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Piezoelectric relaxation in polymer and ferroelectric composites

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Recently, fairly large numbers of studies have been reported on piezoelectric relaxations of polymers. The piezoelectric constants of polymer and ferroelectric composites also show such relaxations. It has been found that both polymer and polymer and ferroelectric composities exhibit typical Debye-type piezoelectric dispersion. Cole–Cole diagrams for the piezoelectric properties of these materials have been drawn and an attempt has been made to interpret the results.

1. Introduction

It is well recognized that studies of dielectric and elastic dispersions provide valuable information about molecular mechanisms of electric and mechanical properties of materials [1]. The dependence of piezoelectricity on dielectric and elastic properties can lead to information about the electromechanical nature of the solids. In fact, piezoelectricity can be defined as a strain dependence of electric polarization [2].

Piezoelectric dispersion occurs in close connection with dielectric and elastic dispersions. Dielectric relaxations can be of various types. The disappearance of various polarizations as the frequency of observation is increased, leads to various relaxation effects, space charge, molecular and electronic polarizations being major contributions, the relaxations due to these polarizations can generally be observed at audible, microwave and optical frequencies, respectively [3]. However, because the frequency of sound waves is much lower compared to the ultraviolet or infrared frequencies, only piezoelectric dispersions associated with molecular motion are observable. The relaxation behaviour manifests itself in the frequency dependence of the piezoelectric constant and also in its temperature dependence. Polymers and their composites with ferroelectric materials are generally heterogeneous. Polymers are heterogeneous because they contain crystallites surrounded by amorphous regions. Polymer and ferroelectric composites are heterogeneous because they are multiphase systems. When the frequency or temperature is varied, local mode motion, side motion and segmental motion of the main chain are activated and electromechanical relaxations occur. Piezoelectric dispersion in polymers, ferroelectrics and compositics of these materials follows Debye-type relaxations. Cole–Cole diagrams have been drawn for piezoelectric constants of these materials, and an attempt is made here to interpret the results.

2. Theory

The piezoelectric stress constant, e, and the piezoelectric strain constant, d, may be defined as follows [2]

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

$$d = \frac{1}{4\pi C}\left(\frac{D}{S}\right)_E = \frac{e}{C} \quad (2)$$

Other piezoelectric constants are

$$h = \frac{4\pi e}{\varepsilon} \quad (3)$$

and

$$g = \frac{4\pi e}{C\varepsilon} \quad (4)$$

where D is the electric displacement, E the electric field, S the strain, T the stress, C the elastic constant, and ε the dielectric constant.

To describe the dynamic response to the sinusoidal excitation, the above constants must be complex

$$\varepsilon = \varepsilon' + j\varepsilon'' \quad (5)$$

$$C = C' + jC'' \quad (6)$$

$$d = d' + jd'' \quad (7)$$

$$e = e' + je'' \quad (8)$$

The piezoelectric dispersion is a typical Debye-type relaxation given by [4]

$$d' = d_\infty + \frac{d_s - d_\infty}{1 + (w\tau)^2} \quad (9)$$

$$d'' = \frac{(d_s - d_\infty)w\tau}{1 + (w\tau)^2} \quad (10)$$

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and

$$\tan \delta_d = \frac{d''}{d'}$$

$$= \frac{d_s - d_\infty}{d_\infty} \frac{w\tau}{1 + (w\tau)^2} \quad (11)$$

If $w\tau = 1$, then

$$2(\tan \delta_d)_{\max} = \frac{d_s - d_\infty}{d_\infty}$$

$$= \frac{\Delta d}{d_\infty} \quad (12)$$

where w is the angular frequency, τ the relaxation time d_s and d_∞ are static and high frequency piezoelectric constants. Satisfaction of Equation 12 implies that the relaxation is of Debye type. Cole–Cole diagrams would be semi-circles for such a relaxation.

Let the representative units in the polymer and ferroelectric composite consist of concentric spheres of radii a and b so that $a^3/b^3 = \phi$ = volume fraction (Fig. 1). The inner sphere represents an inclusion of polymer of dielectric constant ε_2 and elastic constant C_2. The shell around this sphere represents a matrix of constants ε_1 and C_1. The unit is covered with a homogeneous medium of properties ε and C of composite.

