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A poling study of lead zirconate titanate/polyurethane 0–3 composites

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0–3 composites of lead zirconate titanate particles dispersed in a thermoplastic elastomer polyurethane matrix were fabricated. The dielectric permittivity and loss of the composite film were measured and compared to the theoretical values. The composites were polarized by the ac fields at different frequencies. With the application of the Sawyer-Tower circuit, the *D-E* hysteresis loops of the composites can be measured during the poling process. By decreasing the poling frequency, the composite sample shows a larger "remanent" polarization at the same poling field. To evaluate the poling effectiveness, the pyroelectric coefficients of the poled composite samples were measured by a dynamic method. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2767614]

I. INTRODUCTION

Ferroelectric ceramic/polymer composites are a well-established alternative to conventional ferroelectric materials for transducer, actuator, and sensor applications because they can combine the mechanical compliance and flexibility of polymer with the high piezoelectric and pyroelectric activities of ceramic.[1–4] Nevertheless, speeding up the poling process as well as enhancing the properties are still the challenges for manufacturers using the composites in production. It is generally believed that during the poling process, space charges in the polymer phase will drift and accumulate at the particle-matrix interfaces (this is the reason for the long poling time, e.g., 1 h or even longer). The interfacial charges can stabilize the dipole orientation in the ceramic phase, and increase the local electric field in the ceramic phase and the poling efficiency.[5,6] Although the importance of the interfacial charge is widely recognized, there is not too much work studying the resulting effects on the poling process in detail.

Recently, Wong and co-workers[7,8] have developed an analytical model to include the effect of interfacial charge and it has been successfully applied to understand some peculiar experimental observations in ferroelectric composites. They found that higher conductivity in the polymer matrix can shorten the time development of the electric field acting on the ceramic to reach saturation; therefore, poling of the ceramic phase in ferroelectric composite systems can be more efficient. In fact, we have demonstrated that the time scale for fully polarizing the ceramic phase of a PT/P(VDF-TrFE) composite at 120 °C is in the order of 10 s.[9] At 120 °C, P(VDF-TrFE) existed in paraelectric phase has a high conductivity of $\sim 2.5\times 10^{-9}\ \Omega^{-1}\ \mathrm{m}^{-1}$. Sakamoto *et al.*[10] also attempted to improve the poling efficiency of lead zirconate titanate/polyurethane (PZT/PU) composites by doping with graphite filler. By adding about 1% by volume of graphite to increase the electrical conductivity of PU, the PZT phase could be polarized by a lower dc field with a shorter time. However, they have not considered the effect of interfacial charge and have not studied the poling process in detail.

II. COMPOSITE POLING CONSIDERATION

In the poling process, the mobility of charges in the polymer matrix plays an important role. Correspondingly, a parameter τ (known as "relaxation time" of the interfacial charge) in the new analytical model governing the poling process is dependent on the conductivity σ as well as the permittivity ε of the constituents, and is given by:[7]

$$\tau = \frac{\phi 3\varepsilon_p + (1-\phi)(\varepsilon_c + 2\varepsilon_p)}{\phi 3\sigma_p + (1-\phi)(\sigma_c + 2\sigma_p)}, \tag{1}$$

where the subscripts c and p denote ceramic and polymer phases, respectively, and ϕ is the ceramic volume fraction. It has been theoretically shown that if the poling time is sufficiently longer than τ, the ceramic phase can be fully polarized even thought for the case with a small field factor. To speed up the poling process, one way is to decrease τ by using a polymer matrix with high conductivity and a piezoceramic inclusion with low permittivity. For PZT, it has a relative permittivity of ~1800 (at 1 kHz) and electrical conductivity of $0.05\times 10^{-10}\ \Omega^{-1}\ \mathrm{m}^{-1}$.[11] As its relative permittivity is much higher than that of the polymer matrix (in the range of 5–12), τ is dependent obviously with the conductivity of polymer matrix. Figure 1 shows the variation of τ vs σ_p for different PZT volume fractions. The parameter τ can be significantly reduced to several tens of seconds as σ_p increases up to $1\times 10^{-10}\ \Omega^{-1}\ \mathrm{m}^{-1}$. In the present work, composites of PZT particles dispersed in a mildly conductive PU are prepared. The *D-E* hysteresis loops of the composites upon application of ac field at different frequencies are studied. To evaluate the poling effectiveness, the pyroelectric coefficients of the composites are measured and the results are discussed in the next sections.

