Thermal Hysteresis in the Permittivity and Polarization of Lead Zirconate Titanate/Vinylidenefloride-trifluoroethylene 0-3 Composites

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ABSTRACT

The permittivities of 70/30 vinylidene fluoride-trifluoroethylene copolymer and lead zirconate titanate/vinylidene fluoride-trifluoroethylene 0-3 composites have been measured at 1 kHz over the temperature range of 20 to 120°C. Thermal hysteresis was observed for the 0-3 composites and abrupt changes in the permittivities occurred at different temperatures upon heating and cooling. Good agreement was found between the measured permittivities and the predictions of the Bruggeman model. Implications of the thermal hysteresis behavior on the poling of 0-3 composites are also discussed.

1. INTRODUCTION

P IEZOELECTRIC 0-3 composites consist of piezoelectrically active ceramic particles dispersed in a 3-dimensionally connected polymer matrix. 0-3 composites of various compositions have received considerable attention recently because of their potential use as high energy storage capacitor dielectrics [1] and as transducers and sensors in smart systems [2-4]. One of the attractive features of polymeric composites is the ease of assuming a variety of forms, including thin sheets, bars and fibers. 0-3 composites also exhibit a high hydrostatic piezoelectric coefficient d_h and thus have considerable potential in hydrophone and ultrasonic transducer applications [5-10]. Although non-piezoelectric polymer matrices have mostly been used in previous work, 0-3 composites in which both the ceramic and polymer phases are piezoelectric also have attracted some interest [11-14].

In order to produce an electrically polarized composite, it must be poled such that the dipoles are aligned perpendicular to the plane of the composite and there are a number of reports describing the poling of 0-3 composites [15-19]. One of the major considerations in the poling of a 0-3 composite is the ratio ρ_c/ρ_p of the resistivity of the ceramic and the polymer. After a dc field has been applied to the composite for a time long compared to the interfacial relaxation time, the ratio of the electric fields in the two phases estimated from the Maxwell-Wagner model is given [16,18,20] by $E_c/E_p = \rho_c/\rho_p$,

implying that the field acting on the ceramic is controlled by the ratio of the resistivity of the ceramic and the polymer. Consequently, if the ceramic particles in a piezoelectric ceramic/polymer composite have a resistivity which is orders of magnitude lower than that of the polymer, the electric field across the ceramic is a very small fraction of the applied field, and the ceramic will only be partially poled. One way to reduce the resistivity of the polymer is to load it with a conducting or semiconducting filler such as carbon black, silicon, or germanium powder [21]. However, the addition of such a filler tends to increase the dielectric loss of the composite. Another way to improve poling is to exploit the different temperature dependences of the resistivities of the two phases [22]. If the resistivites are such that they converge as temperature increases, there will be a temperature at which poling is optimized.

