

## Enhancement of piezoelectric and pyroelectric properties of composite films using polymer electrolyte matrix

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Composite films consisting of lead zirconate titanate (PZT) inclusions dispersed in a matrix of polymer electrolyte the polyethylene oxide were fabricated. Their piezoelectric coefficients  $d_{33}$  and pyroelectric coefficients  $p$  are increased almost proportional to the volume fraction of the ferroelectric ceramic phase. For 34% PZT composite,  $d_{33}$  and  $p$  are 170 pC/N and 120  $\mu\text{C}/\text{m}^2\text{K}$ , respectively, they are much larger than PZT/polyvinylidene fluoride-trifluoroethylene composite with similar ceramics content. It is believed that the enhancement of the measured coefficients is due to the relatively high electrical conductivity of polymer electrolyte matrix. This is confirmed by theoretical models which consider the conductivity of matrix. © 2007 American Institute of Physics. [DOI: 10.1063/1.2827571]

Composites of polymer matrix mixed with ferroelectric ceramics have been well studied and their pyroelectric and piezoelectric properties are widely applied in various areas.<sup>1-6</sup> The ferroelectric ceramics inclusions play the role to provide the functional effects and the polymer matrix usually serves to provide good protection of the ceramic phase while maintains the compliant mechanical property. The advantages of these polymer composites with piezoelectric or pyroelectric functions are that they can be easily made to large area to increase sensitivity as sensors, they are flexible that intimate contact with the objects to be detected is possible, this is particularly important in vibration sensing application. However, even though the functional ceramics have high piezoelectric and pyroelectric coefficients, the effective coefficients of the composites are relatively low, for example, the pyroelectric coefficients  $p$  of lead zirconate titanate (PZT) (30 vol %)/polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) is 21% of the pure PZT ceramics at room temperature,<sup>7</sup> as their  $p$ 's are 73 and 352  $\mu\text{C}/\text{m}^2\text{K}$ , which hinders the realization of practical use of the polymer composites.

From our previous study,<sup>8</sup> a 0-3 composite of 30 vol % PZT with a thermoplastic polyurethane (PU) shows a pyroelectric coefficient of 90  $\mu\text{C}/\text{m}^2\text{K}$  at room temperature, around 27% of pure PZT, which is much higher than the PZT/PVDF-TrFE composite of the same ceramic volume fraction. As the PU used in the study has a higher electrical conductivity than other insulating polymers, this interesting result reveals the contribution of the electrical conductivity of the matrix which would enhance the pyroelectric coefficient of the composites.<sup>8</sup> It also encourages the application of other polymeric materials which has higher conductivity to further enhance the pyroelectricity or even piezoelectricity. Polyethylene oxide (PEO) is a well known polymer electrolyte which has been demonstrated a useful solid electrolyte for lithium battery.<sup>9</sup> The neat PEO has higher conductivity than PU by three orders of magnitudes. According to the theoretical model developed in the previous study, the PZT/

PEO composite is expected to have even a higher pyroelectric activity than the PZT/PU composite. On the other hand, PEO is a semicrystalline polymer which has a reasonably higher mechanical strength than the elastic PU. This will lead to a better mechanical coupling of the two phases in the composite, therefore, the piezoelectric property of the composites is expected to be enhanced as well.

PEO powder (molecular weight of  $\sim 6 \times 10^5$ ) was purchased from SIGMA-ALDRICH and the presintered PZT powder (Navy Type II 502) was obtained from Piezo Kinetics. The PEO and PZT powders to the designated volume fraction, i.e., 0%, 10%, 16%, 20%, 23%, and 34% were mixed in de-ionized water, the mixtures in a viscous liquid form were cast on the glass substrates for the preparation of the thin films. The samples were then dried in an oven at 48 °C for 12 h. The thicknesses of the dried samples were ranged from 110 to 130  $\mu\text{m}$ . Gold electrodes of 6 mm in diameter were coated on both sides of the samples by sputtering. dc poling was then preformed at 5 MV/m in silicon oil for 1 min at room temperature, this was a short poling process that is benefited by the high conductivity of polymer matrix.<sup>10</sup> The samples were warped with an aluminum foil and grounded for 1 day in order to remove any possible residual spatial charges.

