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Dielectric studies of PZT–polymer composites

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Lead zirconate titanate (PZT)/Nylon 66 composites having 3–3 connectivity have been prepared by a relatively simple fabrication process. The d.c. conductivity and dielectric constant were measured from 30 to 220° C at various frequencies (0.1, 1, 10, 100 kHz). The dielectric constant increased with increasing temperature and PZT-constant of the composite up to 50 vol % PZT, but later showed a decrease due to increase in porosity in the samples. The dielectric constant also increased rapidly at higher temperature (> 100° C) for lower frequencies (0.1 and 1 kHz) due to intergrain polarization. The dielectric loss increased with increasing temperature and with decreasing PZT content of the composite. D.c. conductivity increased continuously with increasing temperature.

1. Introduction

Lead zirconate titanate (PZT) is a well-known piezoelectric material and two decades of research have not succeeded in finding a better one in a homogeneous system. Hence hetero-structure materials, such as composites of ceramics and polymers, have attracted much interest in recent years.

Newham [1] reported the concept of connectivity. Skinner *et al.* [2] developed a flexible PZT–polymer composite transducer in which the two phases formed an interpenetrating three-dimensional network. This form of diphasic connectivity is referred to as 3–3 structure. The composite takes maximal advantage of the useful properties of each phase. The resultant composite has a low density for improved acoustic coupling to water or human tissue, is compliant with better resistance to mechanical shock and provides high damping, can be flexible (depending on the type of polymer) and has a low dielectric constant. Newham [1] succeeded in preparing a 3–3 composite of PZT–silicone rubber and PZT–epoxy by the coral replamine process. Shrout *et al.* [3] investigated a 3–3 composite of the same material prepared by Burned-out Plastic Sphere (BURPS) technique. Safari *et al.* [4] prepared a material by arranging PZT spheres in a close-packed monolayer in a flat plastic container and pouring polymer over the spheres.

Very few studies [5, 6] have been reported on the electrical properties of PZT–polymer composites and no attempt has been made so far to determine the effect of compositional variation of component phases on the electrical properties. The present study reports the d.c. conductivity and dielectric constant of PZT and Nylon 66 (polyhexamethylene adipamide) composite over a wide temperature (30 to 220° C) and frequency range (0.1, 1, 10, 100 kHz) for varying PZT/polymer volume ratio. This polymer is special interest because of the great strength of the interchain forces and of its higher melting point.

2. Experimental details

The method of mixing [2, 7, 8] the powdered ceramic with a polymer is the most convenient way of preparing a composite of any specified composition and geometry. However, because the sample must be poled after its initial preparation in order to produce any piezoelectric effects, the volume fraction, resistivity and dielectric constant of the polymer become important.

Composite discs were prepared by dissolving Nylon 66 in formic acid and then adding PZT powders (0 to 75 μm). Upon slow heating under constant stirring, formic acid evaporates and the solid mass left behind can be formed into any desired shape. Composites having different volume fractions of PZT and polymer were prepared by taking proportional quantities of components. Composites with high volume percentage ($\geqslant$ 80%) of either PZT or polymer posed difficulties for fabrication. After polishing, air-drying silver paint was applied for electroding purposes.

The dielectric measurements were done using a GR-1615A capacitance bridge at frequencies of 0.1, 1, 10 and 100 kHz in the temperature range 30 to 220° C. The temperature of the sample was measured by a Pt/Pt–Rh thermocouple. All measurements were done in three-terminal configuration. Cooling runs were taken for the observations.

The d.c. conductivity was measured using Keithley 610C electrometers in the temperature range 30 to 220° C. A d.c. field of about 25 V cm^{-1} was applied. It is known that absorption of water gives excessive effects on conductivity and dielectric loss, hence measurements were taken in vacuum.

3. Results and discussion

3.1. Dielectric constant

Fig. 1 shows the variation of dielectric constant with temperature at four fixed frequencies (0.1, 1, 10 and 100 kHz) for a 50 vol % PZT composite. The dielectric