If the piezoelectric copolymer vinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) is used as the matrix material, the sign of the piezoelectric constant of the copolymer is opposite to that of the ceramic so that cancellation in piezoelectric properties would occur [11,18]. We have carried out poling studies of 0-3 composites and have shown that it is possible to use a two-step poling procedure [18] to polarize the two phases in opposite directions so that their piezoelectric properties reinforce each other. In our previous report, [18] a long poling time (typically 2 to 4 h) was used. An alternative way of poling 0-3 composites is to apply an electric field for a time comparable to, or shorter than, the interfacial relaxation
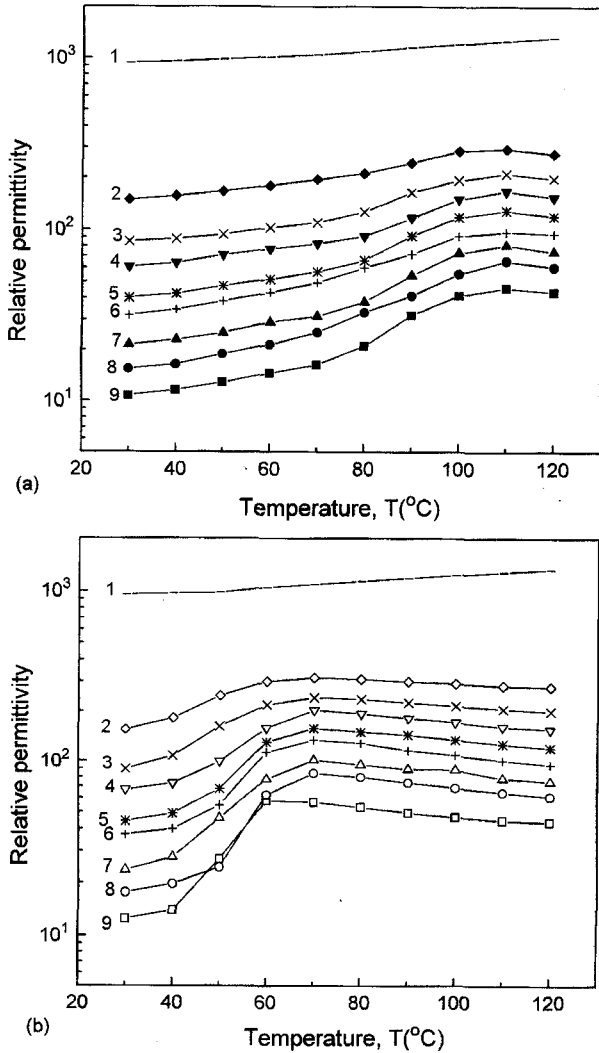
(a)

(b)

Figure 1. (a) Permittivities of 0–3 composites with different volume fractions of ceramic ϕ as functions of temperature upon heating. 1: $\phi = 1$, 2: $\phi = 0.67$, 3: $\phi = 0.56$, 4: $\phi = 0.49$, 5: $\phi = 0.37$, 6: $\phi = 0.28$, 7: $\phi = 0.17$, 8: $\phi = 0.09$, 9: $\phi = 0$. (b) Permittivities of 0–3 composites with different volume fractions of ceramic ϕ as functions of temperature upon cooling.

time τ which is given by [20]

$$\tau = \frac{\varepsilon_o[\varepsilon_p\phi + \varepsilon_c(1 - \phi)]}{\sigma_c(1 - \phi) + \sigma_p\phi} \qquad (1)$$

where ε_o is the permittivity of free space, $\sigma = 1/\rho$ is the conductivity and ε the permittivity of the composite sample. ϕ is the volume fraction of ceramic, and the subscripts p and c denote the polymer and the ceramic phase, respectively. This can be achieved by increasing the voltage acting on the sample from 0 to $+V$, maintaining the voltage at V for a time shorter than the relaxation time τ and then decreasing the voltage from $+V$ to 0, and this procedure is repeated for several times. During this process, the field experienced by each phase will be governed by the permittivities of the constituent phases [20, 23]. Therefore, the permittivities of the ceramic and the composite must be known in order to estimate the electric field experienced by the ceramic particles inside
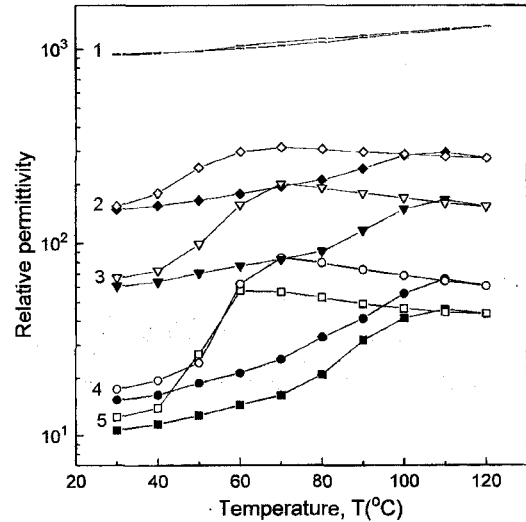

Figure 2. Thermal hysteresis in the permittivities of PZT/P(VDF-TrFE) 0–3 composite with different voulme fractions of ceramic ϕ. 1: $\phi = 1$, 2: $\phi = 0.67$, 3: $\phi = 0.49$, 4: $\phi = 0.09$, 5: $\phi = 0$. The filled and open symbols correspond to heating and cooling, respectively. heating and cooling

the composite.

