Dielectric and pyroelectric properties of lead zirconate titanate/polyurethane composites

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0-3 composite ranging between 0 and 3, of ferroelectric ceramic lead zirconate titanate (PZT) and thermoplastic elastomer polyurethane (PU) were fabricated. The pyroelectric and dielectric properties of the hot-pressed thin film samples of various PZT volume fractions were measured. The experimental dielectric permittivities and losses agreed reasonably well with the Bruggeman model. The room temperature pyroelectric coefficients of the composites were found to increase linearly with PZT volume fraction and substantially larger than expected. For example, for a composite with 30% PZT, its pyroelectric coefficient is about 90 $\mu C/m^2 K$ at room temperature, which is more than tenfold of a PZT/PVDF composite of the same ceramic volume fraction. We propose a model in which the electrical conductivity of the composite system is taken into consideration to explain the linear relationship and the extraordinarily large pyroelectric coefficients obtained. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1787586]

I. INTRODUCTION

Composites of polymers blended with ferroelectric ceramics have been well studied and widely applied in various areas.[1–5] Despite the complicated behavior of such composites in the high electric field regime, their properties under low electric field can be to a certain extent correctly predicted theoretically. Composites made by blending elastomers of high compliance with ferroelectric ceramics, which have yet to be investigated more extensively, may provide applications that have not been achieved with the conventional ferroelectric ceramic-polymer composites. As illustrated in the present study, the blending of lead zirconate titanate (PZT) with the thermoplastic elastomer polyurethane (PU) is such a combination which possesses very high pyroelectric activity.

PZT is a well studied ferroelectric ceramic material. Due to its high piezoelectric coefficient and high Curie temperature, PZT have been widely used for transducer applications. Also, the relatively high pyroelectric coefficient of PZT makes it also suitable for pyroelectric sensor applications. However, the response voltage of a pyroelectric material is directly proportional to its pyroelectric coefficient and inversely proportional to its permittivity. Although PZT has a large pyroelectric coefficient, its permittivity is large as well, thus giving a relatively low figure of merit (the ratio of the pyroelectric coefficient to the permittivity). Therefore, composition with a low permittivity material would be one of the solutions to enhance the pyroelectric voltage output of PZT. Some studies[6,7] have already shown that composites of PZT ceramics and polymers, including polyurethane synthesized in laboratory,[8] do reveal good pyroelectric sensitivity with low permittivity. In the present study a commercial thermoplastic elastomer PU is adopted as the polymer matrix. It is

nonpiezoelectric and would not generate piezoelectric noise due to vibration from the environment; the pliable property of the elastomer also provides a cushion effect, which is able to suppress the vibration of the PZT particles in the composite. This vibration noise has been a nuisance in most piezoelectric ceramic for pyroelectric sensor applications. In this regard, ferroelectric ceramic-elastomer composites will be an alternative selection, which provides pyroelectric capability of relatively high signal to noise ratio.

II. EXPERIMENT

A. Sample preparation

Thermoplastic PU pellets from Dow Chemical (Dow 2103-80AE) were oven-dried at 50 °C for 12 h before processing. A measured amount of the processed PZT powder (Navy Type II 502) was premixed with the dried PU pellets in a grinder, and the mixture was blended in a single screw extruder (Rancastle RCP0250) equipped with a 1/4 in. screw and a 1×40 mm strip die. PZT/PU composites were extruded as a long rectangular sheet. The composite sheet was then cut and refilled into the single screw extruder again for a second extrusion for homogenizing. Finally, PZT/PU composite pellets with 2%, 5%, 13%, 18%, 26%, and 30% in volume of PZT were obtained. Thin film samples of thickness about 100 μm were fabricated by hot press. Circular gold electrodes of 6 mm diameter were coated on both sides of the films by sputtering.

