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# Magnetolectric effect of polymer electrolyte composites with Terfenol-D and lead zirconate titanate inclusions

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The magnetolectric effects of three-phase composites in 0-0-3 connectivity were investigated. The composites consist of particulate Terfenol-D and lead zirconate titanate blended in different polymer matrices. The magnetolectric coefficient  $\alpha_q$ , which is the charge density change in response to a change in the applied magnetic field, of the samples was measured under short circuit condition. The results show that the  $\alpha_q$  of the samples with an electrolytic polymer matrix is larger than that of the samples with an insulating matrix, while samples with an ion-doped electrolytic polymer matrix exhibit the largest  $\alpha_q$ . These results conform with the expectation that higher matrix conductivity has an effect of enhancing the magnetolectric signals. © 2009 American Institute of Physics. [DOI: 10.1063/1.3138133]

The magnetolectric (ME) effect, which is a measure of the electrical response of materials when subjected to an applied magnetic field  $H$ , has long been studied<sup>1-4</sup> as a topic of fundamental interest and for potential electric and magnetic applications. The study on the ME effect of single-phase materials can be traced back to Curie in 1894, but only in the 1960s that a material,  $\text{Cr}_2\text{O}_3$ , was first found to have a ME effect of any significance. Afterward, the attention has turned to materials of laminated magnetostrictive/ferroelectric layered structures since they exhibit very a large ME response compared to the single-phase materials.<sup>5,6</sup> In fact, these composite structures exploit a combination of the magnetostriction and piezoelectric effects from two different materials under applied ac magnetic fields from 100 Hz to several hundreds of-kilohertz (Ref. 1) and the overall “product” effect can be schematically represented as follows:

$$\text{ME effect} = \frac{\text{electric}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}} \quad (1)$$

with the first factor on the right hand side signifying the piezoelectric coupling and the second signifying the magnetostrictive coupling. Likewise, a three-phase particulate composite, comprising of magnetostrictive particles and ferroelectric particles co-dispersed in a polymer matrix, is an alternative method to producing materials with a significant ME response. The polymer binder also serves to provide the stress coupling between the functional inclusions in response to any deformation of the magnetostrictive inclusions due to a change in the applied magnetic field. Although the ME response of this kind of polymer composites is comparatively lower than that obtained from layered structure composites,<sup>7</sup> their flexible structure, simple fabrication, and easy shaping<sup>7-9</sup> provide attractive advantages in ME applications.

In our previous study, we have established that the pyroelectric and piezoelectric coefficients of the 0-3 ferroelectric composites with a conductive polymer matrix<sup>10</sup> and elec-

trolytic polymer matrix<sup>11</sup> are much larger than those of the conventional composites with an insulating polymer matrix. The higher conductivity of the polymers facilitates the accumulation of free charges at the matrix-inclusion interfaces for compensating the bound polarization changes in the ferroelectric inclusions in poling. A variation in the polarization of the inclusions due to stress or temperature change will lead to an adjustment of interfacial charges, resulting in a conduction current that adds to the displacement current for an enhancement of both the pyroelectric and piezoelectric effects of the samples.<sup>12</sup> Evidently, the ME activity of a three-phase magnetostrictive/ferroelectric/electrolytic polymer composite of 0-0-3 connectivity, with a structure similar to the 0-3 composite, is expected to be also able to benefit from the conductive electrolytic-polymer matrix. Therefore we have prepared a series of three-phase composite samples, which consist of the ferromagnetic Terfenol-D (T-D) particles and ferroelectric lead zirconate titanate (PZT) particles blended with the polymer electrolyte polyethylene oxide (PEO) and lithium perchlorate-doped PEO ( $\text{Li}^+$ -PEO) for ME measurements. In addition, samples with the insulating polymer poly(methyl methacrylate) (PMMA) as matrix have also been fabricated for comparison. We aim to evaluate the significance of the matrix conductivity in this ME system.

In the measurement of ME effect of the samples under short circuit, a charge amplifier is commonly used for measuring the induced charge  $\Delta q$  that flow in the external circuit in response to a change in the magnetic field  $H$ . In the short circuit condition, the electric field  $E$  in the sample is identically zero, thus defining a ME voltage coefficient  $\alpha_E$  based on  $dE/dH$  would actually be quite inappropriate; a more convenient definition of ME coefficient  $\alpha_q$  to describe the ME performance can be defined as shown below,

$$\alpha_q = dq/dH(1/A), \quad (2)$$

where  $A$  is the area of the electrodes. This ME coefficient is directly obtained from the measured induced charge density ( $\Delta q/A$ ), independent of other physical parameters such as permittivity. The  $\alpha_q$  can be converted from a ME coefficient  $dP/dH$  (Ref. 4) under short circuit condition,

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$$dP/dH = dD/dH = dq/dH(1/A) = \alpha_q, \quad (3)$$

where  $P$  and  $D$  are the polarization and electric displacement, respectively.  $dP/dH$  is polarization change in response to a change in the magnetic field, therefore, this is also a measurement of ME effect in terms of charge density.

