Electrostriction of lead zirconate titanate/polyurethane composites

K. S. Lam, Y. Zhou, Y. W. Wong,[a] and F. G. Shin
Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Hong Kong SAR, China

Electrostriction of a ferroelectric inclusion/nonferroelectric matrix composite system was studied. The samples were prepared by blending the lead zirconate titanate (PZT) particles with the thermoplastic polyurethane through extrusion and subsequently by hot pressing. Quasistatic cyclic electric fields were applied across the samples while strains and currents were monitored simultaneously. It was found that the electrostriction of the composites depended on the applied electric field in a hysteretic manner. In particular at the high-field regime, the samples exhibited a reversal in the electrostrictive strain. This switching effect occurred at a critical field which was inversely proportional to the PZT content. An associated increase in the displacement current with the critical field was also observed. It indicates that the switching in strain of the composites was mainly due to the flipping of the PZT dipoles in the nonferroelectric polymer matrix. A model was developed for describing the electrostriction behavior of this composite system and the calculated results are comparable to the experimental curves. The success of this theoretical model encourages its application further to the ferroelectric–ferroelectric composite systems. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1906285]

INTRODUCTION

Electrostriction is the effect of electric-field-induced strain in dielectric materials. It is distinguished from the inverse piezoelectric effect in that electrostrictive strain is proportional to the square of the applied electric field and occurs in all dielectric materials irrespective of the crystal symmetry. From a practical point of view, the mechanisms causing this effect include contributions from the electrostatic attraction between the electrodes and space charges injected from the electrodes as well as from the field-induced molecular structural change. The deformation can be exploited for devices such as actuators, microrobots, or other electromechanical transducers.[1]

In the past, the electrostriction in polymeric materials has not attracted much attention due to their relatively low electrostrictive strains ($\sim 0.01\%$) Ref. 2 as well as their low strain energy density. However, in recent years, several polymers with large electrostrictive strain ($>3\%$) have been identified which include the thermoplastic elastomer polyurethane[3] (PU), the rubber polychloroprene,[4] and the electron-irradiated ferroelectric copolymer poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE).[5] For the present study concerned, PU is a block copolymer composed of flexible long chain polyols and rigid diisocyanate components. The molecular chains are predominantly linear with the soft and hard segments distributed alternately. Phase separation usually occurs in the synthesis process. The hard segments segregate to form microphases dispersed in the nonpolar and flexible matrix. This two-phase feature with one phase in the microdomain structure has been regarded as being responsible for the large electrostriction of PU. Nevertheless, due to

the compliance of polymers, the electromechanical stress produced is not competitive with the ceramic counterpart. Thus the ceramic/polymer composites appear as a good alternative. A combination of two electroactive materials will result in composites that benefit from the advantages of both materials. In fact, the composites of (lead zirconate titanate) PZT/PVDF[6] and PZT/PU[7] had been studied extensively, in particular the latter one exhibits significantly large pyroelectric effect as well.[8] It is obvious that there is still much research work toward clarifying the electromechanical mechanisms leading to the large strains and other interesting properties that may evolve from the electroactive ceramic/polymer composites.

EXPERIMENT

The detailed sample preparation process has been previously described.[8] Briefly, the PZT/PU mixture was blended by a single screw extruder then hot pressed to a rectangular sheet of thickness of about 150 μm. The composite films contained PZT in volume fractions ranged from 5%, 13%, 18%, 26%, and 30%.

