton. After cooling, these ceramics were back filled with polymer. These ceramics have better piezoelectric and mechanical properties compared to 1-3 composites of PZT rods and epoxy.

Robert Ting¹⁸ studied the hydroacoustic behaviour of piezoelectric composites of 0-3 and 1-3 connectivity to demonstrate potential of these materials for underwater acoustic applications. Based on the multiple scattering theory¹⁹ and effective medium theory, Ce-Wen Nan²⁰ proposed to treat coupled electromechanical behaviour in composite media. The explicit relations for determining effective behaviour of piezoelectric composites are derived. Models for 1-3 tubular composite for smart transducer applications are worked out by Zhang *et al.*^{21,22}.

Tables 1-4 present the characteristics of various piezoelectric polymer composites available in the literature¹²⁻²¹.

Dielectric properties

When a minor phase is mixed in a major phase the resultant dielectric constant of the mixture as a function of volume fraction, dielectric constants and geometry has been the subject of study of many workers²³⁻²⁶. Rayleigh²⁷ and Maxwell²⁸ used the approach suggested by Clausius and Mosetti and considered a dilute dispersion of isotropic spheres in an isotropic continuum.

Effective medium approximation, also known as self-consistent approximation, was developed by Bruggeman²⁹ and Landauer³⁰. All these theories predict reasonably accurate results for dilute concentrations below 0.2 volume fraction of one of the phases. For higher volume fractions, almost all these equations do not agree with the experimental results.

Yomezawa and Cohen³¹ gave exact relations for dielectric constants of composite for very dilute concentrations of dispersion of particles in a continuous matrix. A small volume fraction (Φ) of spherical particles of dielectric constant (ϵ_2) is dispersed in continuous matrix of dielectric constant (ϵ_1). Solving the Laplace equation for the scalar potential in and around the dispersed spheres and applying the principle of continuity, the expression for the dielectric constant (ϵ) is obtained as:

$$\frac{\epsilon - 1}{\epsilon + \mu} = \sum \Phi_i \frac{\epsilon_i - 1}{\epsilon_i + \mu} \quad (1)$$

Here i is the number of phases present in the composite, μ is a constant which depends on the geometry of the dispersed particles and Φ_i is volume fraction of the i th phase, and ϵ is the dielectric constant of the composite.

For spheres embedded in a medium of dielectric constant ϵ_1 , form factor μ is equal to $2\epsilon_1$. For biphasic solid containing spheroidal minor phase, it has been shown by Rayleigh²⁷ that

$$\epsilon = \frac{2\epsilon_1 + \epsilon_2 - 2\Phi(\epsilon_1 - \epsilon_2)}{2\epsilon_1 + \epsilon_2 + \Phi(\epsilon_1 - \epsilon_2)} \epsilon_1, \quad (2)$$

where Φ is the volume fraction of the second phase.

Table 3. Characteristics of PLZT 5H-PVDF composites¹²

	PLZT 5H	PVDF	1-3 Rod composite (20%)	1-3 Tubular composite (20%)
Density (kg/m ³)	7500	1800	2800	2300
Permittivity	1800	10	780	290000
Loss tangent	2	5	3	3
d_{33} (PC/N)	593	-30	480	> 6000
d_h (PC/N)	45	9	> 100	> 5000
d_{1g_h} (10 ¹⁵ m ² /N)	150	830	> 2000	> 6000

Table 4. Characteristics of PZT-silicone rubber composites¹⁴

	Porosity							
	0.53		0.61		0.64		0.68	
	Air	Si rubber	Air	Si rubber	Air	Si rubber	Air	Si rubber
ϵ/ϵ_0	440.00	440.00	250.00	260.00	210.00	220.00	180.00	200.00
$\tan \delta$	0.026	0.026	0.024	0.024	0.026	0.025	0.026	0.026
K_c	0.16	0.17	0.14	0.15	-	0.12	1.0	0.12
K_t	0.57	0.57	0.57	0.56	0.40	0.51	0.49	0.50

Series and parallel models are well-known and are described respectively by the following equations⁴

$$\varepsilon = \varepsilon_1 \Phi_1 + \varepsilon_2 (1 - \Phi), \quad (3a)$$

$$\varepsilon = \frac{\varepsilon_1 \varepsilon_2}{(1 - \Phi) \varepsilon_1 + \Phi \varepsilon_2}. \quad (3b)$$

Differential effective medium approximation (DEMA) theory is also known as self-consistent approximation, coherent potential approximation and Bruggeman's theory^{29,30,32,33}. DEMA assumes a medium having permittivity ε_h as a host, in which, grains of phase I (ε_1) and phase II (ε_2) are embedded, so that they are well-separated and occupy small volume fraction of the medium. In the next step, grains of larger size than the previous grains of phases I and II are embedded. The process is repeated such that at each step, the new grain sizes are larger than the previous ones and the relative volume fractions of both the phases are adhered to. A limiting process is defined such that the relative sizes become infinite while the number of steps also becomes infinity. The resultant material has effective properties defined by DEMA³⁴. The above process can be thought of as one of the continuous homogenization. At each step, we are replacing an infinitesimal amount of host material by the same amount of materials of phases I and II. The new material is then homogenized and the process is repeated until the whole material is replaced. Thus the properties of host material are irrelevant. The DEMA then predicts ε to satisfy the following equation

$$0 = \sum \left[\frac{(1 - \Phi)(\varepsilon - \varepsilon_1)}{(1 - L_i)\varepsilon + L_i \varepsilon_1} + \frac{\Phi(\varepsilon - \varepsilon_2)}{(1 - L_j)\varepsilon + L_j \varepsilon_2} \right], \quad (4)$$

where the coefficients L_i are the depolarization factors with $L_1 + L_2 + L_3 = 1$ (ref. 35).

For spherical particles $L_1 = L_2 = L_3 = 1/3$ and hence the above equation simplifies to³³

$$(\Phi - 1) \frac{\varepsilon - \varepsilon_1}{2\varepsilon + \varepsilon_1} = \Phi \frac{\varepsilon - \varepsilon_2}{2\varepsilon + \varepsilon_2}. \quad (5)$$

This is same as the equation given by Landauer³⁰.