The pyroelectric coefficients of the series of poled samples were determined by a dynamic method. Details of the experimental setup can be found in our previous work.<sup>8</sup> The sinusoidal heating and cooling cycle of the sample was set at 5 mHz of an amplitude  $T_{\Delta}=1\text{K}$  at temperature  $T_0=299\text{K}$ . The thermally induced current was measured by a digital electrometer (Keithley 617) and was fed to a lock-in amplifier (Stanford Research System, SR 830 DSP) for phase analysis. The current 90° out of phase with the temperature modulation [in phase with the heating rate,  $T'=dT(t)/dt$ ] was the pyroelectric current  $I_p$ , and then the pyroelectric coefficient can be found from the following equation:

$$p = \frac{1}{A} \left( \frac{I_p}{T'} \right), \quad (1)$$

where  $A$  was the area of electrode.

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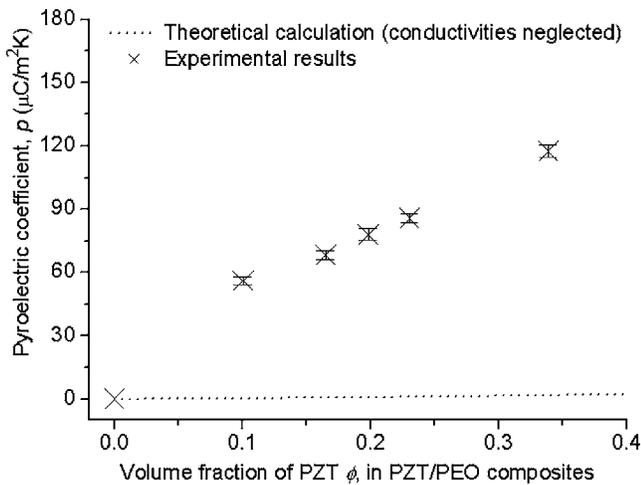


FIG. 1. Pyroelectric coefficients of PZT/PEO composites against PZT volume fraction at 299 K. The crosses refer to experimental results and the dotted line refers to the theoretical calculations that neglect conductivities.

On the other hand, the piezoelectric property of the samples in term of piezoelectric coefficients  $d_{33}$  was measured by using a piezotester (ZJ-3D, Institute of Acoustics Academia Sinica) of which the vibration frequency is 60 Hz.

The ac conductivity of neat PEO film was also measured at two frequencies, i.e., 5 mHz and 60 Hz, respectively. A sinusoidal voltage of the corresponding frequency was applied to the sample which was connected in series with a standard resistor. The voltage across the resistor was measured by a lock-in amplifier, so that the conductivity of samples can be determined.

The pyroelectric coefficients of the composite samples measured by the dynamic method versus PZT volume fractions are plotted, as shown in Fig. 1. It can be clearly seen that the pyroelectric coefficients of the samples are increased almost proportionally with the PZT contents. At 34% volume fraction of PZT, the pyroelectric coefficient reaches about  $120 \mu\text{C}/\text{m}^2\text{K}$ , which is 36% of pure PZT and 30% higher than PZT/PU composites.<sup>8</sup>

As we have pointed out in our previous work, the significant enhancement in pyroelectric current is mainly due to the large conductivity of the polymer matrix. In general, for a composite system with pyroelectric inclusion in a matrix of negligible conductivity, its pyroelectric coefficients<sup>11,12</sup> can be obtained by Maxwell-Wagner's equation,

$$p = \phi B_{ED} p_i, \quad (2)$$

where

$$B_E = \frac{3\epsilon_m}{(2 + \phi)\epsilon_m + (1 - \phi)\epsilon_i}. \quad (3)$$

In Eqs. (2) and (3),  $\phi$  is the volume fraction of inclusion,  $p_i$ ,  $\epsilon_i$ , and  $\epsilon_m$  are the pyroelectric coefficient and the dielectric permittivities of inclusion with subscript  $i$  and matrix material with subscript  $m$ , respectively. For example, in the present PZT/PEO system,  $p_i = 330 \mu\text{C}/\text{m}^2\text{K}$ ,<sup>13</sup>  $\epsilon_m = 6.5\epsilon_0$  and  $\epsilon_i = 1800\epsilon_0$  (Ref. 13), where  $\epsilon_0$  is the permittivity constant in vacuum. By putting these parameters into Eqs. (2) and (3), the theoretical pyroelectric coefficients of various volume fractions of PZT are given as the dotted line shown in Fig. 1. Obviously, the pyroelectric coefficients are far smaller than the experimental results. In other words, the