Figure 1 shows the experimental setup used to measure the electric-field-induced strain of the sample and the current across the sample. The change in the thickness of the sample was monitored by a modified Michelson interferometer. A HeNe laser beam is split into two, one of which was directed to the sample and the other went to the reference mirror. The interference fringes that resulted from the reflected laser beams was projected onto a linear photodiode array of 1024 pixels via an objective lens. The interference pattern was then transferred to a microcomputer for signal processing. The electric field applied to the sample was generated stepwise by a computer-controlled high tension power supply. The change in the thickness of the sample resulted in a shift

[a]Author to whom corresponding should be addressed; electronic mail: apaywwon@polyu.edu.hk

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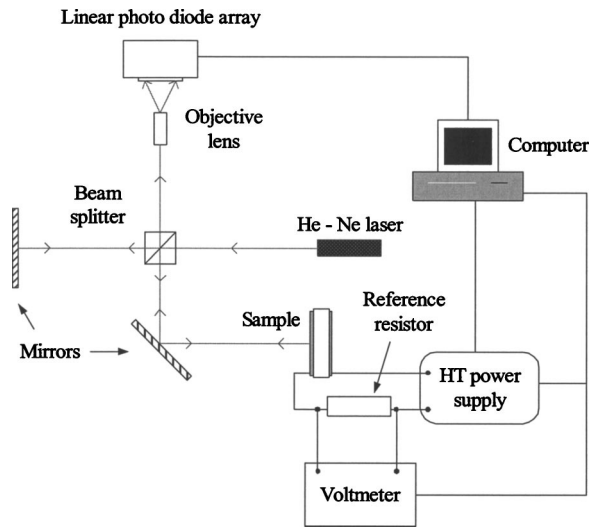FIG. 1. Setup for the electric-field-induced strain and electric current measurement.

FIG. 3. Electrostrictive strain of PU and the composites of PU with PZT of various volume fractions vs the applied electric field. The field was applied from positive to negative in a stepwise cycle.

of the fringe pattern. By measuring the fractional shift magnitude the electric-field-induced strain was deduced. For the setup used in this study, it can resolve $1/30$ of a fringe shift, which is converted to about 10-nm thickness change of the sample. On the other hand, in order to measure the current, a 1-kΩ reference resistor was connected in series with the sample and the voltage drop across the reference resistor was measured by a multimeter (HP 34401A). Since the resistances of the samples are much greater than that of the reference resistor so that it would not affect the voltage applied to the samples.

RESULTS AND DISCUSSION

The electrostrictive response of pure PU is mainly a quadratic relation with the applied electric field. It can be seen from a plot of the electrostrictive strain S against the square of the applied electric field E, as shown in Fig. 2. Therefore S and E can be related by a quadratic equation $S = -ME^2$ where M is called the electrostriction coefficient. The negative sign indicates a contraction response of the polymer. The
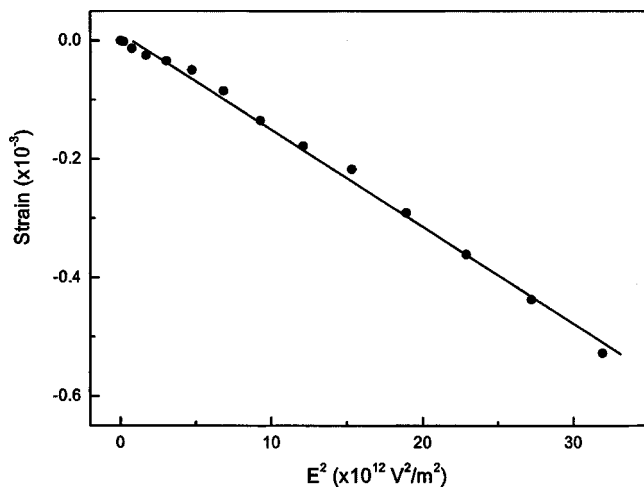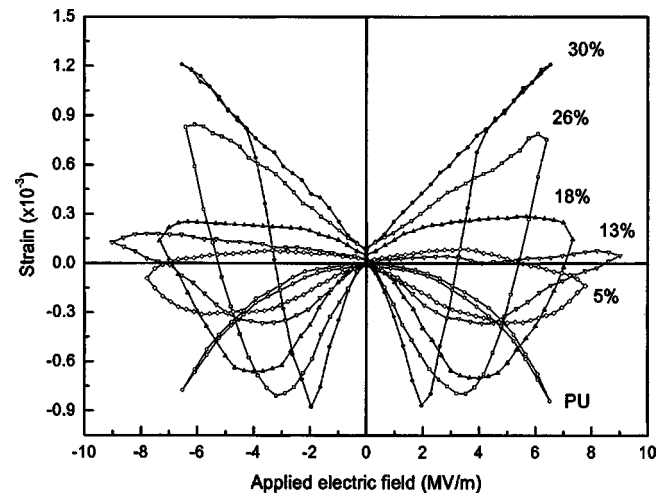