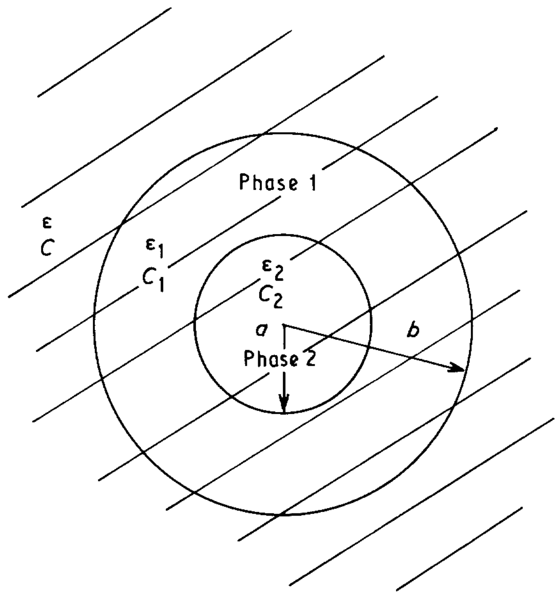

Figure 1 Representative unit of a two-phase system of a matrix with spherical inclusions.

Then we have [5]

$$\varepsilon = \frac{2\varepsilon_1 + \varepsilon_2 - 2(\varepsilon_1 - \varepsilon_2)}{2\varepsilon_1 + \varepsilon_2 + (\varepsilon_1 - \varepsilon_2)} \varepsilon_1 \quad (13)$$