In the differential effective medium theory, infinitesimal grain of material of phase II is added to the material of phase I. The mixture is homogenized and the process is repeated until required volume fraction of phase II is added to the phase I. The general solution obtained by Bruggeman³⁶ for spheres of phase II is given below

$$(1 - \Phi) = \left(\frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 - \varepsilon_1} \right) \left(\frac{\varepsilon_1}{\varepsilon} \right)^{1/3}. \quad (6)$$

Kerner³⁷ developed a formula for dielectric constant of composite in terms of ratio of average electric fields E_1 and E_2 at the materials of phase I and II along the direction of applied field E_0 and it is

$$\varepsilon = \frac{\varepsilon_1(1 - \Phi) + \Phi \varepsilon_2 (E_2 / E_1)}{(1 - \Phi) + \Phi (E_2 / E_1)}. \quad (7)$$

The average electric fields E_1 and E_2 around phase I and II (refs 37, 38) are

$$E_1 = E_0 \quad \text{and} \quad E_2 = \frac{3\varepsilon_1}{2\varepsilon_1 + \varepsilon_2} E_0. \quad (8)$$

Palotto *et al.*³⁹ modified the equation for electric field E_2 as

$$E_2 = \frac{3\varepsilon_2}{(3 - \Phi)\varepsilon_2 + \Phi \varepsilon_1} E_0. \quad (9)$$

Substituting eq. (9) in eq. (7), the composite dielectric constant can be computed as

$$\varepsilon = \Phi \frac{[(1 - \Phi) \varepsilon_1 A^2 + \Phi \varepsilon_2]}{[1 + (1 - \Phi)(A - 1)]^2} + (1 - \Phi) \frac{[(1 - \Phi)\varepsilon_1 + \Phi \varepsilon_2 B^2]}{[(1 - \Phi) + \Phi B]^2}, \quad (10)$$

where

$$A = \frac{3\varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \quad \text{and} \quad B = \frac{3\varepsilon_1}{2\varepsilon_1 + \varepsilon_2}.$$

It can be shown that the theoretical and experimental values of dielectric constant calculated using the above equations agree well for dilute concentrations. For larger concentrations theoretical values are either large or small.

In the composite of piezoelectric spheres dispersed in a continuous medium, where sphere gets polarized by the applied electric field and can be represented as a dipole, the dipole moment of this dipole locally modifies the applied field in the surrounding medium. When only a small volume fraction of spheres is present, the influence of this dipole field on the neighbouring spheres is negligible. However, at larger volume fractions it is no longer valid to neglect the interactive effects of dipoles. Since the models mentioned above do not consider the interactive effects, there is a disagreement between the experimental and theoretical values, particularly at large volume fractions. An expression is developed for dielectric constant of 3-0 (or 0-3) biphasic composite by taking into account these interactive effects of dipoles.

For a composite system, spheres of dielectric constant

ϵ_2 (say piezoelectric, phase II) distributed in a continuum of ϵ_1 (say polymer, phase I), each sphere of phase II of radius acts, as a dipole of moment m . When an external field E_0 is applied, the field inside each sphere is given by E_{2z} (the field inside the isolated sphere). Each sphere then acts as a dipole of moment m positioned at the centre of the sphere. The polarization P in the sphere by definition³⁵

$$P = (\epsilon_2 - \epsilon_1) E_{2z} = \frac{\epsilon_2 - \epsilon_1}{2\epsilon_1 + \epsilon_2} 3\epsilon_1 E_0, \quad (11)$$

and the dipole moment m is

$$m = \frac{4\pi}{3} a^3 P = 4\pi\epsilon_1 a^3 \frac{\epsilon_2 - \epsilon_1}{2\epsilon_1 + \epsilon_2} E_0, \quad (12)$$

where a is the radius of the sphere.

The apparent surface charge distribution on the sphere is

$$\sigma = \frac{3m}{4\pi a^3} \cos \theta = P \cos \theta. \quad (13)$$

Each sphere then interacts with outside dipoles⁴⁰. If the system is assumed to be a distribution of dipoles, the average electric field $\langle E_z \rangle$ due to each dipole is given by multipole expansion as

$$\langle E_z \rangle = \frac{1}{V} \int E_z V = \frac{2m}{R^3}, \quad (14)$$

where V is the volume. R is the radius of an arbitrary sphere of phase I surrounding the dipoles of piezoelectric phase II. If there are n identical dipoles in the sphere of radius R (which contains a dielectric) of dielectric constant ϵ_1 , the electric field is E_{av} (ref. 40)

$$E_{av} = \frac{n 2m}{4\pi\epsilon_1 R^3} = \frac{2m\Phi}{4\pi\epsilon_1 a^3}, \quad (15)$$

where n is the number of dipoles in the volume $(4\pi/3)R^3$ and $(n/R^3) = (\Phi/a^3)$, here Φ is volume fraction of phase II and a is the average radius of the phase II spheres.

Due to the interaction between dipoles, the effective dipole moment is increased by m_i (refs 41, 42).

The increase in the dipole moment is

$$m_i = m(\Phi - 1). \quad (16)$$

From the expression for apparent surface charge density in terms of modified dipole moment can be written following the eq. (16) as

$$\sigma_m = P_m \cos \theta, \quad (17)$$

here P_m represents modified polarization.