FIG. 2. Electrostrictive strain of PU plotted against the square of the applied electric field E with linear regression fitting.

linear regression fitting of the graph in Fig. 2 gives M a value of 1.7×10^{-17} m^2/V^2, which is in the same order of magnitude compared with the reported value.[3] In fact, the measured electrostriction coefficients will depend on several factors. Among which the most important is the sample processing condition, it will affect, in particular for polymeric materials, the elastic modulus of the sample prepared. Secondly, the electrode clamping effect is also a crucial factor that would affect the performance of the sample. In the present study a sufficiently thin gold metal was sputtered on the PU samples as the electrodes. This would minimize the clamping effect.

Despite the neatly quadratic electrostriction of the pure PU sample, the electrostrictive responses of the composite samples were quite different which are discernible in Fig. 3. In general, these composite films contracted the same as the pure PU at low-field regime. However, as the electric field increased to a certain extent, the films reached a maximum contraction and then became expansion as the field increased further. For example, the sample with 5% PZT changed from contraction to expansion at a field around 5.6–5.8 MV/m. It kept on expanding even the applied field starting to decrease. The film expanded to a thickness slightly greater than its original thickness and then restored to zero strain as the field returned back to zero eventually. This electrostriction behavior was almost repeated as the applied field was reversed, thus resulting in a symmetrical strain hysteresis. It should be pointed out that the negative strain obtained at the low-field regime did not follow the quadratic relation. Composite films of other PZT volume fractions experienced similar electric-field cycle exhibiting a similar performance but with a more drastic change in strain, particularly at around the field the sample thickness switched from contraction to expansion. Apparently, there existed a critical field at which the sample thickness started changing from contraction to expansion and is dependent on the PZT contents. Figures 4(a) and 4(b) give the dependences of the critical fields and the corresponding strains on PZT volume fractions, respectively. It can be seen that the higher the PZT volume fraction, the lower is the
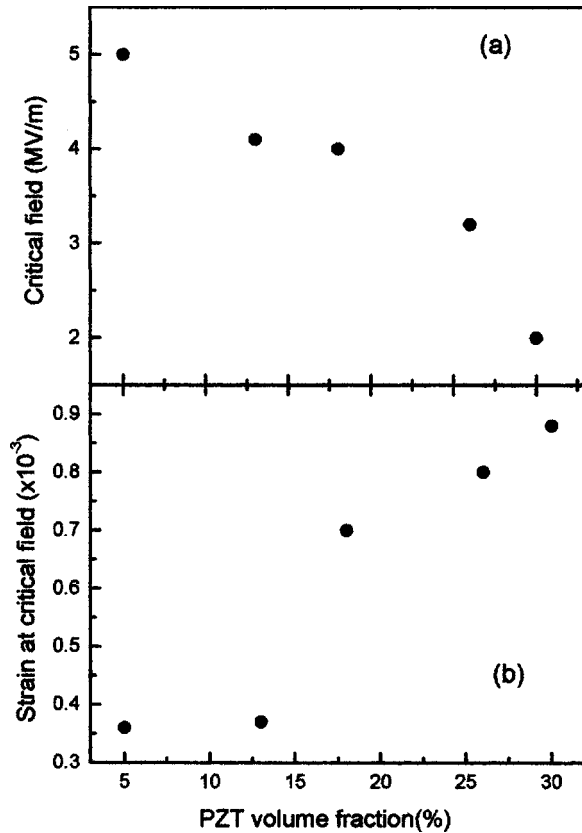
FIG. 4. (a) The critical field of the composite plotted against PZT volume fraction. (b) The strain at critical field plotted against PZT volume fraction.
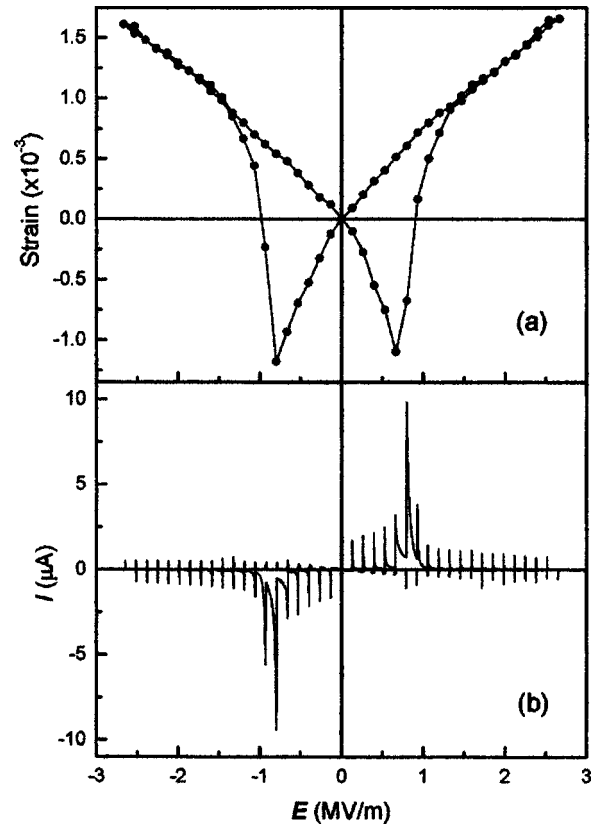