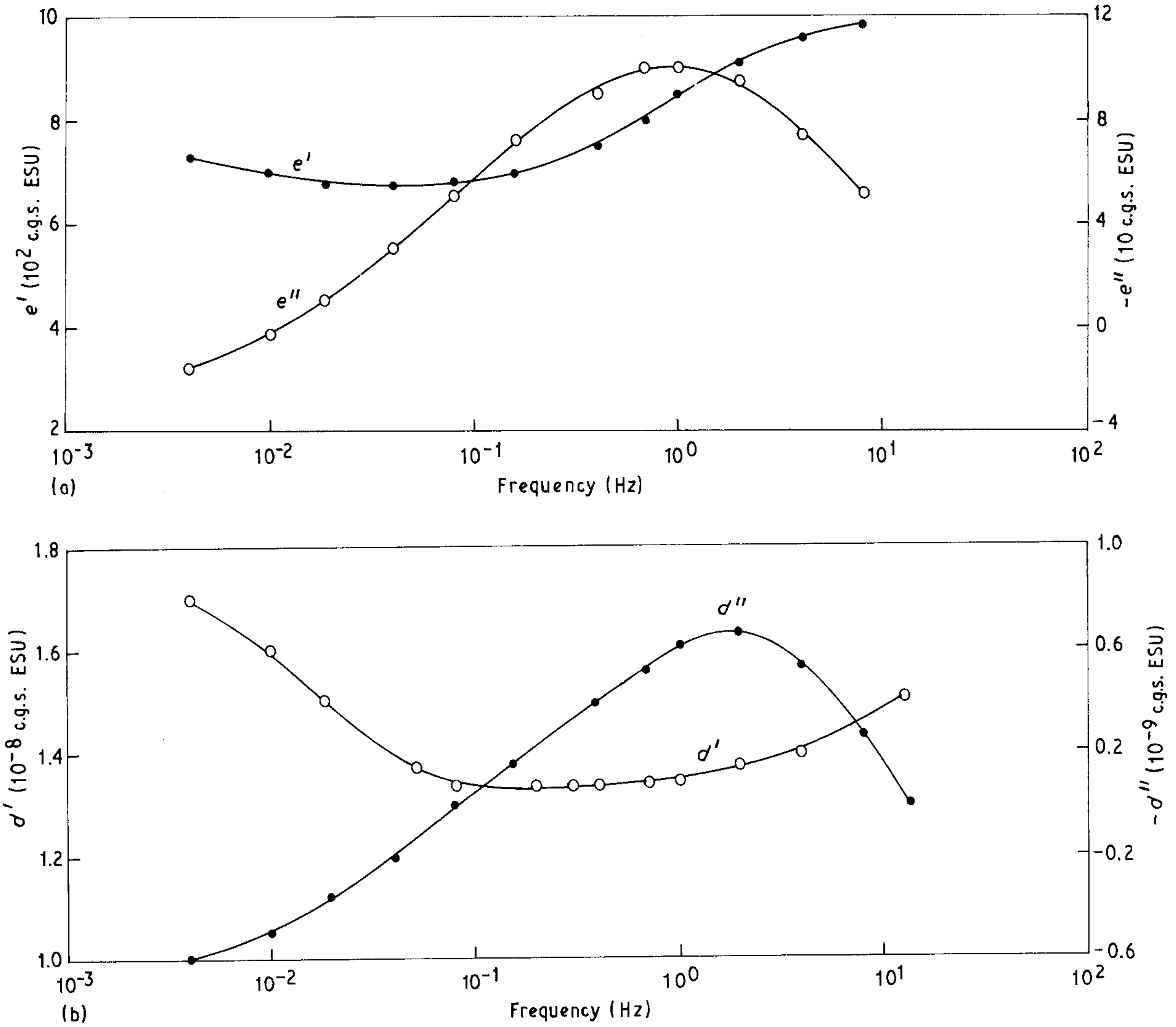

Figure 2 Frequency dependence of piezoelectric constants of PMLG at 12 °C (after Hayakawa *et al.* [6]). (a) e', $-e''$, (b) d', $-d''$, (c) G', $-G''$.

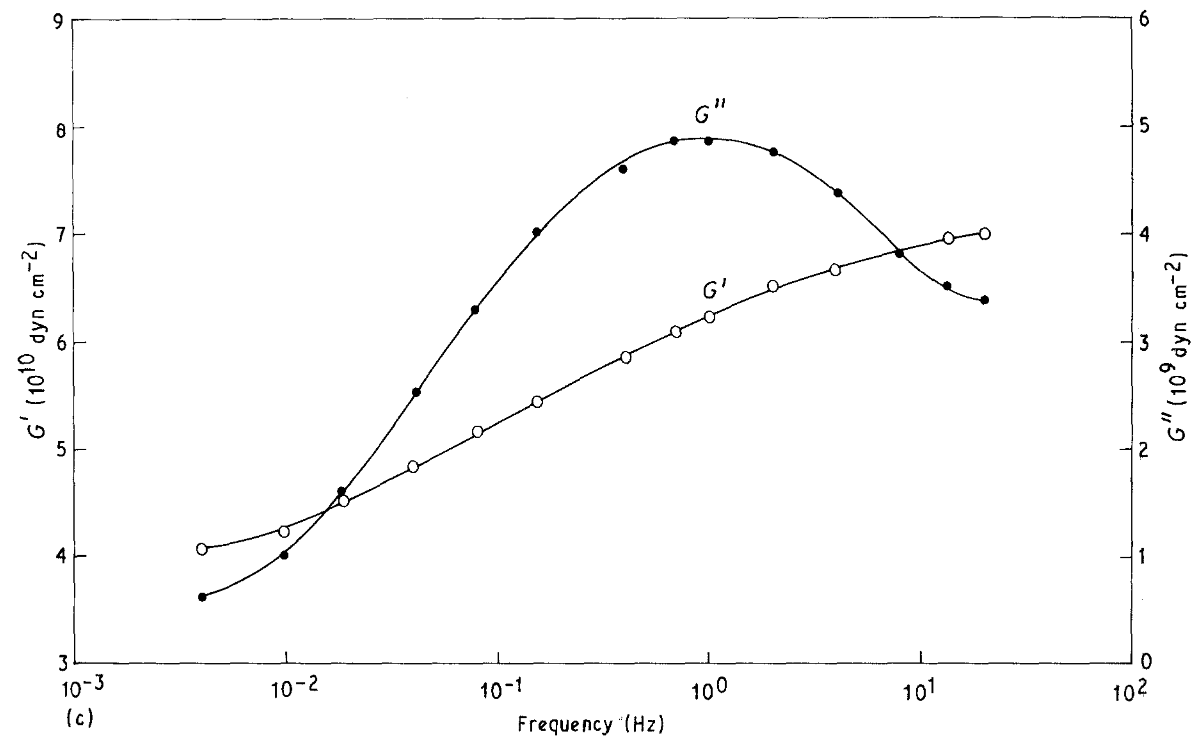

Figure 2 Continued.