The permittivities of P(VDF-TrFE) copolymers have been reported by previous workers [24, 25]. In the present work, a detailed investigation of the permittivities of the ceramic, copolymer, and 0–3 composites is reported and the implication for the poling of 0–3 composites is discussed.

2. FABRICATION OF 0–3 COMPOSITES

The P(VDF-TrFE) copolymer supplied by Atochem North America Inc. has a nominal TrFE content of 30%. The endotherm of the as-received copolymer pellets was measured on a Perkin Elmer DSC7 differential scanning calorimeter at a heating rate of 10°C /min. The Curie transition temperature for the first heating $(T_c^\uparrow)$ is 100°C and the Curie transition temperature on cooling $(T_c^\downarrow)$ is ~ 60°C.

The lead zirconate titanate (PZT) powder was supplied by Zhongshan University in China. The copolymer pellets were first dissolved in methyl-ethyl-ketone (MEK), and then a suitable amount of ceramic powder was blended into the solution. The mixture was then poured onto a petri-dish and, after evaporation of the solvent, the mixture was crushed into small pieces. Then the composite was molded into disks by hot pressing at 200°C in a compression molding machine. The composites disks have a diameter of 12.5 mm and thicknesses ranging from 0.5 to 0.9 mm.

3. PERMITTIVITY MEASUREMENTS

The relative permittivity ε' and dielectric loss ε'' of the unpoled 0–3 composite samples were determined by measuring the capacitance C and dissipation D (loss tangent $\tan \delta$) at 1 kHz using a HP4194 A impedance analyzer. The sample was heated or cooled at
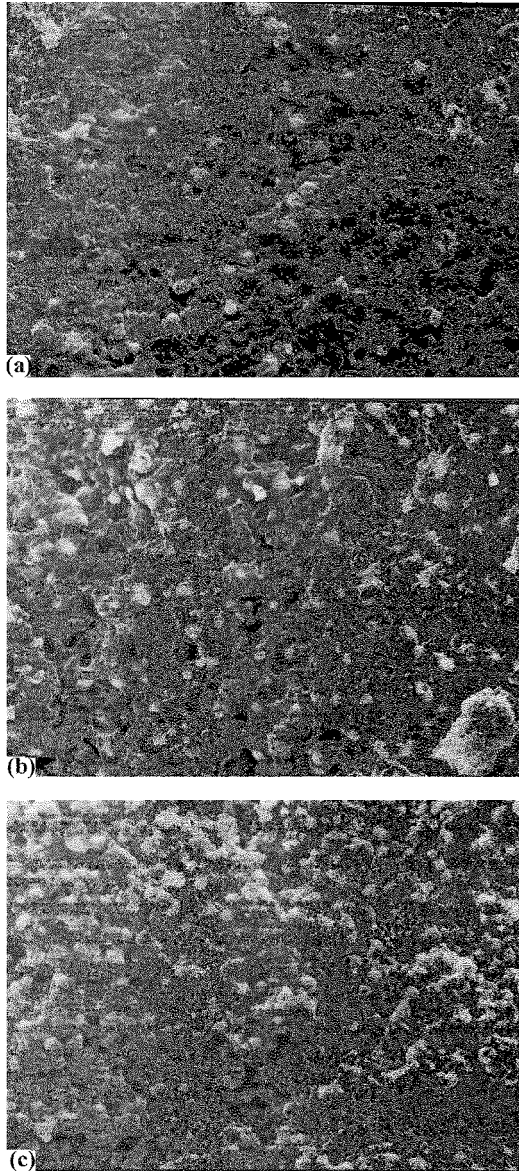
Figure 3. SEM micrographs (×2000) for PZT/P(VDF-TrFE) composites with different volume fractions of ceramic ϕ. (a) $\phi = 0.09$, (b) $\phi = 0.49$, (c) $\phi = 0.67$.