FIG. 5. (a) A plot of the electrostrictive strain against electric field and (b) the current against electric field of pure PZT under the application of the stepwise electric field.

critical field or the external field required in switching the sample deformation. On the contrary, the strain at a critical field was increased with the PZT volume fraction.

Since only the PZT in the composite is a ferroelectric material, it should be the polarizations reversion of this inclusion that is responsible for the strain switching effect. As shown in Fig. 5(a), a pure PZT ceramic sample exhibited strain switching at a field of about 0.85 MV/m as such the polarization of the ceramic changes. This is evident as shown in the current–electric-field ($I–E$) graph of Fig. 5(b). A large current peak was observed at the field of switching, it was the displacement current as a result of the flipping of the PZT dipoles. It should be noted that the smaller sharp peaks shown in the graph are the results of the stepping applied voltage. Despite the relatively low coercive field of PZT, the applied field required to switch the PZT in the composite should be higher than the coercive field. The inclusion in a composite would experience a local field which is much lower than the external applied field due to the high dielectric constant of the inclusion. Thus for the 5% PZT composite, the critical field required to switch the PZT was about 5 MV/m. In addition, unlike the sharp switching occurred in pure PZT, a broader switching was observed in the induced strain of this composite. As a matter of fact, the electrostrictive responses of the composites were the results of the competition between the contraction of PU and the hysteretic electrostriction of PZT. For the composite of 30% PZT, the local field increased correspondingly,[9] therefore a lower applied field (2 MV/m) was sufficient to flip the PZT dipoles

in the composites and this is clearly shown in Fig. 6(a). The $I–E$ curve shown in Fig. 6(b) also provides the evidence that the switch in strain was a result of the dipole flipping which also led to an increase of the displacement current at around the critical field.