B. Measurements

The pure PU and PZT/PU composite films were poled in silicone oil for 1 h under an applied electric field of 20 MV/m at room temperature. The poled samples were then put into an oven and kept at 60 °C for at least 10 h under short circuit condition to remove any trapped charges. The relative permittivities and dielectric losses of the dried

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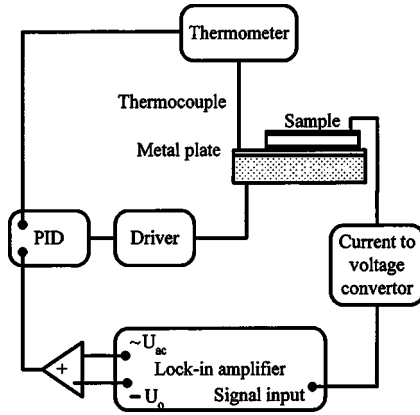J. Appl. Phys., Vol. 96, No. 7, 1 October 2004

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FIG. 1. Schematic diagram of the dynamic pyroelectric measurement setup.

FIG. 3. Dielectric losses of PZT/PU composites as a function of ϕ at room temperature.

samples were measured by an HP 4194A impedance analyzer at room temperature at a frequency of 1 kHz. The results were taken from the average of four samples.

In order to increase the measurement accuracy and suppress the space charge interference in the pyroelectric current, an ac method was used to determine the pyroelectric coefficients of the samples. The schematic diagram of the measurement setup is shown in Fig. 1. A sinusoidal voltage U_{ac} at a frequency f of 5 mHz from the lock-in amplifier superimposed on a dc voltage U_o was employed to drive the Peltier thermoelectric element via a proportional-integral-differential (PID) temperature controller. The sample film was in contact with the Peltier element and experienced a sinusoidally modulated temperature $T(t) = T_o + T_\Delta \sin(\omega t)$, where $\omega = 2\pi f$, with amplitude $T_\Delta = 1$ K at temperature $T_o = 298$ K. The pyroelectric current generated $J(t)$ was measured by an electrometer and the current component 90° out of phase with respect to the temperature modulation (i.e., in phase with the temporal derivative $dT(t)/dt$) was measured by the lock-in amplifier. The pyroelectric coefficient p can then be obtained from the following equation:

$$J(t) = -pT_\Delta \omega \cos(\omega t). \tag{1}$$

III. RESULTS AND DISCUSSION

The relative permittivities and dielectric losses of pure PU and PZT/PU composites with PZT volume fraction ϕ ranging from 0.02 to 0.3 are shown in Figs. 2 and 3, respectively. The samples exhibit an increase in both relative per-
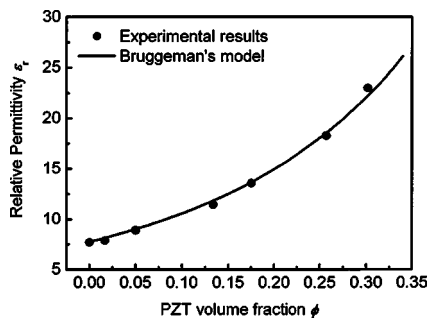
mittivity and dielectric loss with PZT volume fraction. The nonlinear relationship is well described by the Bruggeman formula[9] shown below:

$$\frac{\varepsilon_i - \varepsilon_c}{\varepsilon_i - \varepsilon_m} = (1 - \phi)\left(\frac{\varepsilon_c}{\varepsilon_m}\right)^{1/3}, \tag{2}$$

where ε_i, ε_m, and ε_c are the dielectric permittivity of the particle inclusion, matrix, and composite, respectively, and ϕ is the volume fraction of the inclusions in the composite. Applying the permittivities of PU $\varepsilon_m = 7.7\varepsilon_o$ and of PZT $\varepsilon_i = 1800\varepsilon_o$, ($\varepsilon_o$ is the permittivity in vacuum) the relative permittivities of the composites at room temperature for various PZT contents are calculated and shown as the solid curve in Fig. 2. The good agreement between the theoretical curve and the experimental values indicates that the composites have a good 0–3 connectivity and homogeneity. Similarly, by substituting the complex form of dielectric permittivity with $\varepsilon_m'' = 0.25$ and $\varepsilon_i'' = 0.28$ into Eq. (2) and taking the first order approximation in ε_m'' and ε_i'', the fitting line of the dielectric loss of the composites can be obtained and are shown as the solid curve in Fig. 3.