From eq. (8) since

$$E_0 = \frac{3\epsilon_1}{2\epsilon_1 + \epsilon_2} E_{av}$$

and from eq. (11), we have

$$\sigma_m = 3\epsilon_1 \Phi \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} E_0 \cos \theta, \quad (18)$$

and

$$P = (\epsilon_2 - \epsilon_1) E_z = \frac{(\epsilon_2 - \epsilon_1) 3\epsilon_1 E_{av}}{\epsilon_2 + 2\epsilon_1}. \quad (19)$$

Solution of Laplace equation can be found for the scalar potential inside V_{in} and outside V_{out} the spherical inclusions in terms of Legendre polynomials³⁸. Using the following boundary conditions the constants A , B , and C can be evaluated

$$V_{out} \rightarrow E_{av} Z = -E_{av} r \cos \theta \text{ as } r \text{ tends to infinity.}$$

$$V_{in} = V_{out} \text{ at } r = a$$

$$\epsilon_2 \frac{dV_{in}}{dr} = \left[\epsilon_1 \left(\frac{dV_{out}}{dr} \right) + \sigma_m \right] \text{ at } r = a$$

$$V \text{ is finite at } r = 0.$$

These boundary conditions are the same as those for an isolated sphere except for the apparent charge density σ_m . Using these boundary conditions, solving for internal potential and electric field E_{int} , the internal electric field at the piezoelectric spheres can be obtained as

$$\begin{aligned} E_{internal} &= E_{local} + E_{int} \\ &= \frac{3\epsilon_1}{\epsilon_2 + 2\epsilon_1} \left[1 + 3\Phi \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} \right] E_0. \end{aligned} \quad (20)$$

Substituting eq. (20) in eq. (7), we get the following equation⁴¹.

$$\epsilon =$$

$$\frac{\epsilon_1(1 - \Phi) + \epsilon_2\Phi [3\epsilon_1/(\epsilon_2 + 2\epsilon_1)] [1 + 3\Phi(\epsilon_2 - \epsilon_1)/(\epsilon_2 + 2\epsilon_1)]}{(1 - \Phi) + \Phi(3\epsilon_1)/(\epsilon_2 + 2\epsilon_1) [1 + 3\Phi(\epsilon_2 - \epsilon_1)/(\epsilon_2 + 2\epsilon_1)]}. \quad (21)$$

This is the modified equation for the dielectric constant of a composite with the interactive effects taken into consideration. In Figure 3 experimental values⁴³⁻⁴⁵ for PVDF-PLZT composites are compared with those in the present model along with those of Kerner³⁷. This

Figure shows that theoretical values computed from the present model are in good agreement with experimental values even up to 70% of piezoelectric phase in the composite⁴¹.

Electromechanical properties

Models have been developed for electromechanical characteristics of piezoelectric polymer composite materials with 2-2 connectivity. The constitutive equations of these composites are complicated and their analytical solution is difficult. Earlier models assumed either stress or strain components to be constant. Among earlier models, the Vogit's model assumes constant strain whereas Reuss's model assumes constant stress⁴⁶. More refined models are series parallel model⁴⁷, Cubes model⁴⁸ and Unsworth method⁴⁹.

In our model the assumptions are: (i) the samples have complete stress-free boundary conditions at the polymer piezoelectric interfaces, (ii) the materials are lossless, (iii) the coordinate axis are pure mode propagation directions, (iv) the electric potential and the displacements are assumed to be independent degrees of freedom, (v) the coordinates are pure mode propagation directions, (vi) piezoelectric polymer composite material has extended faces normal to the X_3 direction and poled along this direction.

With these assumptions the equation for electrical impedance of a 2-2 composite was developed and for cylindrical geometry the electric impedance is given by⁵⁰

$$z = \left(\frac{1}{j\omega c_0} \right) \left(1 - \left[\frac{\alpha h_{33}}{\beta_{33}^s + \beta_{33}^{s'}} \right] \left[\frac{(h_{31} C'_{33} - h_{33} C'_{13}) J_0(\alpha a)}{J_a C'_{33} - C'_{13} \alpha J_0(\alpha a)} \right] \right)$$

$$- h_{33} \left[\frac{\{J_a h_{33} - h_{31} C'_{13} \alpha J_0(\alpha a)\} \tan(\alpha_3 a_3)}{\{(\beta_{33}^s + \beta_{33}^{s'}) J_a C'_{33} - C'_{13} \alpha J_0(\alpha a)\} \alpha_3 a_3} \right],$$

where

$$C_0 = \frac{\pi a^2}{(\beta_{33}^s + \beta_{33}^{s'}) a_3}, \quad \alpha = \frac{\omega}{V} \quad \alpha_3 = \frac{\omega}{V_3}, \quad (22)$$

and for rectangular geometry⁵¹

$$z = \frac{1}{j\omega c_0}$$

$$\times \left[1 - \frac{h_{31}}{\beta_{33}^s + \beta_{33}^{s'}} \left\{ \frac{h_{31} C'_{33} - h_{33} C'_{13}}{(C'_{11} + C'_{12}) C'_{33} - 2C'_{13}} \right\} \right]$$

$$\times \left\{ \frac{1}{\cos(\alpha a_1)} + \frac{1}{\cos(\alpha a_2)} \right\} \left[\right]$$

$$- \frac{K^2}{j\omega c_0} \left[\left\{ \frac{1 - 2 \frac{h_{31} C'_{13}}{h_{33} (C'_{11} + C'_{12})}}{1 - 2 \frac{C'^2}{(C'_{11} + C'_{12}) C'_{33}}} \right\} \frac{(\tan(\alpha_3 a_3))}{\alpha_3 a_3} \right] \quad (23)$$

In Figure 4 we present a plot of Z as a function of frequency for rectangular geometry. We find resonance and anti-resonance peaks at a fundamental frequency and a number of overtones. We show only two of them in this figure. From these resonance peaks electromechanical coupling coefficients can be obtained from the following equations⁵²

$$\frac{k_p^2}{1 - k_p^2} = \frac{(1 - \sigma^E) J_1(\Phi(1 + \frac{\Delta f}{f})) - \Phi(1 + \frac{\Delta f}{f}) J_{11}(\Phi(1 + \frac{\Delta f}{f}))}{(1 + \sigma^E) J_1(1 + \frac{\Delta f}{f})} \quad (24)$$

where Δf = resonant frequency, f = band width, σ^E = Poisson's ratio.