Although it is quite clear that the PZT plays a dominant role in the electrostrictive response of the composite, a model given in the following section will be elaborated further in detail the electrostrictive response of a 0-3 composite comprising ferroelectric ceramic particles embedded in a nonferroelectric polymer matrix. It would enhance the understanding of the performance of the PZT/PU composites which may be useful for sensor and actuator applications.

MODEL ON ELECTROSTRICTIVE STRAIN OF THE 0-3 COMPOSITE

It is assumed that the 0-3 composites under consideration do not possess high ceramic loading so that the theory may be kept sufficiently simple. Our previous work[9] has demonstrated that the effect of accumulated charges at the inclusion-matrix interface is essential to understand some characteristics of ferroelectric 0-3 composites. Here the same mechanism is employed in the model being developed. In addition, the composite is assumed to be free from external mechanical stresses. Since particles are assumed to be well dispersed within the matrix, they can be represented by a
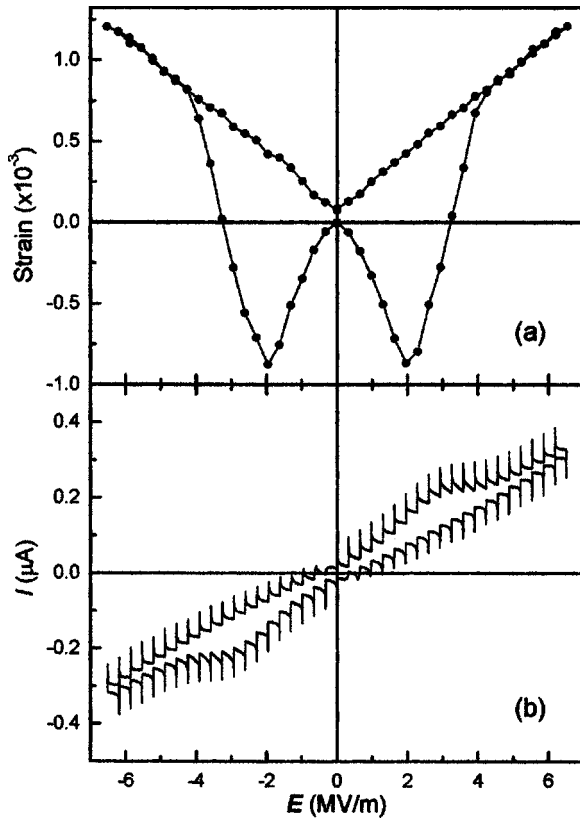
FIG. 6. (a) A plot of the electrostrictive strain against electric field and (b) the current against electric field of the 30% PZT/PU composite under the application of the stepwise electric field.

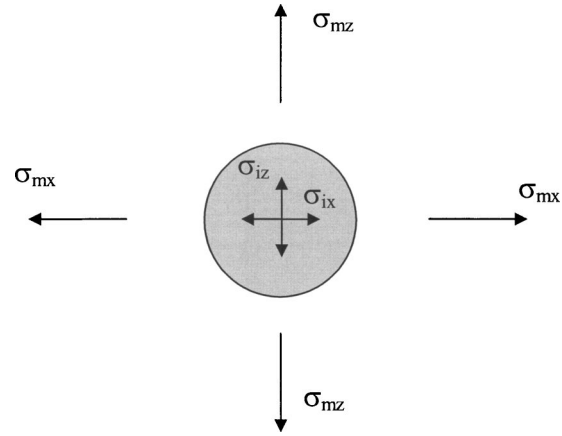FIG. 7. Schematic diagram to show a single inclusion in the matrix under stresses in the *x*, *y*, and *z* directions. The *y*-direction stress not shown in the graph is perpendicular to the paper.

single inclusion embedded in the matrix as depicted in Fig. 7. The subscripts *i* and *m* with the variables denote the inclusion and matrix, respectively.