If both phases are incompressible,

$$C = \frac{3C_1 + 2C_2 - 3(C_1 - C_2)}{3C_1 + 2C_2 + 2(C_1 - C_2)} C_1 \quad (14)$$

Because Equations 5 and 7 indicate that ε and C are complex, one can separate the real and imaginary parts of Equation 13 as follows

Real part

$$\varepsilon' = \frac{\varepsilon_1'(X_1X_2 + Y_1Y_2) + \varepsilon_1''(X_1Y_2 - Y_1X_2)}{X_1^2 + Y_1^2} \quad (15)$$

Imaginary part

$$\varepsilon'' = \frac{\varepsilon_1'(X_2Y_1 - X_1Y_2) + \varepsilon_1''(X_1X_2 + Y_1Y_2)}{X_1^2 + Y_1^2} \quad (16)$$

where

$$X_1 = 2\varepsilon_1' + \varepsilon_2' - 2\phi(\varepsilon_1' - \varepsilon_2') \quad (17a)$$

$$Y_1 = 2\varepsilon_1'' + \varepsilon_2'' - 2\phi(\varepsilon_1'' - \varepsilon_2'') \quad (17b)$$

$$X_2 = 2\varepsilon_1' + \varepsilon_2' + \phi(\varepsilon_1' - \varepsilon_2') \quad (17c)$$

$$Y_2 = 2\varepsilon_1'' + \varepsilon_2'' + \phi(\varepsilon_1'' - \varepsilon_2'') \quad (17d)$$

3. Results and discussion

Fig. 2 shows the dispersion of piezoelectric constants e and d as a function of frequency for poly (γ-methyl-*L*-glutamate) (PMLG). It also gives frequency variation of the piezoelectric constants G' and G''. All these properties show a strong frequency dependence with loss peaks around 1 Hz frequency. Fig. 3 shows the complex piezoelectric strain constant, d, for PZT ceramic samples (poled at $10\,\mathrm{kV\,cm^{-1}}$) as a function of temperature.

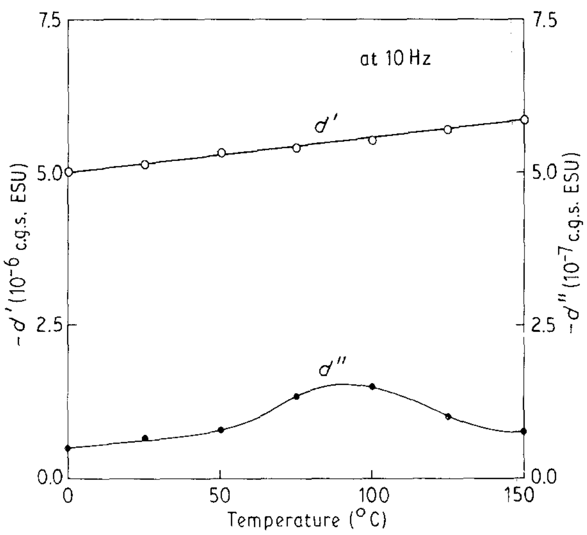

Figure 3 Temperature dependence of d of PZT ceramic samples poled at $10\,\mathrm{kV\,cm^{-1}}$ (after Furukawa *et al.* [7]).

A peak in d'' data can be observed around 90 °C. Variation of the piezoelectric constant of PZT and epoxy resin composite with temperature (poled at $100\,\mathrm{kV\,cm^{-1}}$) is given in Fig. 4. The loss peak is observed at much lower temperature compared to the PZT sample.

Cole–Cole diagrams of PMLG, PZT and PZT–epoxy resin composite are shown in Figs 5–7, respectively. Because the relaxation time increases with increasing temperature, the temperature increase at a fixed frequency has an effect equivalent to a frequency decrease at a fixed temperature. Hence the temperature variation of d at fixed frequency is used for drawing Figs 6 and 7.

The piezoelectric effect in polymers is generally attributed to their heterogeneity and to trapped charges.