a rate of ~ 1 K/min in a temperature controlled oven until a certain temperature was reached, and then kept at that temperature for half an hour before a measurement was made. The resulting permittivities for various volume fractions of ceramic are shown as functions of temperature in Figure 1. Figure 1(a) shows that the relative permittivity of the ceramic is ~ 1000 at 30°C and it increases with temperature. For the copolymer, a relaxation peak was observed near the Curie temperature upon heating ($T_c^\uparrow \sim 100$°C) but the peak becomes less conspicuous as the volume fraction of ceramic ϕ increases. Figure 1(b) shows the permittivities upon cooling. A relaxation peak occurs near the Curie transition temperature upon cooling ($T_c^\downarrow \sim 60$°C) and the peak also becomes shallower as ϕ increases. If the heating and the cooling curves are plotted together (Figure 2), a thermal hysteresis loop is observed not only

for the copolymer [24, 25] but also for the 0–3 composites. When the copolymer is heated, the sample is ferroelectric below $T_c^\uparrow$ and the permittivity increases with temperature. At temperatures above $T_c^\uparrow$, ε_p becomes fairly constant and equal to the value of ε_p for the para-electric phase. Upon cooling, the permittivity remains fairly constant (with a value characteristic of the paraelectric phase) until $T_c^\downarrow$ is reached. Then it decreases with temperature and returns to its original value at room temperature. In a composite, which is a mixture of the two phases, thermal hysteresis only occurs in the copolymer phase. Hence as the amount of copolymer decreases, the thermal hysteresis becomes less conspicuous.

4. COMPARISON WITH THE BRUGGEMAN MODEL

Figures 3(a) to (c) show scanning electron micrographs of the fracture surfaces of composites with ceramic volume fractions of 0.09, 0.49 and 0.67, respectively. It is seen that the ceramic particles are roughly spherical and are dispersed quite uniformly in the polymer matrix. Therefore the permittivities of the composites can be understood in terms of the Bruggeman equation [20, 26]

$$\frac{\varepsilon_c - \varepsilon}{(\varepsilon)^{1/3}} = \frac{(1 - \phi)(\varepsilon_c - \varepsilon_p)}{(\varepsilon_p)^{1/3}} \qquad (2)$$

where ε_c, ε_p and ε are the permittivities of the ceramic, copolymer and composite, respectively. In the derivation of Equation (2), it is assumed that the concentration of the dispersed spherical particles is gradually changed by infinitesimal increments, and simultaneously the permittivity of the medium around a particle slowly changes from ε_p to ε.

Since the ceramic, copolymer and composite exhibit dielectric losses, the quantities ε_c, ε_p and ε are complex and can be written as

$$\varepsilon_c = \varepsilon_c'(1 - i \tan \delta_c) \qquad (3)$$

$$\varepsilon_p = \varepsilon_p'(1 - i \tan \delta_p) \qquad (4)$$

$$\varepsilon = \varepsilon'(1 - i \tan \delta) \qquad (5)$$

where the real quantities ε_c', ε_p' and ε' are now called the permittivities, and $\tan \delta_c$, $\tan \delta_p$ and $\tan \delta$ are the corresponding loss tangents. Since the loss tangents are small (< 0.05), we expand Equation (2) in powers of the loss tangents and and keep only terms up to the first order. Then the permittivity ε' and loss $\varepsilon'' = \varepsilon' \tan \delta$ of a composite are given by

$$\frac{\varepsilon_c' - \varepsilon'}{(\varepsilon')^{1/3}} = \frac{(1 - \phi)(\varepsilon_c' - \varepsilon_p')}{(\varepsilon_p')^{1/3}} \qquad (6)$$

$$\varepsilon'' = \frac{(\varepsilon_c' - \varepsilon')(\varepsilon_c' + 2\varepsilon_p')\varepsilon'}{(\varepsilon_c' - \varepsilon_p')(\varepsilon_c' + 2\varepsilon')\varepsilon_p'}\varepsilon_p'' + \frac{3(\varepsilon' - \varepsilon_p')\varepsilon'}{(\varepsilon_c' - \varepsilon_p')(\varepsilon_c' + 2\varepsilon')}\varepsilon_c'' \qquad (7)$$