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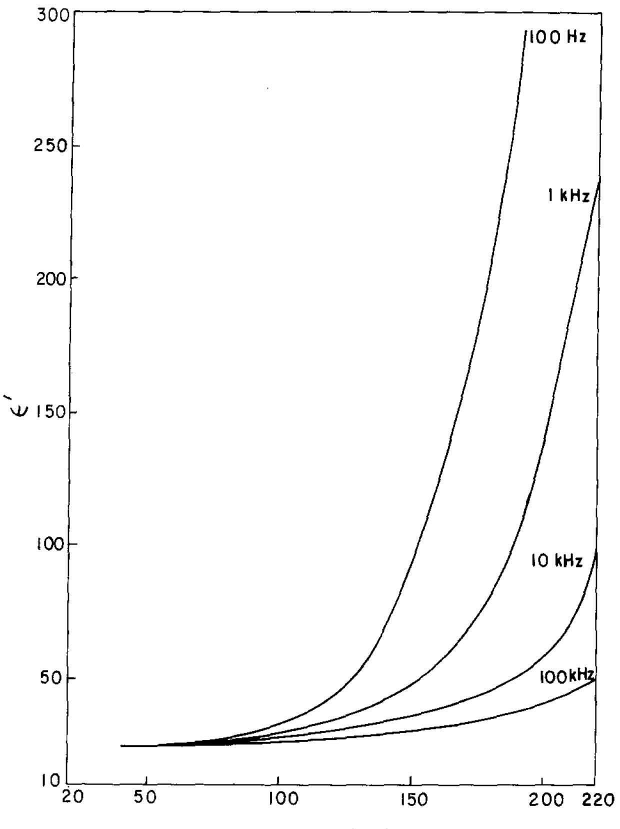

Figure 1 Temperature dependence of dielectric constant (ε′) for PZT–Nylon 66 (50 vol % PZT) at various frequencies.

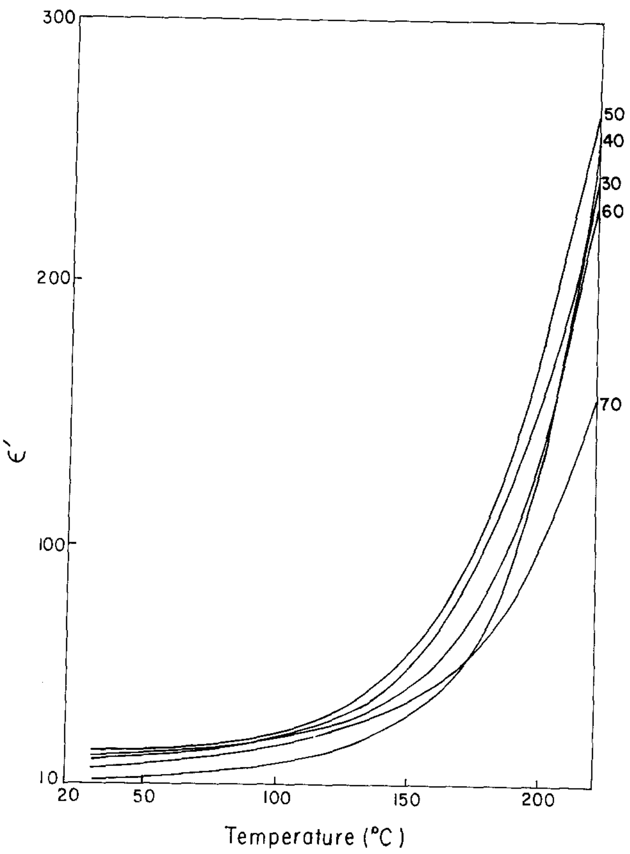

Figure 2 Temperature dependence of dielectric constant (ε′) of PZT–Nylon 66 composites of various compositions (30, 40, 50, 60, 70 vol % PZT) at a fixed frequency of 1 kHz.

constant shows a weak frequency dispersion and temperature dependence up to 130° C. Above 130° C, it shows a strong temperature dependence and frequency dispersion. Similar reports [7, 8, 9] exist in the literature for PZT–epoxy and PZT–PVDF (Polyvinylidene Fluoride) composites. At low frequencies (0.1 and 1 kHz) the dielectric constant rises very sharply above 130° C due to intergrain polarization. Furukawa *et al.* [10] reported that the accumulation of ionic impurities at the interface of the PZT–PVA composite and electrode polarization are responsible for the increase in dielectric constant at low and high temperature, respectively.