The pyroelectric properties of the composites are experimentally and also theoretically investigated. As mentioned in the previous section, pyroelectric coefficients of the composites were determined by the ac method at room temperature. The results of the pure PU and PZT/PU composites are shown in Fig. 4. The open- and solid-circles are data for the unpoled samples and poled samples, respectively. It is obvious that those unpoled are not pyroelectric active, whereas the poled samples exhibit significantly large pyroelectric co-

FIG. 2. Relative permittivities of PZT/PU composites as a function of ϕ at room temperature.
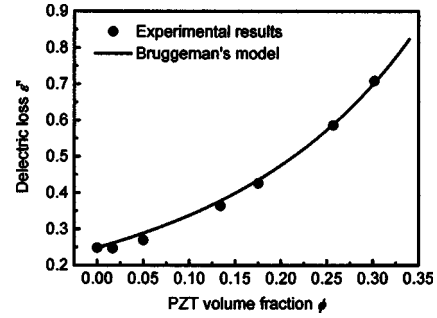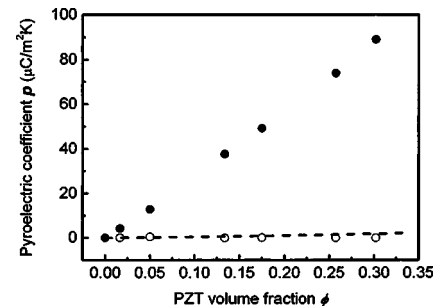

FIG. 4. Pyroelectric coefficients of pure PU and PZT/PU composites at room temperature. The open circles and the solid circles refer to the experimental results of the samples before and after poling, respectively. The dotted line refers to the theoretical calculations that neglect conductivities.

efficients. As a matter of fact, they are almost linearly proportional to the PZT contents and reach about 90 μC/m^{2}K when $\phi=0.3$. This is more than tenfold larger than the pyroelectric coefficients of PZT/PVDF and PZT/P(VDF-TrFE) composites of the same PZT volume fraction measured at room temperature.[11] This result is quite unexpected. Compared with a composite of lead titanate (PT)/P(VDF-TrFE) with 27% PT as reported in Ref. 11, the room temperature pyroelectric coefficient of this system was just about 40 μC/m^{2}K even though both ferroelectric phases were properly polarized.

Several models had been developed to calculate the effective pyroelectric coefficients p of 0–3 composites with non pyroelectric matrices.[10–12] A common one is described by the following equation:[12]

$$p = \phi B_E p_i, \tag{3}$$

where

$$B_E = \frac{3\varepsilon_m}{(2+\phi)\varepsilon_m + (1-\phi)\varepsilon_i}. \tag{4}$$

In Eqs. (3) and (4), ϕ, p_i, and ε_i are the volume fraction, the pyroelectric coefficient, and the dielectric permittivity of the inclusion material, respectively, and ε_m is the dielectric permittivity of the matrix. The expression for B_E is derivable from the Maxwell-Wagner approach for small ϕ. Putting $\varepsilon_m=7.7\varepsilon_o$, $\varepsilon_i=1800\varepsilon_o$, and $p_i=330$ μC/m^{2}K into Eqs. (3) and (4), the pyroelectric coefficients of the PZT/PU composites of various ϕ's can be obtained. The results are shown as the dotted line in Fig. 4. It is obvious that the calculated values are far smaller than the experimental values. We consider that the discrepancy arises from the fact that the model assumes negligible electrical conductivities both for inclusion and matrix. However, this may not be the case for our PZT/PU composites. Thus a model for composites of considerable conductivity is discussed below.