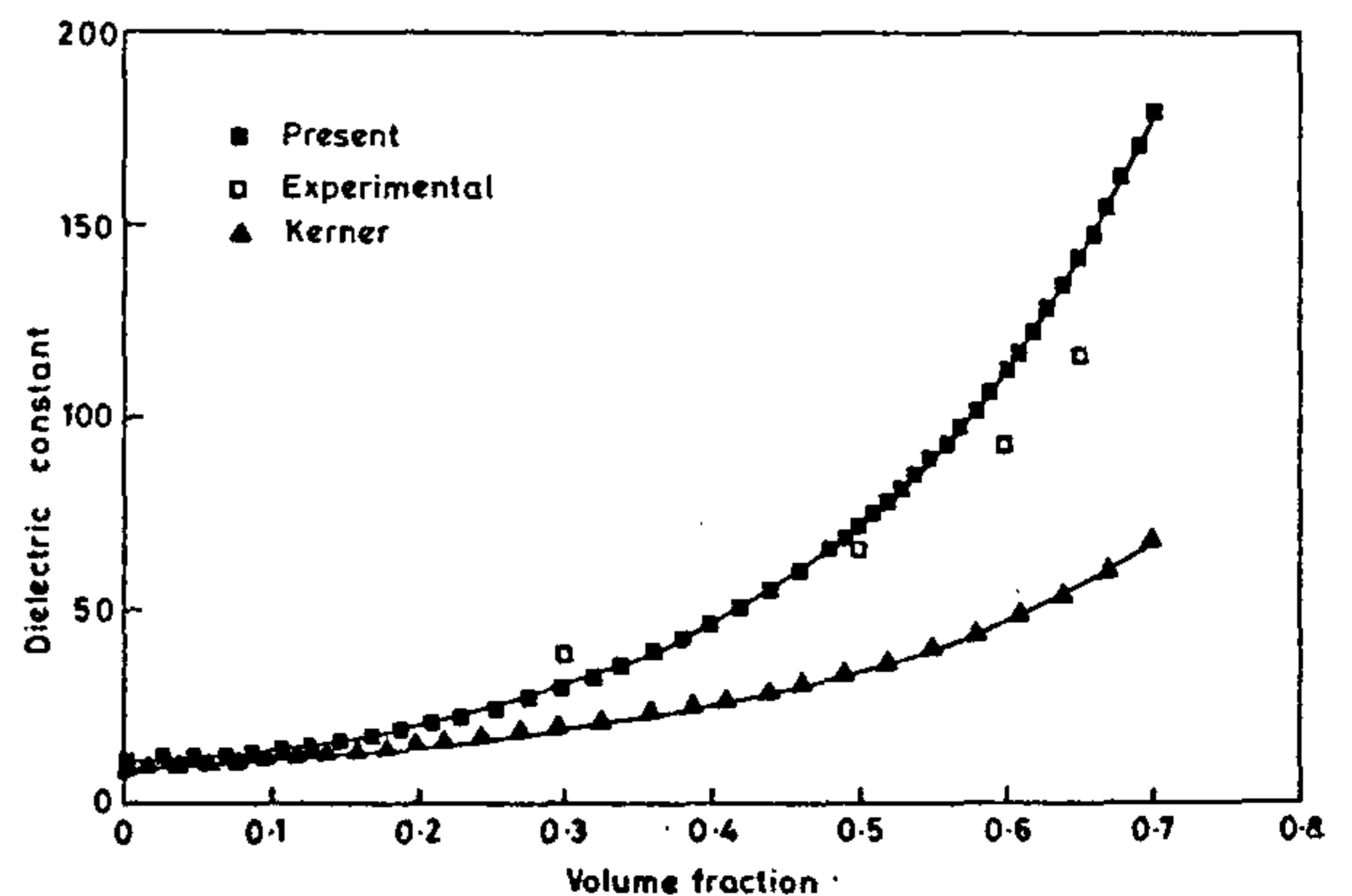


Figure 3. Comparison of experimental and theoretical values of dielectric constants for PLZT-PVDF composite. Experimental values are after ref. 44.

Planar coupling coefficient is¹¹

$$K_p^2 = \frac{f_a^2 - f_r^2}{f_a^2} \quad (25)$$

Here f_a and f_r are anti resonance and resonance frequencies.

$$k_{31} = 0.5(1 - \sigma^E) K_p^2, \quad (26)$$

$$d_{31} = k_{31} (\epsilon_{33}^T S_{11}^E)^{1/2}. \quad (27)$$

Piezoelectric properties of composites

The basic reason for observation of piezoelectric effect in polymer piezoelectric composites (PPE) is due to their heterogeneity. PPE composites often show piezoelectric relaxations in addition to dielectric and elastic relaxations. These composites can be fabricated with

different connectivities and the relaxation observed depends on the type of connectivity. In this paper we discuss the piezoelectric relaxation of 0-3 and 2-2 composites. Since the piezoelectricity is a result of variation of electric polarization with strain, study of dielectric and elastic properties can lead to the understanding of piezoelectricity⁵³.

The relaxation behaviour manifests itself in the frequency and temperature dependence of the property. Dielectric relaxations can be studied even up to optical frequencies. Hence dielectric relaxations due to dipoles, molecules and electrons can be studied. But since frequency of the sound waves is much smaller, only relaxations due to molecular motions are observable in piezoelectric relaxations. Since the piezoelectric properties respond and relax under the alternating strain fields they, like dielectric and elastic properties, can be represented as

$$e^* = e'(w) + ie''(w)$$

and

$$d^* = d'(w) + ie''(w), \quad (28)$$

where e^* and d^* are piezoelectric stress and strain constants. These are defined as follows

$$e = \frac{1}{4\pi} \left(\frac{D}{S} \right)_E = - \left(\frac{T}{E} \right)_S; \quad d = \frac{1}{4\pi C} \left(\frac{D}{S} \right)_E = \frac{e}{S}, \quad (29)$$

where e^* and d^* describe the dynamic response of piezoelectric properties of the composite. d' and e' are real parts and d'' and e'' are imaginary parts of these properties. The piezoelectric dispersion can be characterized with the typical Debye type behaviour which is characterized by⁵³

$$d' = d_\infty + \frac{d_s - d_\infty}{1 + (\omega\tau)^2}; \quad d'' = \frac{(d_s - d_\infty)\omega\tau}{1 + (\omega\tau)^2}, \quad (30)$$

$$\tan \delta = \frac{d''}{d'}, \quad (31)$$

$$\text{if } \omega\tau = 1 \text{ then } 2(\tan \delta)_{\max} = \Delta d / d_\infty. \quad (32)$$

Here d_s and d are static and high frequency piezoelectric constants and τ is relaxation time.