Figures 4(a) to (c) show the comparisons between the observed permittivities ε' and the predictions of the Bruggeman model (Equation (6)) for the composites at 30, 80 and 100°C (upon heating), respectively. The predictions of the parallel and series models
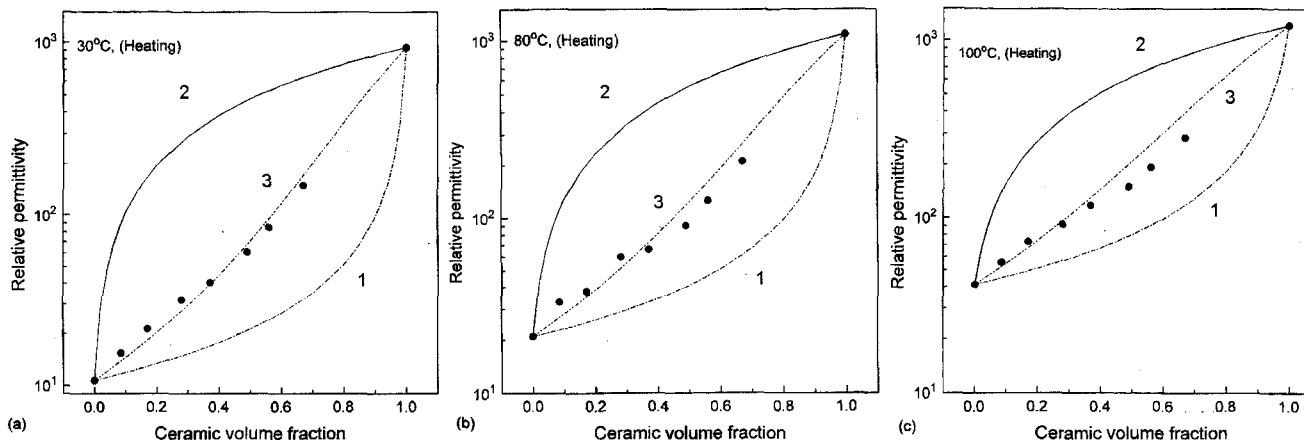
Figure 4. (a) Permittivity of PZT/P(VDF-TrFE) 0–3 composites as a function of the volume fraction of ceramic ϕ at 30°C upon heating. (b) Permittivity of PZT/P(VDF-TrFE) 0–3 composites as a function of the volume fraction of ceramic ϕ at 80°C upon heating. (c) Permittivity of PZT/P(VDF-TrFE) 0–3 composites as a function of the volume fraction of ceramic ϕ at 100°C upon heating. Experimental data (●), 1: Series model, 2: Parallel model, 3: Bruggeman model prediction (Equation (6))

are also plotted in these Figures. It is clear that the upper and lower bounds calculated from the parallel and series models are too wide to provide an accurate estimate of the permittivity. On the other hand, the Bruggeman model agrees reasonably well with the experimental data and thus can be used to predict the permittivity.

Figure 5 shows a comparison of the observed dielectric loss ε'' with the prediction of Equation (7). Although the experimental data show some scatter it is clear that the Bruggeman equation also provides reasonably accurate description of the dielectric loss.