In the preparation of the samples, T-D disks (ETREMA) were first ground to small particles with an average size of about  $50 \mu\text{m}$ . PZT (type II 502 from Piezo Kinetics) with size of about  $3 \mu\text{m}$  were presintered before mixing with the PEO powder (MW= $6 \times 10^5$ , Sigma-Aldrich), Li<sup>+</sup>-PEO (which has a molar ratio of [ethylene oxide]:[Li<sup>+</sup>]= $1.24 \times 10^3:1$ ), or PMMA. The compositions of all samples were controlled to a fixed volume ratio of 3% T-D to 27% PZT, with the remaining 70% being the polymer matrix. The polymers were dissolved into a mixture of chloroform and propan-2-ol solution. The T-D and PZT particles were then added to the polymer solution. The mixtures were cast into films on glass, which were then annealed at  $45^\circ\text{C}$  for 12 h. The films were further hot pressed to a controlled thickness, between 200 and  $280 \mu\text{m}$ . Aluminum electrodes of 6 mm in diameter were thermally evaporated on both sides of the samples. The samples with PMMA matrices were poled at 5 MV/m for 3 h, while the other composite samples with conductive matrices were poled at 5 MV/m for 1 min at room temperature, the latter short poling process is sufficient because of the high conductivity of the matrices.<sup>11,12</sup> The samples after poling were allowed to stabilize under short circuit condition for 1 day. For ease of reference, the composite samples of T-D/PZT/Li<sup>+</sup>-PEO, T-D/PZT/PEO, and T-D/PZT/PMMA are abbreviated as Li<sup>+</sup>-PEO<sub>c</sub>, PEO<sub>c</sub>, and PMMA<sub>c</sub>, respectively.

The ac conductivities of the samples were obtained from the dielectric measurements. A sinusoidal voltage of 1 V was applied on the sample in series with a standard resistor. The in phase and out of phase voltages across the standard resistor, obtained from a lock-in amplifier (Stanford Research System, SR 810 DSP), were used to determine the permittivity and conductivity. The ME signals of the composites were measured by applying a 5 Oe ac magnetic field of various frequencies under a dc magnetic biased field  $H_{\text{dc}}$  applied parallel to surface of the samples. The induced charges in the external circuit were measured by using a charge amplifier (Kistler, 5011), with output sent to the lock-in amplifier for further enhancing the signal to noise ratio.  $\alpha_q$  can then be obtained by Eq. (2).

The conductivities against frequency of neat PEO and Li<sup>+</sup>-PEO polymers are given in Fig. 1. It can be seen that at 100 Hz the conductivity of PEO after doping is about  $3.9 \times 10^{-5}$  S/m, which is about one order of magnitude higher than the neat PEO's of  $4.1 \times 10^{-6}$  S/m. The conductivity of PMMA is of the order of  $10^{-9}$  S/m at 100 Hz,<sup>13</sup> which is far below the electrolytic polymers and has not been shown in the graph.

Figure 2 shows the  $\alpha_q$  of the three samples at 100 Hz against various  $H_{\text{dc}}$ . The  $\alpha_q$  values of Li<sup>+</sup>-PEO<sub>c</sub> are the highest among all samples, with a maximum at around  $1100 \text{ pC/m}^2 \text{ Oe}$  at  $H_{\text{dc}}$  of 1200 Oe. PEO<sub>c</sub> has a peak value of  $330 \text{ pC/m}^2 \text{ Oe}$  at the same bias field. The  $\alpha_q$  of PMMA<sub>c</sub> has only a value of  $100 \text{ pC/m}^2 \text{ Oe}$  at around 1300–1400 Oe. Considered together with the foregoing conductivity results, it is obvious that the higher the conductivity of the composite, the higher its ME  $\alpha_q$  coefficient. The enhancement can be