III. EXPERIMENTS

Modified PZT powder from Piezo Kinetics (Type PKI502) was sintered at 1280 °C for 1 h. To obtain a finer

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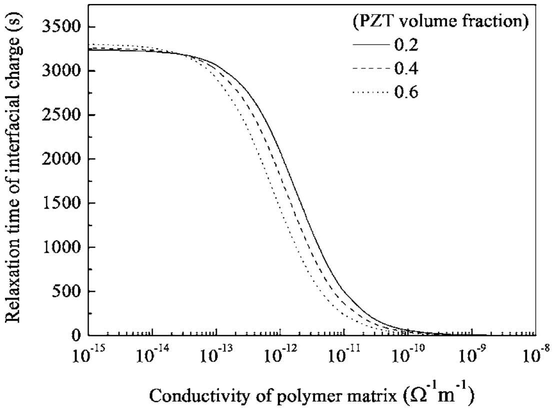

FIG. 1. Variation of the τ with σ_p for PZT/polymer composites.

powder, the sintered particles were ground by ball milling. Thermoplastic PU pellets supplied by Dow Chemicals (Pellethane® 2103-80AE) were dried at 60 °C for 12 h before subsequent processing. A predetermined amount of the PZT powder was blended with the dried PU in a twin-screw HAAKE MiniLab II microcompounder (Thermal Fisher Scientific) at ~170 °C for 15 min, and PZT/PU composite fiber was then extruded at ~160 °C. The fiber was cut into small pellets and fabricated into thin film samples with thickness ranged between 40 and 55 μm by hot compression molding. The ceramic volume fraction of the composite sample, as calculated using the density of PZT (=7700 kg/m^3) and PU (=1130 kg/m^3) provided by the manufacturer and the measured density of composite film, was about 0.19. For subsequent poling process, gold electrodes with 3 mm of diameter were sputtered on both sides of the samples. The cross-section morphology of the PZT/PU composite was studied using a field-emission scanning electron microscope (FESEM) (Cambridge Stereoscan 440).

By mean of a Sawyer-Tower circuit,[12] the samples were poled by several cycles of an ac field at room temperature, and the remanent polarization P_r of the samples was also measured at the same time. The poling field E_a was increased progressively to a maximum value (before sample breakdown) in a step of 2.5 MV/m. At each step, a few cycles of the ac voltage were applied to the sample until the observed hysteresis loop became unchanged. The P_r was determined as the observed polarization value at the end of the application of the E_a field. In the present work, the composite samples were poled at different frequencies ranged from 0.2 to 0.013 Hz. For comparison, the composites were also poled by a dc field for 1 h at room temperature. All poled samples were put into an oven and kept at 60 °C for at least 10 h under short circuit condition to remove any unwanted trapped charge.

The dielectric property of the sample was measured as a function of frequency at room temperature using an HP4194A impedance/gain-phase analyzer. To separate the real pyroelectric response from the thermally stimulated discharge in polymeric materials, an ac method[13,14] was used to determine the pyroelectric coefficients of the samples. The experimental setup is schematically shown in Fig. 2. A sinusoidal voltage V_{ac} at a frequency f of 5 mHz from the lock-in amplifier superimposed on a dc voltage V_{dc} was applied to drive the Peltier thermoelectric element via a proportional-integral-derivative (PID) temperature controller. The sample, placed on the Peltier element, experienced a sinusoidal temperature modulation $T(t)=T_0+T_\Delta \sin(\omega t)$ with amplitude T_Δ of 1.2 °C at the temperature T_0=26 °C. The induced pyroelectric current $J(t)$ was measured with an electrometer and lock-in amplifier. The pyroelectric coefficient p is then calculated using the component of the observed current 90° out of phase with the temperature modulation [i.e., in phase with the heating rate $dT(t)/dt$],