Variation of imaginary part of piezoelectric constant d'' with real part d' would be a semicircle⁵³. These are Cole-Cole diagrams. Temperature increase at a fixed frequency has the same effect equivalent to frequency increase at a fixed temperature. Hence the temperature variation of d at fixed frequency is used to draw the Figure 5. The relaxational behaviour in the piezoelectric polymer composites may be due to (i) relaxation of piezoelectric phase and/or (ii) relaxation of non-piezo-

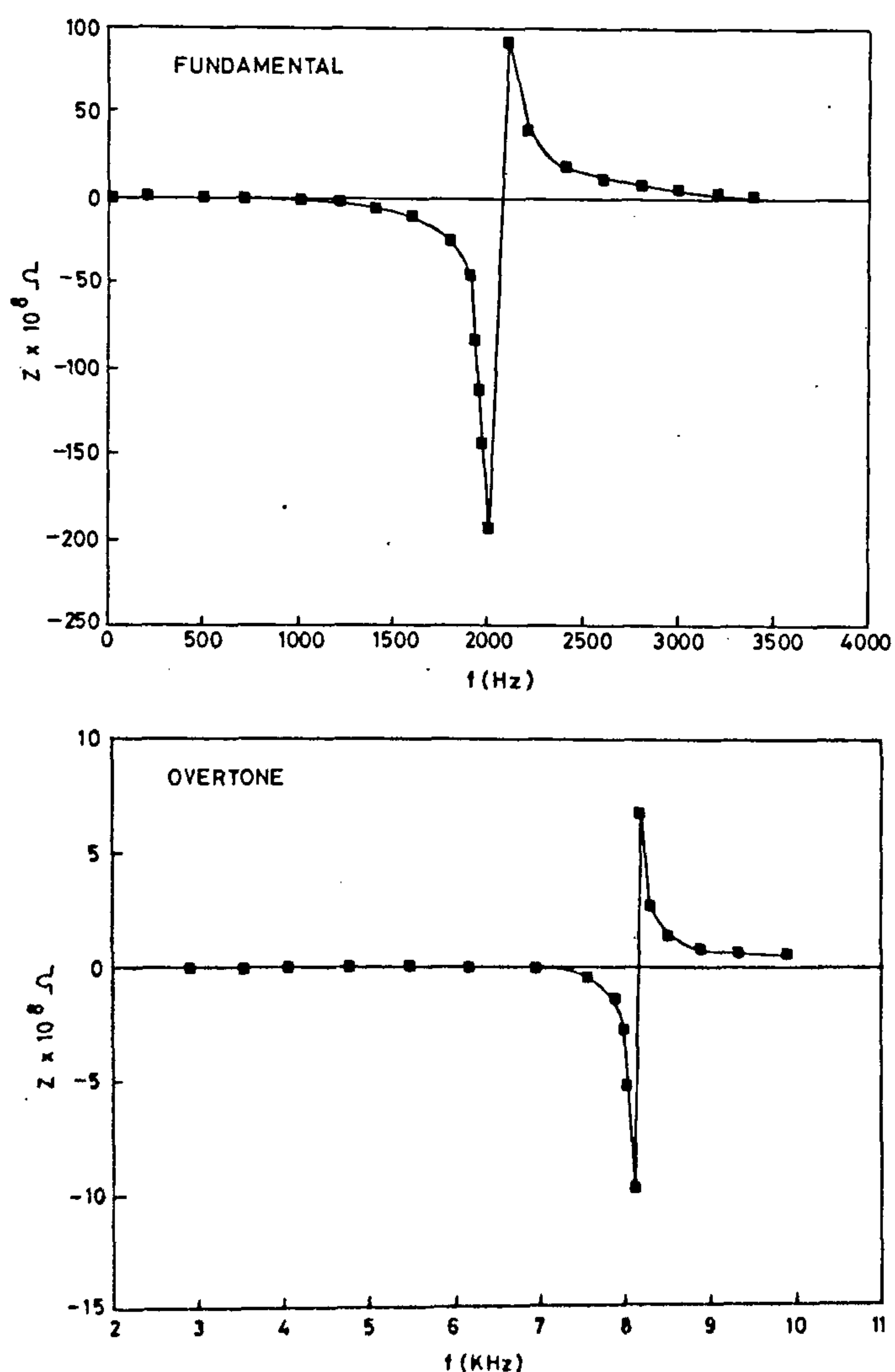


Figure 4. Impedance variation with frequency for a polymer piezoelectric composite.

electric phase. As a consequence, the whole system exhibits the relaxation.

As discussed in the earlier sections the dielectric constants of composite materials can be calculated using various models. If both phases in the composite are incompressible then the elastic constant of the composite is given by⁵

$$C = \frac{3C_1 + 2C_2 - 3\phi(C_1 - C_2)}{3C_1 + 2C_2 + 2\phi(C_1 - C_2)} C_1. \quad (33)$$

Here C_1 and C_2 are elastic constants of the individual phases and ϕ is the volume fraction of phase II.