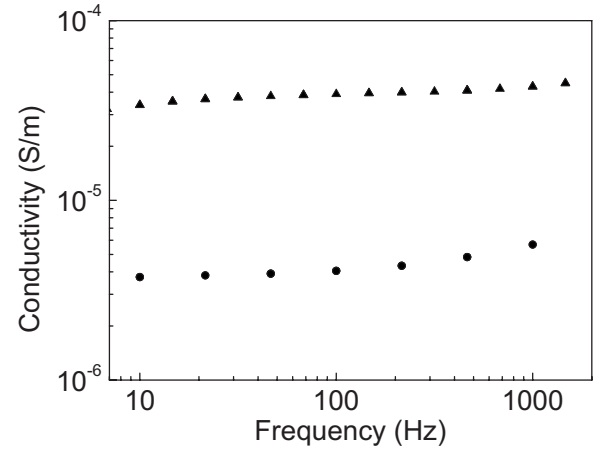


FIG. 1. Conductivity of matrices, PEO (●) and Li<sup>+</sup>-PEO (▲), as a function of frequency.

attributed to the free charges accumulated at the PZT/conductive polymer interface, which were able to participate in conduction to enhance the current. Therefore, for the present three-phase composites, their  $\alpha_q$  increases as a result of the increased conductivities of their matrices. In Ref. 14 we have given a formulation and an analysis of the mechanism to predict the ME coefficients of these composites with significant conductivity. The insulating composite as represented by the PMMA<sub>c</sub>, which has an insignificant conductivity, gives the smallest ME effect. These results further confirm the role played by the free charges in the ME effect enhancement. In addition, the  $\alpha_q$  of the PMMA<sub>c</sub> sample tend to reach its maximum only at a higher bias field than the other two samples. This can be explained by the higher elastic modulus of the PMMA matrix, which imposes a larger mechanical constrain on the T-D particles against their deformation, thus requiring a higher bias magnetic field to reach the maximum slope of the strain-magnetic field profile.

In evaluating the ME effect of a material system, many authors used a ME voltage coefficient  $\alpha_E \equiv dE/dH$ , where the change in the electric field  $E$  in the sample (often the voltage  $V$  across the sample) is to be measured in an open circuit. If the sample of thickness  $t$  can be regarded as an ideal capacitor,  $\alpha_E$  can be further expressed in terms of the change in electrode charges,

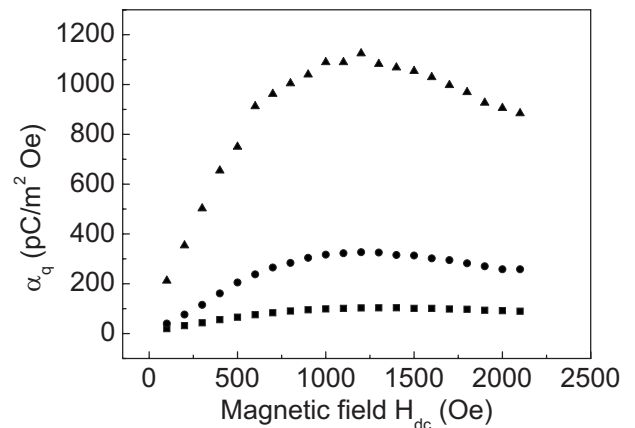


FIG. 2. ME coefficients  $\alpha_q$  of Terfenol-D/PZT/polymer composites, the matrices are PMMA (■), PEO (●), and Li<sup>+</sup>-PEO (▲), under 5 Oe at 100 Hz sinusoidal magnetic field, as a function of biasing magnetic field.

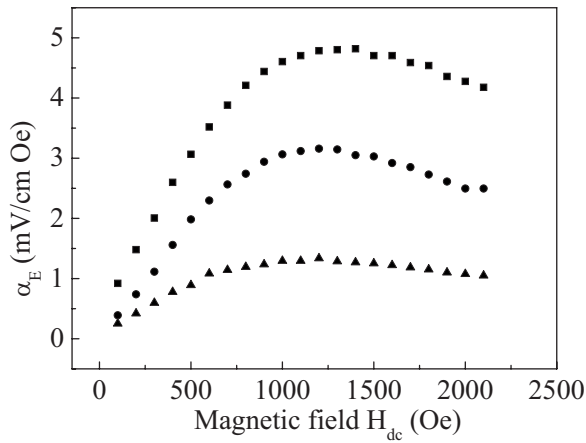


FIG. 3. ME voltage coefficients  $\alpha_E$  of Terfenol-D/PZT/polymer composites, the matrices are PMMA (■), PEO (●), and Li<sup>+</sup>-PEO (▲), under 5 Oe at 100 Hz sinusoidal magnetic field, as a function of biasing magnetic field.