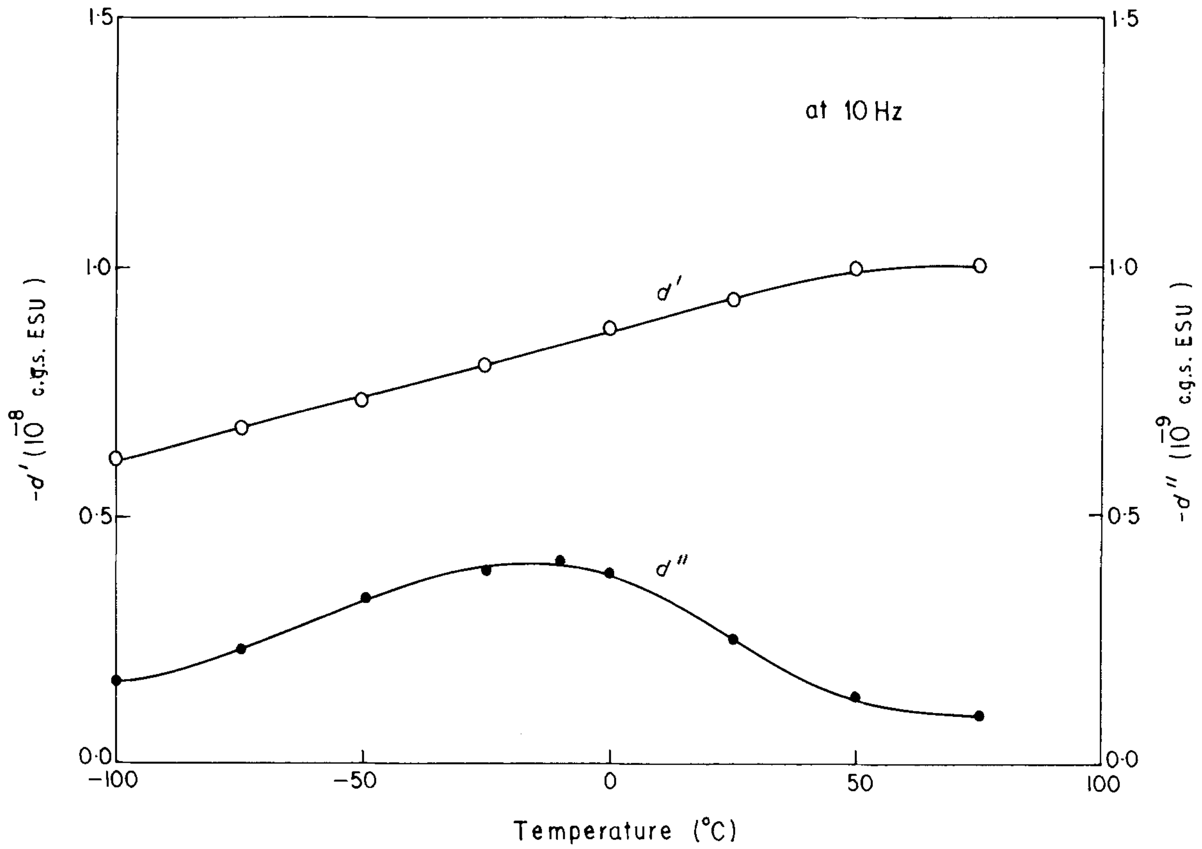

Figure 4 Temperature dependence of PZT–epoxy resin composite with $\phi = 0.131$ poled at $100\,\mathrm{kV\,cm^{-1}}$ (after Furukawa *et al.* [7]).