Many theoretical investigations on binary systems like polymer piezoelectric composites have been performed in regard to piezoelectric constants^{4,20,21,43-45}. Most of them assumed characteristics of continuous medium and/or that the volume fraction of one of the phases is small. Recently one line of theoretical study of piezoelectric composites is focused on the development of micromechanics models. Schulgasser⁵⁵ and Benveniste and Dvorak⁵⁶ have extended these models for 1-3 composites. Dunn and Taya⁵⁷ have generalized this model to 0-3 and 1-3 composites. All these models are valid for smaller volume fractions and without considering the interaction between the particles of different phases. Nan⁵⁸ has, however, proposed a model using multiple scattering theory and effective medium theory, which agrees well with experimental results up to 0.5 volume fraction. In the following we present essence of the model we have reported for calculation of piezoelectric constants⁴¹.

Average electric displacements in the composite and the phase I and phase II, when an electric field E is applied, are given by

$$\begin{aligned} D &= D_0 + \epsilon E, \\ D_1 &= D_{01} + \epsilon_1 E_1, \\ D_2 &= D_{02} + \epsilon_2 E_2. \end{aligned} \quad (34)$$

Here D_0 , D_{01} and D_{02} are the displacements at zero applied electric field. E , E_1 and E_2 are the electric fields at composite, phase I and phase II respectively. To a good approximation we can also write,

$$D = (1 - \Phi)D_1 + \Phi D_2, \quad (35)$$

$$E = (1 - \Phi)E_1 + \Phi E_2. \quad (36)$$

If $D_{01} = D_0 = D_{02} = 0$, from eqs (34) and (35) we have

$$\epsilon E = (1 - \Phi)\epsilon_1 E_1 + \Phi\epsilon_2 E_2. \quad (37)$$

In an analogous way, for elastic fields we can write

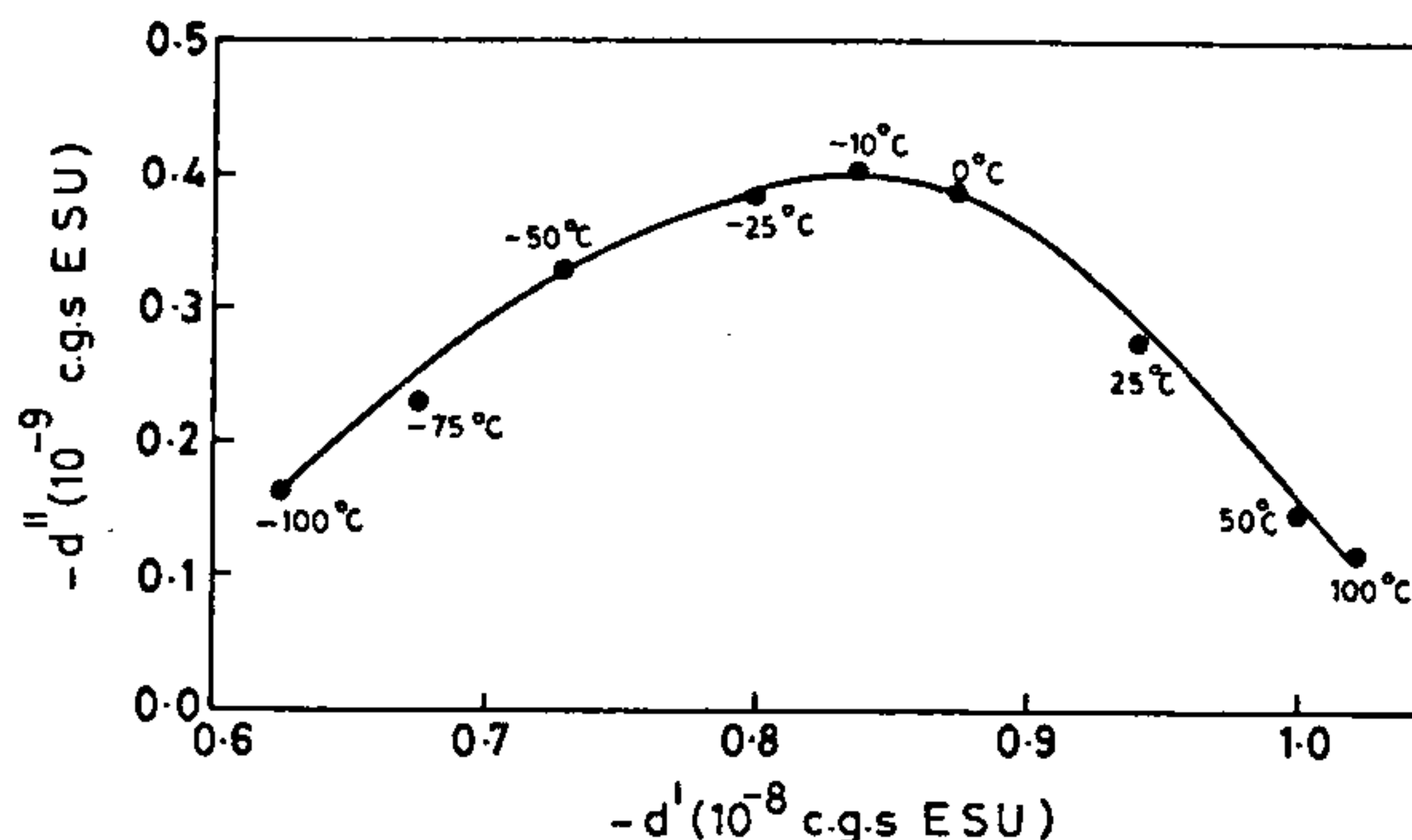


Figure 5. Cole-Cole plot of PZT-epoxy resin poled at 100 kV/cm (data after ref. 44).

relations for stress (T), strain (S) and compliance (C). Here suffixes 1 and 2 refer to phases I and II respectively:

$$T = T_0 + C,$$

$$T_1 = T_{01} + C_1 S_1 \quad \text{and} \quad T_2 = T_{02} + C_2 S_2,$$

and

$$T = (1 - \Phi) T_1 + \Phi T_2,$$

$$S = (1 - \Phi) S_1 + \Phi S_2. \quad (38)$$

When inclusions in the composite are piezoelectric, we observe piezoelectricity as gross property of the composite. In order to relate gross property to that of the inclusions, the following assumptions are made⁴¹: (i) The piezoelectric constants of the inclusions are one-dimensional and relate the dielectric variables alone on polar axis and elastic variables perpendicular to the polar direction. (ii) The inclusions are spherical and their dielectric and elastic properties are isotropic and incompressible. (iii) The dielectric constants of constituents are independent of mechanical states and vice versa.