Similar characteristics were observed for all other composites having 30, 40, 60 and 70 vol % PZT. Fig. 2 shows the variation of dielectric constant with temperature for various composites at a fixed frequency of 1 kHz. Fig. 3 is drawn to show the low-temperature region (⩽ 130° C) with clarity. It is seen that the dielectric constant increases with increasing PZT content of the composite until PZT attains 50 vol % and then decreases with increasing PZT volume fraction. This may be due to the fact that porosity in the sample decreases with increasing PZT volume fraction up to 50% and then shows an increase and the composite becomes a three-phase system with air acting as the third phase. The continuous increase of dielectric constant with PZT volume fraction in PZT–PVDF composite reported by other workers [8] is due to the absence of porosity because the composite was prepared by pressing at high temperature

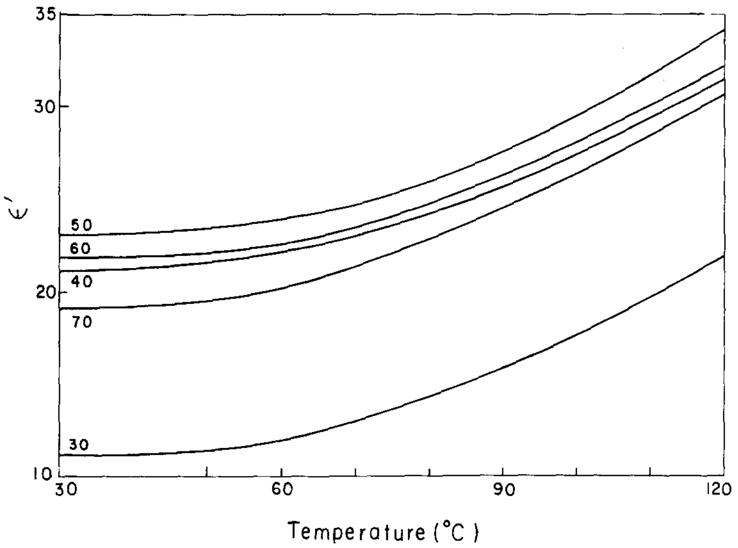

Figure 3 Temperature dependence of dielectric constant (ε′) pf PZT–Nylon 66 composites of various compositions (30, 40, 50, 60, 70 vol % PZT) in the low-temperature range at a frequency of 1 kHz.

TABLE I Comparison of dielectric constants of PZT (ε = 98)-Nylon 66 (ε = 10) composites

PZT (Vol %)	Dielectric constant		
	Experimental value	Equation 1	Equation 2
30	11.16	18.64	18.04
40	19.2	22.75	22.91
50	23.16	27.84	26.0
60	21.75	34.29	30.2
70	21.23	42.76	33.23

(200° C). But in our case, no pressure was applied, thereby leaving pores in the composite due to evaporation of the solvent.

Several authors [5, 7, 11] have calculated the dielectric constant, ε, of a two-phase system, particularly PZT–polymer composites using the following formula

$$\varepsilon = \frac{2(1-x)\varepsilon_1 + (1+2x)\varepsilon_2}{(2+x)\varepsilon_1 + (1-x)\varepsilon_2}\,\varepsilon_1 \qquad (1)$$

where x is the volume fraction of the inclusion. But in our case the composites have lower values of dielectric constant (Table 1) at room temperature than the values obtained using the above formula. This discrepancy decreases if we apply the following three-phase mixture theory [12] and reducing this formula for spherical inclusions with three phases, because air acts as the third phase for our porous composites

$$\left(\frac{\varepsilon-\varepsilon_1}{\varepsilon_1}\right) = \left(\frac{\varepsilon-\varepsilon_1}{\varepsilon_1}\right)\left(\frac{E_2}{E}\right)\left(\frac{V_2-V_3}{V_1}\right) + \left(\frac{\varepsilon_3-\varepsilon_1}{\varepsilon_1}\right)\left(\frac{E_3}{E}\right)\left(\frac{V_3}{V_1}\right) \qquad (2)$$

The volume ratios V_2/V_1 and V_3/V_1 are the volume fractions occupied by materials $\varepsilon_2 + \varepsilon_3$ and ε_3, respectively, and E_2 and E_3 are average fields in materials ε_2 and ε_3, respectively. Dielectric constant increases with increasing PZT content of the composite (up to 70 vol %) (Table I) if we apply Equation 2 taking porosity into account, but in our case the dielectric constant attains a maxima at 50 vol % PZT and then decreases even if the PZT content is increasing. This may be due to some critical bonding that takes place between the components at this composition. The assumption that component phases are spherical also may not be true. Such results of a critical maxima have been reported [9] for a BT–PVDF composite.

3.2. Dielectric loss

Fig. 4 shows the variation of dielectric loss (tan δ) with temperature for various frequencies (0.1, 1, 10, 100 kHz) for a 50–50 composite. The loss increased with increasing temperature. The increase in loss factor with decreasing frequency is due to the contribution of d.c. conductivity caused by the presence of ionic impurities present in the composite. Similar observations exist in the literature [10] for a PZT–polymer composite. The loss also increased with decreasing PZT content of the composites. Dasgupta and Doughty [5] have observed that dielectric loss increases with increasing PZT content of the composite, due to decreased steric hindrance of the polymer.