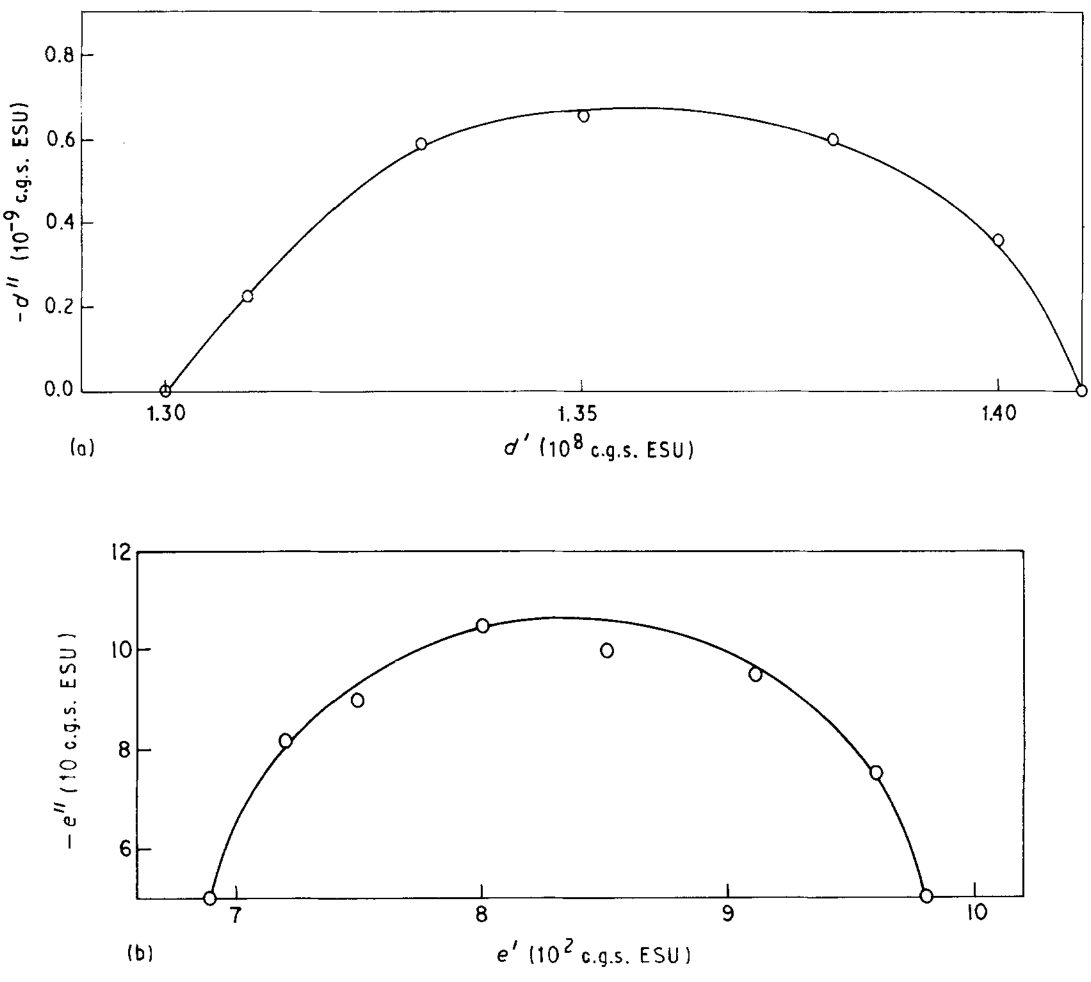

Figure 5 Cole–Cole diagram of PMLG.

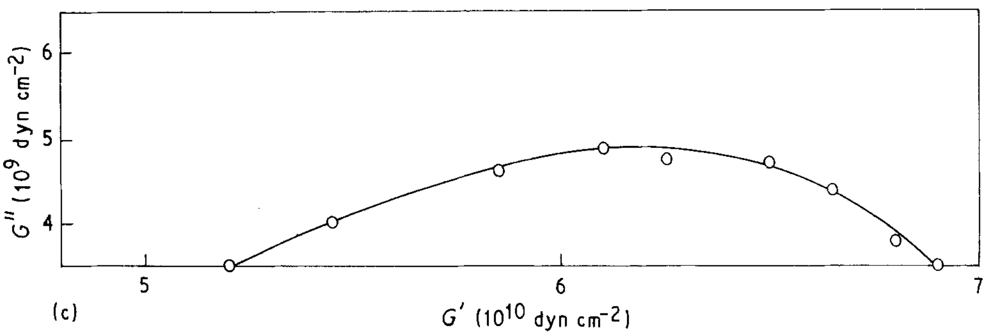

Figure 5 Continued.