The piezoelectric direct effect coefficient e is a result of the following three effects: (i) Strain S applied to a composite produces S_2 strain in the piezoelectric inclusions. (ii) The strain S_2 gives rise to displacement D_{02} to these inclusions. (iii) This D_{02} is observed as an increase of macroscopic electric displacement D_0 .

Therefore the piezoelectric constant e can be written as⁴¹

$$\begin{aligned} e &= \frac{1}{4\pi} \frac{D}{S} = \left(\frac{D_0}{D_{02}} \right) \left(\frac{D_{02}}{4\pi S_2} \right) \left(\frac{S_2}{S} \right) \\ &= \left(\frac{D_0}{D_{02}} \right) \left(\frac{S_2}{S} \right) e_2. \end{aligned} \quad (39)$$

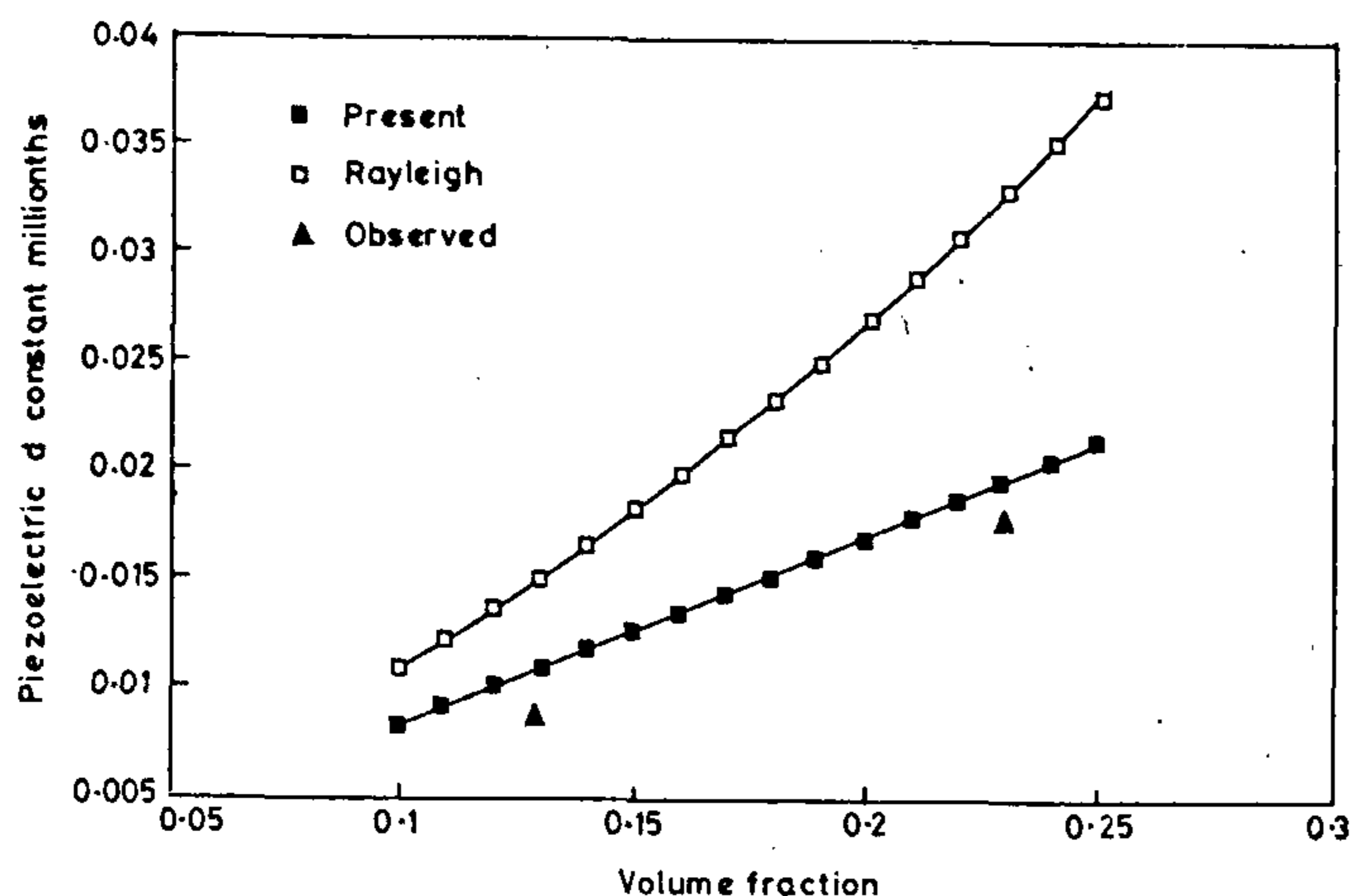


Figure 6. Comparison of experimental and theoretical values of piezoelectric d constant for PZT-PVDF composite. Experimental values are after Furukawa *et al.* (ref 44).

From the eqs (35) and (36) we have

$$\frac{E_2}{E} = \left(\frac{1}{\Phi} \right) \frac{(\epsilon_1 - \epsilon)}{(\epsilon_1 - \epsilon_2)} \quad (40)$$

If the displacement is completely due to piezoelectric phase only, then only D_{02} exists, so that $E = E_1 = E_2$, and we can show

$$\frac{D_0}{D_{02}} = \frac{(\epsilon_1 - \epsilon)}{(\epsilon_1 - \epsilon_2)} \quad (41)$$

Considering the analogous equations, we can have for elastic constants,

$$\frac{S_2}{S} = \frac{1}{\Phi} \frac{(C_1 - C)}{(C_1 - C_2)} \quad (42)$$

Finally the piezoelectric constant of composite using the eqs (41) and (42) in the eq. (39) can be written as

$$e = \frac{1}{\Phi} \left[\frac{C_1 - C}{C_1 - C_2} \right] \left[\frac{\epsilon_1 - \epsilon}{\epsilon_1 - \epsilon_2} \right] e_2 \quad (43)$$

In the above equation by using the equations for composite's dielectric constant ϵ and elastic constant C , the piezoelectric constant of the composite can be calculated.