The ceramic particles are surrounded by the matrix medium in which the asymptotic uniform stresses σ_{mx}, σ_{my}, and σ_{mz} act in the *x*, *y*, and *z* directions, respectively. Within the particle, the corresponding stresses σ_{ix}, σ_{iy}, and σ_{iz} are uniform. In the region close to the particle the stresses in the matrix become nonuniform due to the presence of the particle.[9] The stresses and deformation in the matrix and in the inclusion have to be matched at the inclusion-matrix interface. Since both the elasticity equations and the interface conditions are linear equations involving stresses and deformation, it is therefore possible to relate the asymptotic matrix stresses and strains to the uniform stresses and strains in the inclusion. A similar approach but in a dielectric context has been employed in previous works.[11,12] The relations are

$$\sigma_{ix} - \sigma_{mx} = A \times (e_{ix} - e_{mx}) + B \times (e_{iy} - e_{my})$$
$$+ B \times (e_{iz} - e_{mz}), \tag{1}$$

$$\sigma_{iy} - \sigma_{my} = B \times (e_{ix} - e_{mx}) + A \times (e_{iy} - e_{my})$$
$$+ B \times (e_{iz} - e_{mz}), \tag{2}$$

$$\sigma_{iz} - \sigma_{mz} = B \times (e_{ix} - e_{mx}) + B \times (e_{iy} - e_{my})$$
$$+ A \times (e_{iz} - e_{mz}), \tag{3}$$

where e_{il} and e_{ml} (l:*x*, *y*, and *z*) are strains of the inclusion and matrix, respectively. The constants *A* and *B* can be solved by employing Eqs. (1)–(3) in special cases such as hydrostatic compression,[13] pure shear,[14] and simple tension.[10] After some manipulation, the coefficients *A* and *B* are obtained which depend on the matrix elastic properties only:

$$A = \frac{10}{9}\mu_m\left(-3 + \frac{2\mu_m}{k_m + 2\mu_m}\right), \tag{4}$$

$$B = \frac{1}{9}\mu_m\left(-3 - \frac{10\mu_m}{k_m + 2\mu_m}\right), \tag{5}$$

where μ_m and k_m are shear and bulk moduli of the matrix, respectively, they can be obtained from the Poisson's ratio ν and the Young's modulus *Y* as given in Table I.

The results of the single inclusion problem are now extended to a composite with a dilute suspension of inclusion particles to allow the electrostriction strain to be solved in terms of the dielectric and elastic properties of its constituents. Since the composite is subjected to an electric field in the *z* direction, only the variables in the *z* direction need to be concerned and also only the variables in the *x* direction are listed due to the transverse isotropy, i.e., $\sigma_{ix} = \sigma_{iy}$, $\sigma_{mx} = \sigma_{my}$, $e_{ix} = e_{iy}$, and $e_{mx} = e_{my}$. Thus

TABLE I. Properties of the constituents for the PZT/PU 0-3 composites.

	Relative permittivity $\varepsilon/\varepsilon_0$	Electrical conductivity $\xi(\Omega^{-1}\ m^{-1})$	Remanent polarization $P_r(C/m^2)$	Saturation polarization $P_s(C/m^2)$	Coercive field $E_c(MV/m)$	Young's modulus $Y(GPa)$	Poisson's ratio ν
PZT	1800	5×10^{-12}	0.35	0.4	0.85	36[a]	0.3[a]
PU	6.8	9×10^{-10}	⋯	⋯	⋯	0.03	0.49

[a]Reference 15.

$$\sigma_{ix} - \sigma_{mx} = (A + B) \times (e_{ix} - e_{mx}) + B \times (e_{iz} - e_{mz}) \qquad (6)$$

and

$$\sigma_{iz} - \sigma_{mz} = 2B \times (e_{ix} - e_{mx}) + A \times (e_{iz} - e_{mz}). \qquad (7)$$