$$\alpha_E = dE/dH = dV/dH(1/t) = dQ/dH(1/\epsilon A), \quad (4)$$

where  $\epsilon$  is the permittivity of the composite. According to Eq. (4),  $\alpha_E$  can be converted from the charge measurement by multiplying  $\alpha_q$  with  $1/\epsilon$ . From the results of the dielectric measurements, the relative permittivities of the composites at 100 Hz are found to be  $\epsilon'_{\text{PMMA}_c} = 24$ ,  $\epsilon'_{\text{PEO}_c} = 117$ , and  $\epsilon'_{\text{Li}^+\text{-PEO}_c} = 951$ , respectively.  $\alpha_E$  was calculated and the results are shown in Fig. 3. Since  $\epsilon'_{\text{Li}^+\text{-PEO}_c}$  is the largest compared to the other two, the ME response of Li<sup>+</sup>-PEO<sub>c</sub> based on  $\epsilon_E$  becomes the smallest, with a peak value of 1.3 mV/cm Oe at 1200 Oe. Due to the smaller relative permittivities, the PEO<sub>c</sub> has a peak of 3.2 mV/cm Oe at the same  $H_{dc}$ , while  $\alpha_E$  of PMMA<sub>c</sub> reaches a peak value of 4.8 mV/cm Oe at around 1300–1400 Oe. These results seem to match the trends illustrated in Ref. 8, viz., the higher the conductivity of the composite, the lower its ME voltage response. However, we believe that in a short circuit measurement,  $\alpha_q$  is a more suitable parameter to represent the ME response, whereas  $\alpha_E$  may not be appropriate for this purpose as  $E$  is zero in the short circuit condition. From a practical point of view, a more conductive ME material gives a stronger ME signal out of a charge amplifier which will make it a more useful material for magnetic sensing applications.

The room temperature frequency response from 10 to 1000 Hz of the samples has been measured under 1 kOe bias magnetic field with a 5 Oe ac modulation. The  $\alpha_q$  versus frequency relations are plotted in Fig. 4. The  $\alpha_q$  of the composite with Li<sup>+</sup>-PEO matrix remains the highest within this frequency range compared to the other two samples, although it drops gradually after reaching a maximum at around 50 Hz. The PEO<sub>c</sub> sample drops from 10 to around 300 Hz, but it rises at the higher frequencies. The generally decreasing trends of the two PEO based composites can be understood from the conductivity as explained in the previous section. The cyclic stresses coupled to the piezoelectric phase lead to the adjustment of interfacial charges that will contribute to the total change in charges at the electrodes. The higher the frequency of the stresses, the shorter the time allowed for the interfacial charges move to the electrodes,

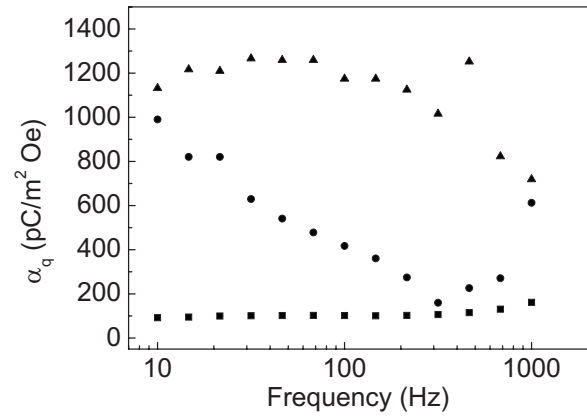


FIG. 4. ME coefficient  $\alpha_q$  of Terfenol-D/PZT/polymer composites, the matrices are PMMA (■), PEO (●), and Li<sup>+</sup>-PEO (▲), under 5 Oe sinusoidal magnetic fields superimposed with 1 kOe magnetic field in various frequencies.

thus resulting in a weaker signal measured. On the other hand, the  $\alpha_q$  of PMMA<sub>c</sub> sample, despite their lowest values, increases slightly against frequency within this frequency range. It can be explained by the higher modulus of the PMMA at higher frequency, which will increase the stresses coupling between the magnetostrictive and the piezoelectric phases in this composite.

In conclusion, composite samples of magnetostrictive Terfenol-D powder and piezoelectric PZT powder blended with three types of matrices—PMMA, PEO, and Li<sup>+</sup>-PEO—were fabricated and their ME coefficients were measured accordingly. The  $\alpha_q$  of composites with PEO and Li<sup>+</sup>-PEO matrices are significantly higher than those of the composite sample with an insulating PMMA matrix. The large  $\alpha_q$  is a result of high conductivities of polymer electrolytes.

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