Consider a composite with a dilute dispersion of particle inclusions in a continuous matrix. The average electric field E and displacement D in the composite can be written as follows:[12,13]

$$E = \phi E_i + (1-\phi)E_m, \tag{5}$$

$$D = \phi D_i + (1-\phi)D_m, \tag{6}$$

where the subscripts i and m denote inclusion and matrix, respectively. The relations of displacement D and polarization P of the inclusion and matrix[14] are

$$D_i = P_i + \varepsilon_i E_i, \tag{7}$$

$$D_m = P_m + \varepsilon_m E_m, \tag{8}$$

Putting Eqs. (7), (8), and $P_m=0$ (for a nonpyroelectric matrix such as PU) into Eq. (6), the electric displacement and its time derivative can be written, respectively, as

$$D = \phi(\varepsilon_i E_i + P_i) + (1-\phi)\varepsilon_m E_m, \tag{9}$$

and

$$\frac{\partial D}{\partial t} = \phi\left(\varepsilon_i\frac{\partial E_i}{\partial t} + \frac{\partial P_i}{\partial t}\right) + (1-\phi)\varepsilon_m\frac{\partial E_m}{\partial t}. \tag{10}$$

According to Wong, Poon, and Shin,[15] for a dilute dispersion of spherical inclusions of permittivity ε_i and electrical conductivity σ_i in a matrix of permittivity ε_m and electrical conductivity σ_m with an electric field E applied along the thickness direction, the following equations can be obtained:

$$\frac{\partial E_i}{\partial t} + \frac{E_i}{\tau} = \frac{3\left(\sigma_m E + \varepsilon_m\frac{\partial E}{\partial t}\right) - (1-\phi)\frac{\partial P_i}{\partial t}}{\phi 3\varepsilon_m + (1-\phi)(\varepsilon_i + 2\varepsilon_m)}, \tag{11}$$

where

$$\tau = \frac{\phi 3\varepsilon_m + (1-\phi)(\varepsilon_i + 2\varepsilon_m)}{\phi 3\sigma_m + (1-\phi)(\sigma_i + 2\sigma_m)}, \tag{12}$$

In the pyroelectric current measurement, the sample is connected in short circuit condition; as a result the electric field $E=0$. Equation (11) can be simplified to

$$\frac{\partial E_i}{\partial t} + \frac{E_i}{\tau} + \frac{(1-\phi)\frac{\partial P_i}{\partial t}}{\phi 3\varepsilon_m + (1-\phi)(\varepsilon_i + 2\varepsilon_m)} = 0 \tag{13}$$

and Eq. (5) becomes

$$E_i = \frac{-(1-\phi)}{\phi}E_m. \tag{14}$$

Substituting E_i into Eq. (13) gives

$$\frac{\partial E_m}{\partial t} + \frac{E_m}{\tau} - \frac{\phi\frac{\partial P_i}{\partial t}}{\phi 3\varepsilon_m + (1-\phi)(\varepsilon_i + 2\varepsilon_m)} = 0. \tag{15}$$

As shown in the preceding paragraph, the pyroelectric current was measured by an ac method. Therefore, the time derivative of polarization equals $\partial P_i/\partial t = -p_i\omega T_\Delta\cos\omega t$ for a sinusoidal $T_\Delta=\sin\omega t$ variation in temperature. E_i and E_m must also be sinusoidal at steady state, so that the first order differential Eqs. (13) and (15) can be solved with the solutions

$$E_i = \frac{(1-\phi)p_i T_\Delta}{\phi 3\varepsilon_m + (1-\phi)(\varepsilon_i + 2\varepsilon_m)}\frac{\omega\tau}{1+\omega^2\tau^2}(\cos\omega t + \omega\tau\sin\omega t), \tag{16}$$

$$E_m = -\frac{\phi p_i T_\Delta}{\phi 3\varepsilon_m + (1-\phi)(\varepsilon_i + 2\varepsilon_m)}\frac{\omega\tau}{1+\omega^2\tau^2}(\cos\omega t + \omega\tau\sin\omega t). \tag{17}$$