The constitutive equations including electrostriction effect for the two materials are given by

$$\sigma_{ix} = \left(2k_i + \frac{2}{3}\mu_i\right)e_{ix} + \left(k_i - \frac{2}{3}\mu_i\right)e_{iz} - f_{ix}(E_i), \qquad (8)$$

$$\sigma_{mx} = \left(2k_m + \frac{2}{3}\mu_m\right)e_{mx} + \left(k_m - \frac{2}{3}\mu_m\right)e_{mz} - f_{mx}(E_m), \qquad (9)$$

$$\sigma_{iz} = \left(2k_i - \frac{4}{3}\mu_i\right)e_{ix} + \left(k_i + \frac{4}{3}\mu_i\right)e_{iz} - f_{iz}(E_i), \qquad (10)$$

$$\sigma_{mz} = \left(2k_m - \frac{4}{3}\mu_m\right)e_{mx} + \left(k_m + \frac{4}{3}\mu_m\right)e_{mz} - f_{mz}(E_m), \qquad (11)$$

where $f_x(E)$ and $f_z(E)$ denotes the electric field E-induced stresses perpendicular and parallel to the applied field direction, respectively. For a given material the functional form of $f(E)$ can be determined from experiment, usually for the case of zero external stress, i.e., $\sigma=0$. Since the composite in the present study is assumed to be free from external mechanical stresses, thus if ϕ is the inclusion volume fraction then

$$\phi\sigma_{ix} + (1 - \phi)\sigma_{mx} = 0 \qquad (12)$$

and

$$\phi\sigma_{iz} + (1 - \phi)\sigma_{mz} = 0. \qquad (13)$$

The strain of the composite in the z direction can be obtained from

$$\phi e_{iz} + (1 - \phi)e_{mz} = e_z. \qquad (14)$$

It has been shown that electrical conduction is essential to the behavior of the ferroelectric composites[9] thus the conductivity ξ should also be included in the model for consideration. It will appear in the time evolution of the electric field of the inclusion E_i in the composite as shown in the following equations:[8]

$$\frac{\partial E_i}{\partial t} + \frac{E_i}{\tau} = \frac{3\left(\xi_m E + \varepsilon_m \frac{\partial E}{\partial t}\right) - (1 - \phi)\frac{\partial(P_i - P_m)}{\partial t}}{\phi 3\varepsilon_m + (1 - \phi)(\varepsilon_i + 2\varepsilon_m)} \qquad (15)$$

and

$$\tau = \frac{\phi 3\varepsilon_m + (1 - \phi)(\varepsilon_i + 2\varepsilon_m)}{\phi 3\xi_m + (1 - \phi)(\xi_i + 2\xi_m)}, \qquad (16)$$

where ε and P denote the permittivity and polarization, respectively.

After all, Table I gives the properties of the constituents of the composite used in this model. In the calculation, $P_m = 0$ because PU is nonferroelectric while P_i is generally not a simple function of E_i. We assume that the PZT particles are fully polarized initially, i.e., $P_i(t=0) = -P_r$, the remanent po-
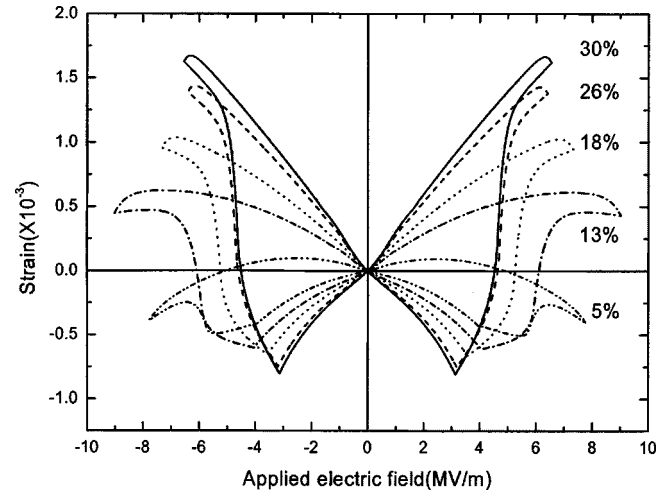

FIG. 8. The calculated curves for the electrostrictive strains of PZT/PU composites of various PZT volume fractions.

larization. The model equation[16] for a saturated hysteresis loop of a ferroelectric material adopted in the calculation is

$$P_i = P_s \tanh\left[\frac{E_i - E_c}{2E_c} \ln\left(\frac{1 + P_r/P_s}{1 - P_r/P_s}\right)\right], \qquad (17)$$

where E_c and P_s are the coercive field and saturation polarization, respectively.