4. D.c. conductivity

The d.c. conductivity study is shown in Fig. 5 where log $\sigma_{\text{d.c.}}$ is plotted against $10^3/T$(K) in the temperature range 100 to 220° C. It is seen that d.c. conductivity increases continuously with increasing temperature. PZT behaves as a ferroelectric in this temperature range, but the plot of log $\sigma_{\text{d.c.}}$ against $10^3/T$(K) is not linear, rather a continuous curve. Such continuous curves have been reported by Seanor [13], and McCall and Anderson [14] for Nylon 66. The direct current conductivity which becomes large as the temperature is raised is due to the motion of ions in the polymer. The d.c. activation energy decreases from 0.93 eV at 100° C to 0.46 eV at 220° C for a 30 vol % PZT composite and from 0.64 eV at 100° C to 0.48 eV at 220° C for a 70 vol % PZT composite. This is in agreement with the values reported for PZT [15] and Nylon 66 [13]. The electrical conduction in a crystalline ceramic such as PZT is ionic and in a semicrystalline polyamide such as Nylon 66 is also ionic [16]. Low values of

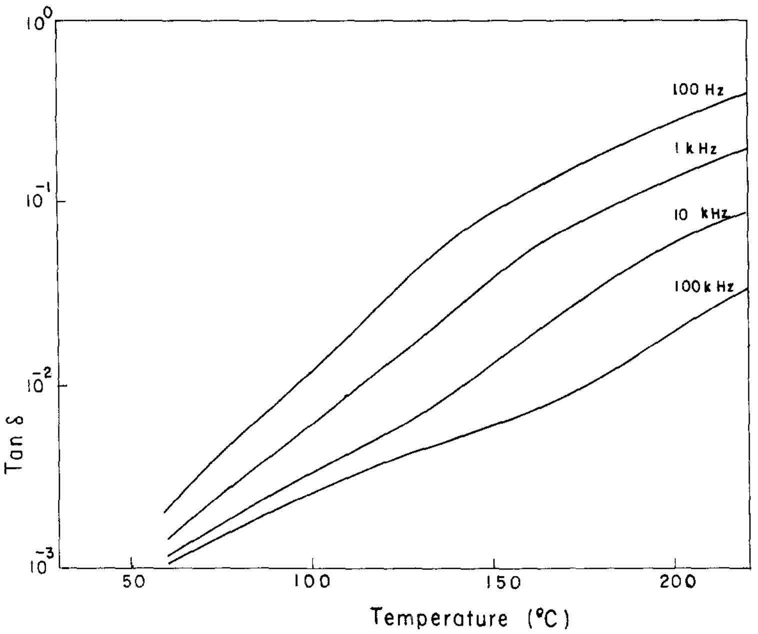

Figure 4 Temperature dependence of tan δ of PZT–Nylon 66 composite (50 vol % PZT) at various frequencies.

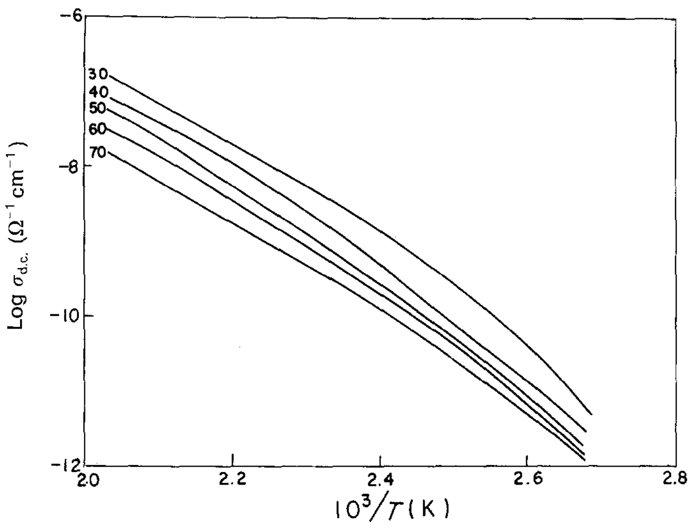

Figure 5 Variation of d.c. conductivity with temperature.

conductivity for PZT–ecogel polymer have also been reported by Sa-Gong [17]. Due to sharp rise in conductivity at higher temperatures, our study was confined to temperatures up to 220° C.

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