On the other hand, the current density J is the sum of the conduction current density j and the displacement current $\partial D/\partial t$. The conduction current can be expressed in terms of E as

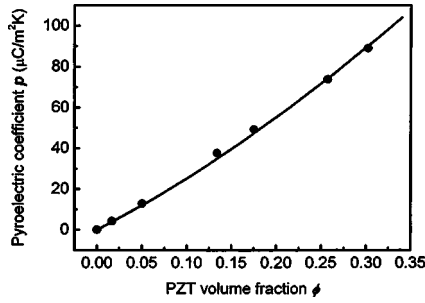$$j = (1-\phi)\sigma_m E_m + \phi\sigma_i E_i, \tag{18}$$

therefore,

FIG. 5. Pyroelectric coefficients of PZT/PU composites versus ceramic volume fraction. The solid circles refer to the experimental results. The solid line refers to theoretical calculations that consider conductivities.

$$J = (1 - \phi)\sigma_m E_m + \phi\sigma_i E_i + \frac{\partial D}{\partial t}. \tag{19}$$

Substituting Eqs. (16) and (17) into Eq. (19) and collecting the terms in $\cos(\omega t)$, we obtain

$$J^{\cos} = -\omega T_\Delta \cos(\omega t)\phi p_i$$
$$\times \left[1 - \frac{(1 - \phi)}{3\phi\varepsilon_m + (1 - \phi)(\varepsilon_i + 2\varepsilon_m)} F \right], \tag{20}$$

where

$$F = \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}(\varepsilon_i - \varepsilon_m) + \frac{\tau}{1 + \omega^2 \tau^2}(\sigma_i - \sigma_m), \tag{21}$$

$J^{\cos}$ is the cosine component of the current density $J(t)$ from which p is obtained [see Eq. (1)]. As a result, the pyroelectric coefficient is

$$p = \phi p_i \left[1 - \frac{(1 - \phi)}{3\phi\varepsilon_m + (1 - \phi)(\varepsilon_i + 2\varepsilon_m)} F \right]. \tag{22}$$

If the conductivities of the inclusions and matrix are small, for example, of the order of $10^{-12}\ \Omega^{-1}\ \mathrm{m}^{-1}$, then τ is large and F approximately equals $(\varepsilon_i - \varepsilon_m)$, so that Eq. (22) reduces to Eq. (3). However, in the present study, the electrical conductivity σ_m of the PU sample was found to be $2.3 \times 10^{-10}\ \Omega^{-1}\ \mathrm{m}^{-1}$. Substituting this value and the conductivity of PZT $\sigma_i (5 \times 10^{-12}\ \Omega^{-1}\ \mathrm{m}^{-1}$; Ref. 16) into Eq. (22), the pyroelectric coefficients of PZT/PU composites as a function of PZT volume fraction can be obtained. The results are shown as the solid line in Fig. 5. It is evident that a very good agreement between the experimental and the theoretical values is obtained. This result on the one hand explains the origin of the large pyroelectric coefficient of the PZT/PU

system and on the other hand it implies that a considerably large electrical conductivity of the composite could enhance its pyroelectric property.

IV. CONCLUSIONS

PZT/PU composites of PZT content up to 30% were fabricated. The dielectric permittivities and losses of the samples were found to increase as the PZT content increased. The results can be well fitted by the Bruggeman model. It indicates that the PZT particles are well dispersed within the composites. The pyroelectric coefficients of the samples were determined by the ac method. They were found to increase linearly with the PZT volume fraction and could be as high as 90 $\mu\mathrm{C}/\mathrm{m}^2$ K for $\phi = 30\%$. This value is much larger than the value obtained from the conventional pyroelectric ceramic/polymer composites. When the conductivities of both inclusion and matrix materials of the composite are taken into account, the theoretical results show a good fit with the experimental pyroelectric coefficient. The calculation indicates that large electrical conductivity may enhance the pyroelectricity of the composite system.

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