5. ESTIMATION OF THE ELECTRIC FIELD ACTING ON THE CERAMIC PARTICLES INSIDE A COMPOSITE

When an electric field E_o is applied to a composite containing a sphere of permittivity ε_c embedded in a continuous medium of permittivity ε, the local or internal field E_c experienced by the spherical particle is given by [27],

$$E_c = \frac{3\varepsilon E_o}{2\varepsilon + \varepsilon_c} \qquad (8)$$

The value of ε can be determined either experimentally or by calculation using a suitable model. Since there is good agreement between experimental values and the predictions from the Bruggeman model, the permittivities calculated using Equation (6) were inserted into (8) to estimate E_c. Values of the local field coefficient E_c/E_o for three different volume fractions of ceramic ($\phi = 0.09$, 0.17 and 0.67) were calculated and are shown in Figure 6. The relation between the electric field ratio (or local field coefficient) and the poling of 0–3 composites is discussed in the next Section.

6. 0–3 COMPOSITE POLING

The calculated local field coefficient E_c/E_o also exhibits thermal hysteresis. With proper heat treatment, it is possible to make use of the thermal hysteresis effect to maximize the poling field E_c experienced by the ceramic particles. For example, it is seen from

Table 1. Results on 0–3 composite poling. Poling temperature 110°C.

Ceramic vol.frac. ϕ	Appl.field E_0 kV/mm	E_c kV/mm	τ s	Ceramic poling ratio α
0.09	26.9	3.2	10	0.52
0.17	28.6	4.0	6	0.52
0.67	8.0	3.7	0.7	0.70

Figure 6 that if we first heat the composite with $\phi = 0.09$ or 0.17 to 110°C, cool it to 60°C and then apply an electric field, the ceramic particles would experience close to 20% of the total field. For these two composites, the highest applied electric field E_o without breakdown is ~ 27 kV/mm, hence $E_c \sim 5$ kV/mm, which will be high enough to pole the ceramic. It was found experimentally that the highest applied electric field without breakdown becomes smaller as ϕ increases. However, the E_c/E_o ratio increases as ϕ increases and is as high as 0.5 for $\phi = 0.67$. This overcomes the effect of the lower applied field.

Experimentally, three composite samples with $\phi = 0.09$, 0.17 and 0.67 were heated to 110°C (above $T_c^\uparrow$ of the copolymer) and then poled by increasing the applied voltage manually from 0 to $+V$ and almost immediately decreasing the applied voltage from $+V$ to 0. This procedure was repeated for five times and it took ~ 1.5 min to complete the whole poling process. As the estimated local electric field E_c was high enough (Table 1) at 110°C, we chose not to pole the sample upon cooling to 60°C. The electric field was switched off at 110°C and then the samples were cooled to room temperature. This ensured that the copolymer phase was not poled and the piezoelectric properties of the samples was contributed only by the ceramic. The poling (or polarization) ratio α of the ceramic was calculated from the peak heights of the (200) and (002) X-ray reflections associated with the PZT ceramic using the relation [16, 28]

$$\alpha = \frac{I_{002}}{I_{002} + I_{200}} \qquad (9)$$

where I_{002} and I_{200} are the intensities of the (002) and (200) reflections, respectively. A domain shift of 180°, *i.e.* from anti-parallel to parallel to the applied field, would not affect the diffraction pattern because there would be no change in the population of diffracting lattice planes. The X-ray pattern cannot tell the difference before and after a 180° rotation of polar axes, hence Equation (9) is only an approximate expression. For a fully poled ceramic, $\alpha \approx 0.8$ [16].
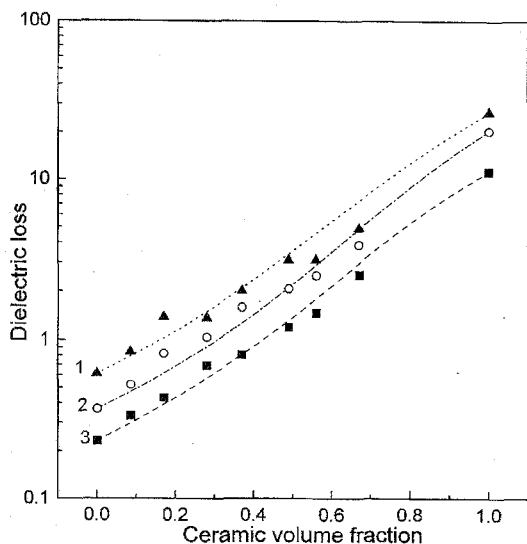