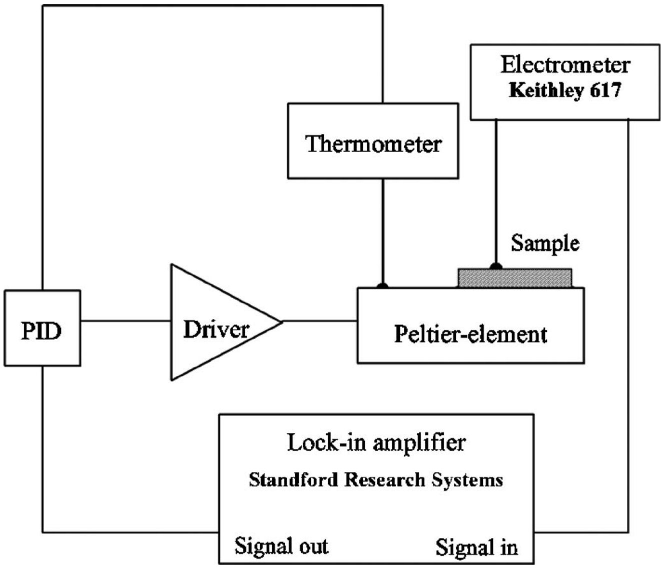

FIG. 2. Schematic diagram of the setup for dynamic pyroelectric measurement.

$$J(t) = -pT_\Delta \omega \cos(\omega t). \tag{2}$$

IV. RESULTS AND DISCUSSION

The FESEM image of the PZT/PU composite is shown in Fig. 3. It can be seen that the PZT powder disperse uni-

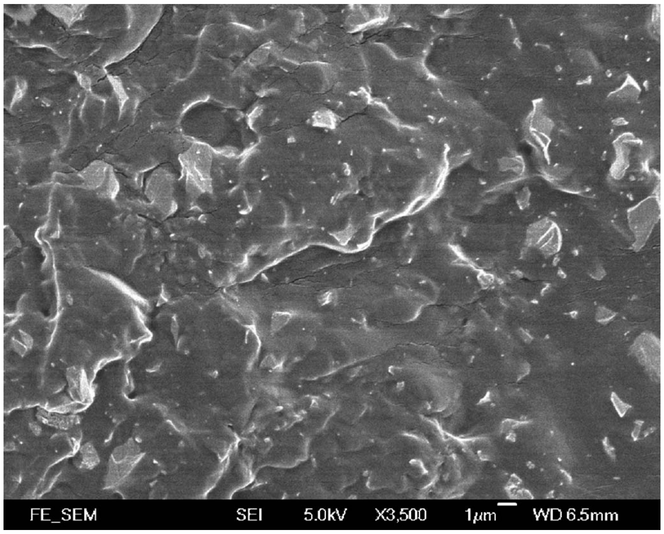

FIG. 3. FESEM micrograph of the fracture surface of the 0–3 PZT/PU composite film.

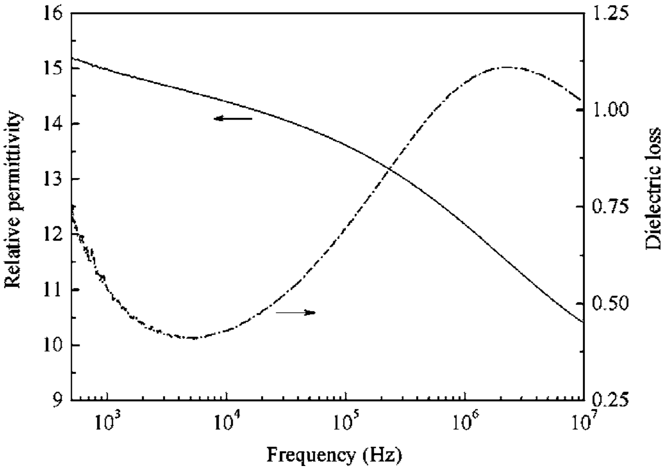

FIG. 4. Relative permittivity and dielectric loss of PZT/PU composite as a function of frequency at room temperature.