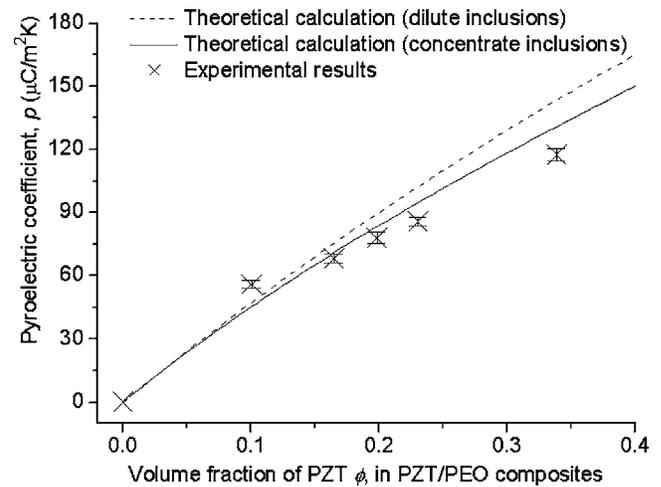


FIG. 2. Pyroelectric coefficients of PZT/PEO composites against PZT volume fraction at 299 K. The crosses refer to experimental results, the dash line refers to the theoretical calculations that consider conductivities only, and solid line considers both concentrations of inclusion and conductivities.

Maxwell-Wagner approach is not appropriate to describe a composite system with significantly large conductivity.

Then, we apply our previously developed model as given in Ref. 8. It points out that the polarization of the poled ferroelectric particles in the matrix are stabilized by the spatial charges adhered. Any change in polarization of the particles thus changing the adhered charge density which contributes to the displacement current of the samples under a short-circuit measurement mode. Therefore, the electrical conductivities,  $\sigma_i$  and  $\sigma_m$ , of both inclusion and matrix, respectively, should be taken into account in the derivation of the pyroelectric coefficients. As a result, the pyroelectric coefficients of the composite system at different volume fractions of inclusion,  $p$  has to be expressed in terms of the  $\sigma_i$  and  $\sigma_m$ , as shown in the following equations:

$$p = \phi p_i \left[ 1 - \frac{(1 - \phi)}{3\phi\epsilon_m + (1 - \phi)(\epsilon_i + 2\epsilon_m)} F \right], \quad (4)$$

where

$$F = \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} (\epsilon_i - \epsilon_m) + \frac{\tau}{1 + \omega^2 \tau^2} (\sigma_i - \sigma_m), \quad (5)$$

and

$$\tau = \frac{\phi 3\epsilon_m + (1 - \phi)(\epsilon_i + 2\epsilon_m)}{\phi 3\sigma_m + (1 - \phi)(\sigma_i + 2\sigma_m)}, \quad (6)$$

where  $\omega$  is the angular frequency of the applied thermal cycle in the measurement.

As shown in Fig. 2, the dash line is the results calculated by Eq. (4) with  $\sigma_m = 2.5 \times 10^{-7} \Omega^{-1} \text{m}^{-1}$ ,  $\sigma_i = 5 \times 10^{-12} \Omega^{-1} \text{m}^{-1}$ ,<sup>14</sup>  $\epsilon_m = 6.5\epsilon_0$ , and  $\epsilon_i = 1800\epsilon_0$ , it matches fairly well with the experimental results. This suggests that the role played by the conductivity of the samples as emphasized in the model is correct. Nevertheless, this model assumes only dilute dispersion of particle inclusion in a continuous matrix, it explains that the calculated curve exhibits a larger deviation from the experimental results at higher PZT contents. In a more recent work given by Wong and Shin,<sup>10</sup> composite of high inclusion content was considered in their model. The pyroelectric coefficient of the composite can be obtained from the following equation:

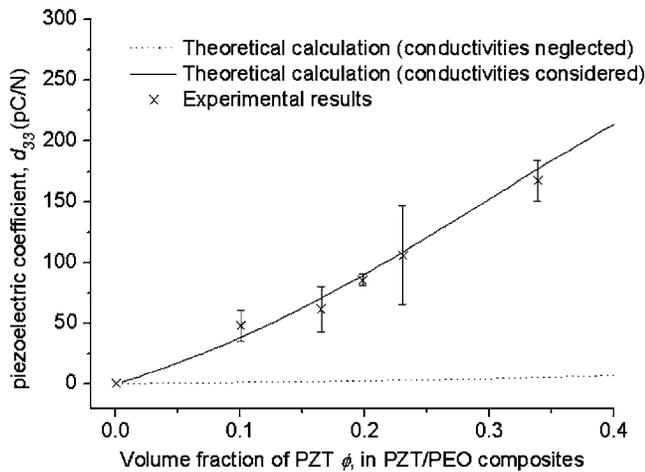


FIG. 3. Piezoelectric charge coefficients of PZT/PEO composites against PZT volume fraction. The crosses refer to experimental results, the dotted line refers to the theoretical calculations that neglect conductivities, and the solid line refers to the theoretical calculations that consider both concentrations of inclusion and conductivities.

$$p = \phi[1 - \Gamma_p^{\text{ac}}(1 - L_E)]p_i, \quad (7)$$

where  $\Gamma_p^{\text{ac}}$  and  $L_E$  are factors that involved frequency of thermal cycle, conductivities, and permittivities of the constituents. Details can be found in Ref. 10. The solid line plotted in Fig. 2 was calculated from Eq. (7). It shows an even better agreement with the measured data. It indicated that this latter model is more satisfactory to describe the enhancement of the composite samples. Regarding the success of the modeling to describe the high pyroelectric performance of composites with either PU or PEO matrix, this will widen the study of composites with many other matrices with high conductivity and on the other hand to extend applications of composite materials with functional inclusions.

Other than the pyroelectric coefficients, the piezoelectric coefficients of the PZT/PEO composites were measured. The results are shown in Fig. 3. Same as the pyroelectric coefficients,  $d_{33}$  are also enhanced significantly. At 34% of PZT, the  $d_{33}$  of the composite is found to be 167 pC/N, it is much larger than the 24 pC/N for 70% by weight of PZT in a PZT/PVDF composite as given in Ref. 15. In the same model as mentioned Ref. 10, it has also illustrated the formulation of  $d_{33}$  of the composite to high inclusion content, as shown in the equation given below,

$$d_{33} = \phi[1 - \Gamma_d(1 - L_E)](F_T''d_{33i} + 2F_T^\perp d_{31i}), \quad (8)$$

where  $\Gamma_d$  and  $L_E$  are factors that involved frequency of mechanical stress cycle, conductivities, and permittivities of constituents.  $F_T''$  and  $F_T^\perp$  are terms related to mechanical properties of the constituents. The  $d_{33i} = 400$  pC/N,

$d_{31i} = -175$  pC/N,<sup>13</sup> and  $\sigma_m = 1.68 \times 10^{-6} \Omega^{-1} \text{m}^{-1}$  at 60 Hz are substituted into Eq. (8). The dotted and solid lines in Fig. 3 show the theoretical  $d_{33}$  of neglected and considerable conductivities of constituents, respectively. The model that considers conductivities is in good agreement with the experimental results. It further confirms that the piezoelectricity of the 0–3 composites can also be enhanced by the considerable large conductivity of the matrix.

In conclusions, PZT/PEO composites were fabricated up to volume fraction of 34% of PZT. The pyroelectric coefficients of the samples were greatly enhanced compared with other PZT polymer composites with negligible conductivity. In addition, the piezoelectric coefficients of the samples were measured as well. Similar to the pyroelectric coefficients, a significant enhancement in piezoelectric coefficients is observed. Both coefficients are much larger than the values obtained from the conventional ferroelectric ceramic/polymer composites with insulating polymer matrix. These results are confirmed by the theoretical models which take the conductivities of the constituents into consideration. It is expected that both the study and applications of the sensors or actuators that make use of these composite materials will be benefited from the understanding of the role playing by the conductivity of the materials.

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