The equations for other piezoelectric constants d , g and h can also be obtained from the following relations

$$d = e/C; \quad h = 4\pi e/\epsilon; \quad g = 4\pi e/C\epsilon \quad (44)$$

Figures 6 and 7 present the variation of piezoelectric constants as a function of volume fraction. These constants are calculated by substituting Rayleigh's eq. (2) and eq. (22) for dielectric constant of composite for PZT-PVDF composite. The experimental data are taken

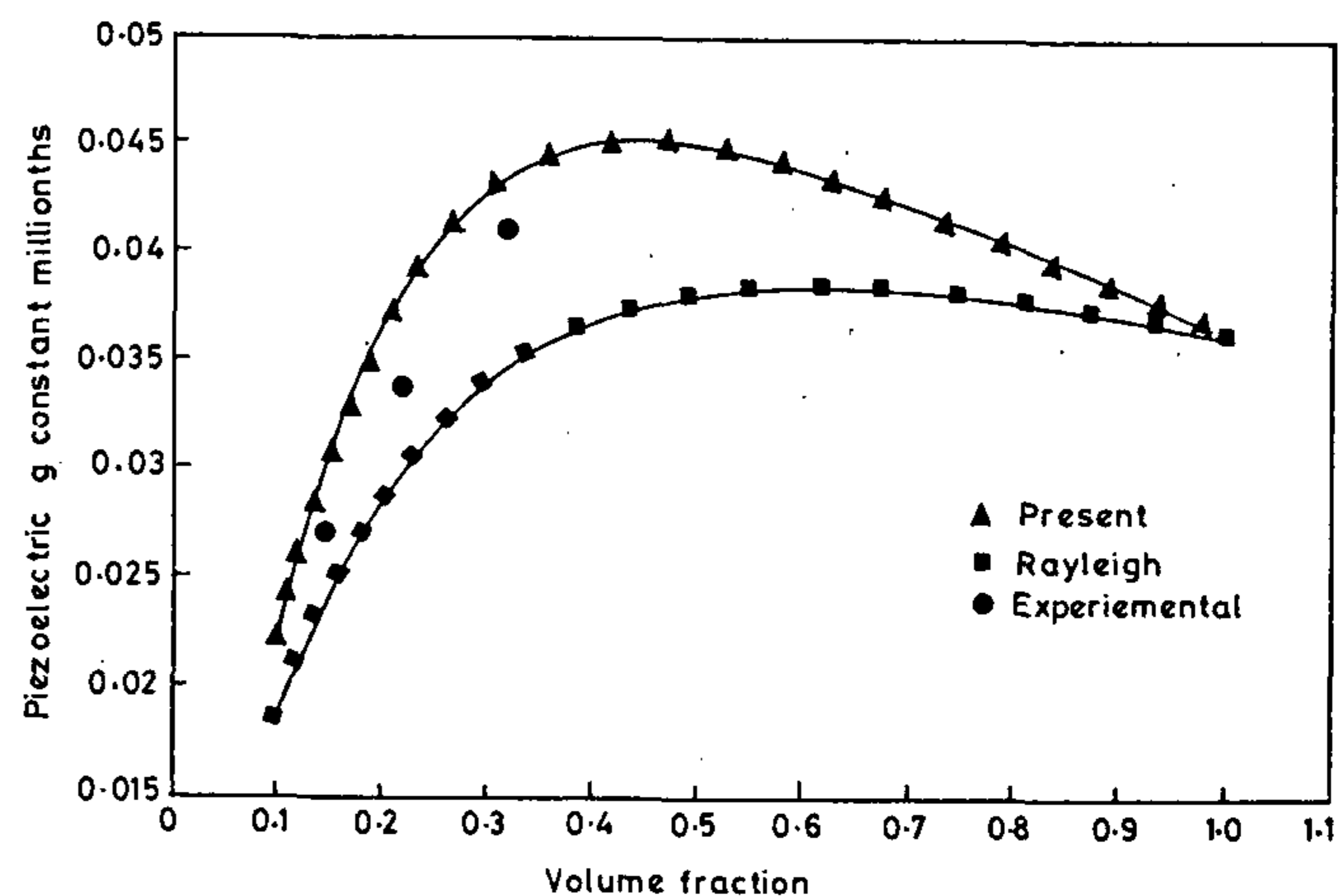


Figure 7. Comparison of experimental and theoretical values of piezoelectric g constant for PZT-PVDF composite (ref. 44).

from ref. 44. It can be seen that the piezoelectric d coefficients calculated using eq. (25) for composite's dielectric constant in eq. (42) agree well with the experimental values.

Conclusions

In summary, the mixture rules of dielectric properties of these composites with 0-3 or 3-0 connectivity are modified taking into account the local field interactions. Theoretical values of dielectric constants of 3-0 and 0-3 polymer piezoelectric composites calculated using the present model are in good agreement with the experimental values even up to 70% of piezoelectric phase in the composite. A model for estimation of impedance and electromechanical coupling coefficients of these composites with 2-2 connectivity for circular and rectangular geometry is presented. The piezoelectric constants of these materials exhibit Debye-type relaxations. Cole-Cole plots using real and imaginary components of piezoelectric constants have been drawn. A stress field applied to the piezoelectric polymer composite material can produce an overall piezoelectricity. Piezoelectric constant of these materials is related to the elastic and dielectric properties of the component phases. Using the modified equations piezoelectric properties of the composite are estimated.

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MEETINGS/SYMPOSIA/SEMINARS

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Speech acoustics; Underwater acoustics; Ultrasonic and NDT; Acoustic emission; Acoustic imaging, etc.

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