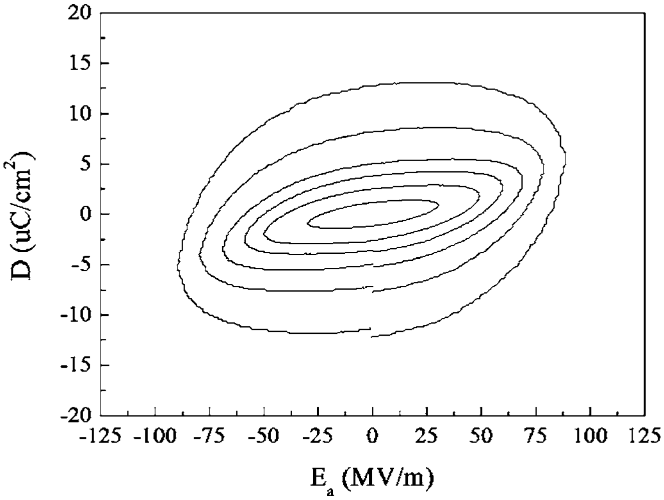

FIG. 5. The polarization hysteresis loops of PZT/PU composite film measured during the ac poling at a frequency of 0.2 Hz.

formly, without serious agglomeration, in the polymer matrix. The grain size is found in the range from 0.8 to 2 μm. Figure 4 shows the relative permittivity and dielectric loss of the composite as a function of frequency. The relative permittivity decreases with the frequency. At 1 kHz, the values of ε' and ε'' are found to be $14.9\varepsilon_0$ (ε_0 is the permittivity in vacuum) and 0.53, respectively. The theoretical permittivity of the 0–3 composite can be predicted by using Bruggeman's equations[15] as shown below,

$$\frac{\varepsilon'_c-\varepsilon'}{(\varepsilon')^{1/3}}=\frac{(1-\phi)(\varepsilon'_c-\varepsilon'_p)}{(\varepsilon'_p)^{1/3}}, \tag{3}$$

$$\varepsilon''=\frac{(\varepsilon'_c-\varepsilon')(\varepsilon'_c+2\varepsilon'_p)\varepsilon'\varepsilon''_p}{(\varepsilon'_c-\varepsilon'_p)(\varepsilon'_c+2\varepsilon')\varepsilon'_p}+\frac{3(\varepsilon'-\varepsilon'_p)\varepsilon'\varepsilon''_c}{(\varepsilon'_c-\varepsilon'_p)(\varepsilon'_c+2\varepsilon')}, \tag{4}$$

where subscripts c and p refer to the particle inclusion and matrix, respectively, and ϕ is the volume fraction of the inclusions in the composite. By substituting the permittivity and dielectric loss for PZT ($\varepsilon_c'=1800\varepsilon_0$ and $\varepsilon_c''=0.279$) and those values for PU ($\varepsilon_p'=7.7\varepsilon_0$ and $\varepsilon_p''=0.25$), the theoretical values of ε' and ε'' for the composite are obtained ($\varepsilon'=14.4\varepsilon_0$ and $\varepsilon''=0.48$). The good agreement between the measured and theoretical values implies that the composite has a good 0–3 connectivity and homogeneity.

The polarization hysteresis loops of PZT/PU composite film measured during the ac poling at 0.2 Hz are shown in Fig. 5. The observed hysteresis loops are slightly different to the typical *D-E* loop in ferroelectrics. Since the polymer has high electrical conductivity, the rounded ends of the loops are due to the electrical conduction in the polymer matrix. As expected, when the electric field increases, the hysteresis loop grows and the remanent polarization increases. Figure 6 shows the variation of the remanent polarization P_r with the electric field E_a for all composite samples. At low frequency ($f \geqslant 0.1$ Hz), the observed P_r value remains almost zero until E_a=50 MV/m, and it then increases obviously with increasing E_a, reflecting that that the electric field is high enough to switch the dipoles of the ceramic phase. The observed P_r value increases significantly with decreasing the poling frequency at each E_a. For the frequency down to 0.03 Hz, the observed P_r value starts to increase at a much lower poling field, E_a=20 MV/m. However, electrical breakdown occurs when the electric field increases to $E_a\sim 70$ MV/m.