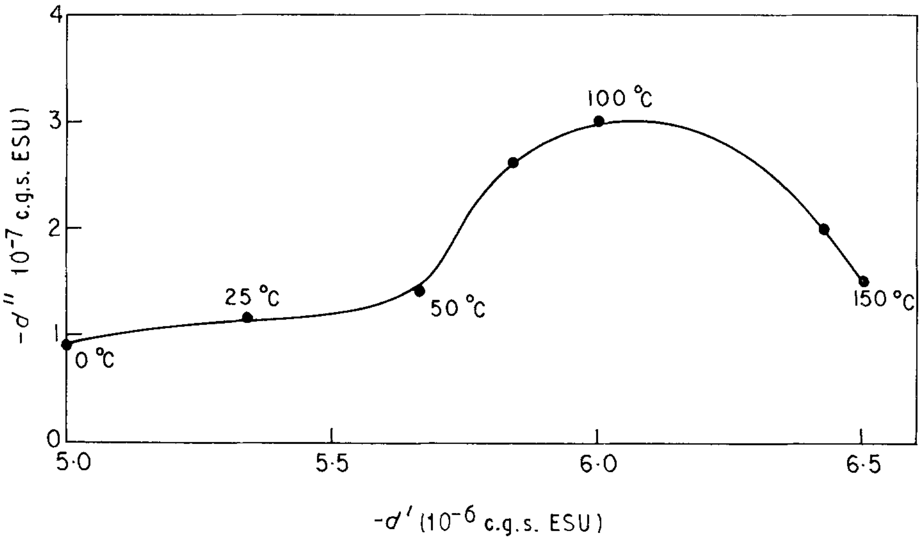

Figure 6 Cole–Cole diagram of PZT poled at $10\,kV\,cm^{-1}$.

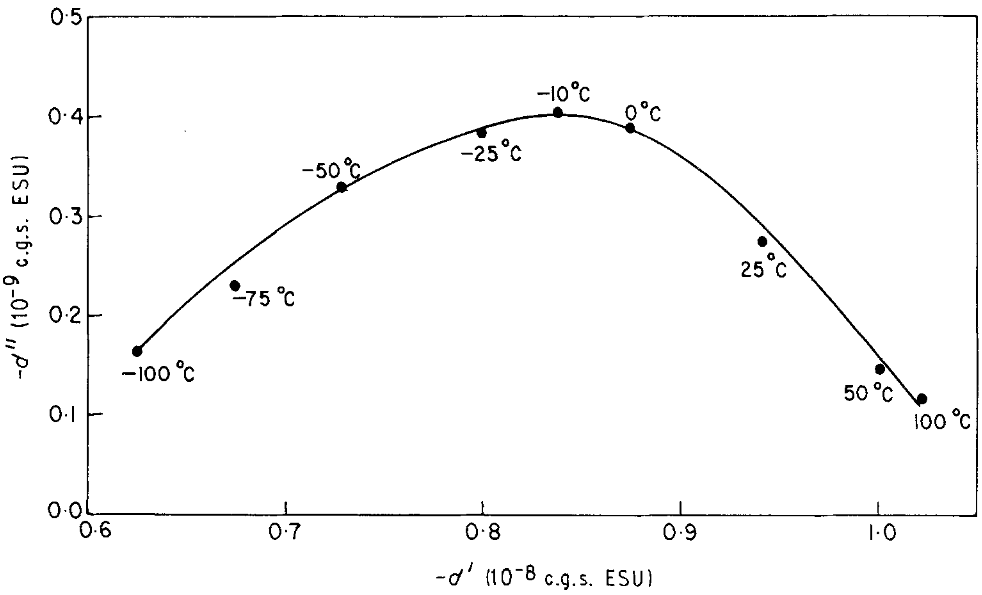

Figure 7 Cole–Cole plot of PZT–epoxy resin poled at $100\,kV\,cm^{-1}$.

PZT and epoxy resin composites show piezoelectricity if they are poled with high d.c. electric fields, because ferroelectric PZT exhibits spontaneous polarization, P_s, and this polarization is changed due to application of strain resulting in piezoelectricity. Piezoelectricity in composites arises due to hetrogeneity and trapped charges in the interfaces [8]. The relaxations reflected in piezoelectric properties are related to the hetrogeneity and nature of trapped charges. Therefore, a systematic study of piezoelectric relaxations through Cole–Cole plots can lead to an understanding of the origin of piezoelectricity in composites.

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