Figure 5. Dielectric loss ($\varepsilon'' = \varepsilon' \tan \delta$) of PZT/P (VDF- TrFE) 0–3 composites as a function of the volume fraction of ceramic ϕ upon heating and Bruggemen model prediction (dotted lines, Equation (7)). 1: 100°C, 2: 80°C, 3: 30°C.
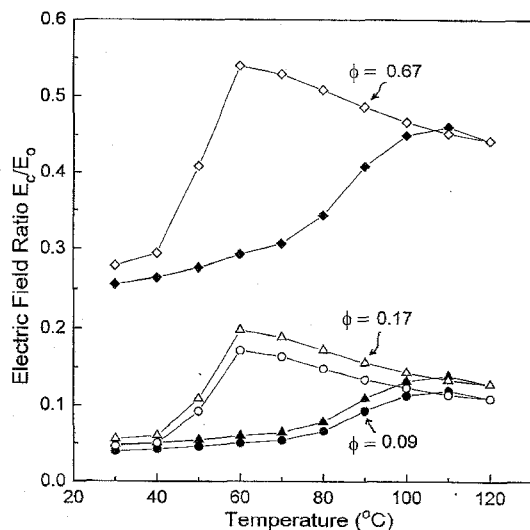

Figure 6. Local field coefficient (E_c/E_o) calculated as a function of temperature using Equations (6) and (8) upon heating and cooling of three PZT/P(VDF-TrFE) 0–3 composites. The filled and open symbols correspond to heating and cooling, respectively.

Table 1 shows the magnitudes of the electric field E_o applied to the samples, the relaxation time τ at 110°C calculated using Equation (1), the field across the ceramic phase as predicted by the Bruggeman model and the resulting ceramic poling ratio α. These results show that by using a varying electric field, it is possible to pole the ceramic inside a 0–3 composite. The two composites with

low volume fractions of ceramic have $\alpha = 0.52$ while the composite with $\phi = 0.67$ is almost fully poled ($\alpha = 0.7$). In order to fully polarize the ceramic, the time spent at the peak voltage V is quite critical. As the volume fraction of ceramic decreases, τ becomes larger, so the peak voltage must be applied for a longer period of time in order to improve the poling ratio.

We are now automating the poling equipment to enable the cycling of the poling field at a pre-determined rate. Once an effective way of poling the ceramic particles has been developed, the next step is to polarize the copolymer matrix in the same direction as or in the opposite direction to the polarization of the ceramic and to measure the piezoelectric and pyroelectric properties of the composites. We are also exploring various means of estimating the degree of poling in the copolymer matrix and more experimental poling studies will be reported in the future.

7. DISCUSSION AND CONCLUSION

THE permittivities of PZT ceramic, 70/30 P(VDF-TrFE) copolymer and PZT/P(VDF-TrFE) 0–3 composites with various volume fractions of ceramic ϕ have been determined from 20 to 120°C. The permittivity of the composites exhibits a thermal hysteresis behavior which is reported here for the first time. The measured permittivities and dielectric loss agree quite well with the predictions of the Bruggeman model. The local field coefficients of the composites were calculated as functions of temperature. The magnitude of the local field coefficient indicates that it is possible to pole the ceramic particles inside a 0–3 composite if we apply a sufficiently high electric field to the composite for a time comparable to or shorter than the interfacial relaxation time of the system. This poling method has a distinct advantage in that it is quicker than poling the sample in the resistivity controlled regime and is easier to apply. By choosing an appropriate thermal treatment before poling, it is possible to pole the ceramic inside a 0–3 composite for all values of ϕ.

ACKNOWLEDGMENT

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