The poling effectiveness was evaluated by measuring the pyroelectric coefficient p of the composite samples and the result is tabulated in Table I. For comparison, the pyroelectric response of the composite samples polarized with a long time poling method (i.e., under dc field at room temperature for 1 h) was measured and the result is also shown in Table I. The p value increases obviously with decreasing the poling frequency. For poling frequency of 0.2 Hz (sample A), the p value is 15 μC/m^2 K. When the poling frequency decreases to 0.03 Hz (sample E), the p value increases by twice. At the poling frequency of 0.02 Hz (sample F), the highest p value is obtained (=32 μC/m^2 K) which is nearly 80% to that observed in the dc poled composite samples. This implies that the ceramic phase is fully poled by the ac field. Further decrease in the poling frequency, similar p value is obtained with lower poling field (i.e., 60 MV/m). As mentioned

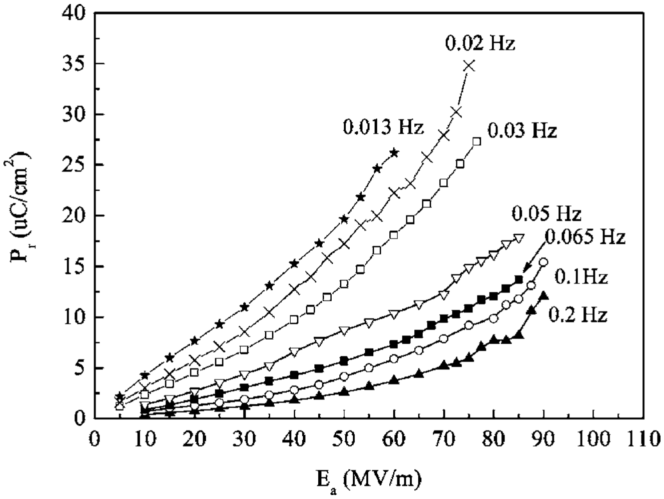

FIG. 6. Variation of the "remanent" polarization P_r with the electric field E_a for all composite samples (measuring frequencies: 0.2, 0.1, 0.065, 0.05, 0.03, 0.02, and 0.013 Hz).

TABLE I. Pyroelectric coefficient of the composite samples poled at different frequencies.

Sample	f (Hz)	$1/f$ (s)	E_a (MV/m)	p (μC/m^2 K)
A	0.2	5	90	15
B	0.1	10	90	20
C	0.065	15.4	85	23
D	0.05	20	85	26
E	0.03	33.3	75	30
F	0.02	50	75	32
G	0.013	77	60	28
H	⋯	⋯	dc 20 (for 1 h)	38
I	⋯	⋯	dc 40 (for 1 h)	40

above, the parameter τ (relaxation time of the interfacial charge) is an important factor for the poling process. By substituting the electrical conductivity of the PU ($\sigma_p=2.3\times10^{-10}\ \Omega^{-1}\ \mathrm{m}^{-1}$, Ref. 16) and PZT ($\sigma_c=0.05\times10^{-10}\ \Omega^{-1}\ \mathrm{m}^{-1}$, Ref. 11) into Eq. (1), the τ value is found to be 25.7 s. Thus, when the poling frequency down to 0.03 Hz (i.e., $1/f=33.3$ s, which is longer than τ), the ceramic phase can be easily poled. This has been successfully demonstrated in the result of the pyroelectric measurement. By using a high conductive polymer as the matrix of the composite, the ceramic phase can be polarized effectively with an ac field at room temperature. It has been found that the poling time can be significantly reduced from an hour to several tens of seconds.

V. CONCLUSIONS

PZT/PU 0–3 composites with ceramic volume fraction of 0.19 have been fabricated. The relative permittivity and dielectric loss of the composite film were measured. The experimental values agree well with the calculated values derived from the Bruggeman model, implying that the PZT particles can be well dispersed within the composites. The poling behavior of the composite upon application of ac field has been studied. For the poling frequency down to 0.03 Hz, the observed "remanent" polarization starts to increase at much lower electric field (i.e., 20 MV/m), and a pyroelectric coefficient of ~30 μC/m^2 K is observed. The present work has provided an experimental evidence that by using the polymer matrix with good conductivity, the ceramic phase can be almost poled within several tens of seconds.

ACKNOWLEDGMENTS

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