With the substitution of Eq. (15) into Eq. (17), the relation $\partial P_i / \partial t = \partial P_i / \partial E_i \, \partial E_i / \partial t$ is employed. In Eqs. (8)–(11), the electrostriction functions $f(E)$ have to be determined, this is done by comparing the measured longitudinal and transverse strains of the pure materials subjected to electric fields, under zero external stresses, i.e., $\sigma_x = \sigma_y = \sigma_z = 0$. Experimental data on the transverse electrostrictive strain responses of PU and PZT are not readily available in the literature. Therefore, in the present study the ratios of the transverse strain to longitudinal strain of PU and PZT in the range from -0.1 to -10 were tried in Eqs. (8)–(11) for fitting the experimental longitudinal strains. It shows that the results actually are not sensitive to these ratios. Nevertheless, the calculated strain-electric-field curves of PZT/PU composites with different PZT volume fractions are depicted in Fig. 8. The simulation results give the strain-electric-field loops in butterfly shape same as those observed in experiment. It can be seen that the critical fields of the composites under applied electric fields decrease while the electrostriction strain magnitudes increase with increasing PZT volume fraction, which is in good agreement with the experimental results. Despite the slight deviation in strain magnitudes and shapes for $\phi=0.13$, the simulation results show all the essential features of the hysteretic curves obtained from experiment.

CONCLUSIONS

The electromechanical response of pure PU follows a simple quadratic relation with the applied electric field and the electrostriction coefficient is about 1.7×10^{-17} m^2/V^2. The electromechanical response of pure PZT shows a conventional hysteresis loop in butterfly shape. A combination of the two components forms the 0-3 composite of which a

switching feature in electrostrictive strain was observed. This feature occurs at a critical field which decreases with PZT volume fraction. The measured displacement current exhibited a large increase at around the critical field. It indicates that the PZT dipole flipping is responsible for the strain reversal of the composite. A model based on elasticity in associate with the ferroelectricity of both components in the composite was proposed to calculate the theoretical electrostrictive strain of the composite for various PZT volume fractions. It successfully reveals all the essential features of the measured hysteretic electrostrictive strains of such a composite system of ferroelectric particles in nonferroelectric matrix. These results encourage the extended application of the model to a system of ferroelectric matrix.

ACKNOWLEDGMENTS

[1] R. E. Pelrine, R. D. Kornbluh, and J. P. Joseph, Sens. Actuators, A **64**, 77 (1998).
[2] T. Furukawa and N. Seo, Jpn. J. Appl. Phys., Part 1 **29**, 675 (1990).
[3] Z. Ma, J. I. Scheinbeim, J. W. Lee, and B. A. Newman, J. Polym. Sci., Part B: Polym. Phys. **32**, 2721 (1994).
[4] Y. Ma and D. H. Reneker, Rubber Chem. Technol. **69**, 674 (1996).
[5] Q. M. Zhang, V. Bharti, and X. Zhao, Science **280**, 2101 (1998).
[6] D. K. Das-Gupta, Ferroelectrics **118**, 165 (1991).
[7] W. K. Sakamoto, S. T. Shibatta-Kagesawa, and W. L. B. Melo, Sens. Actuators, A **77**, 28 (1999).
[8] K. S. Lam, Y. W. Wong, L. S. Tai, Y. M. Poon, and F. G. Shin, J. Appl. Phys. **96**, 3896 (2004).
[9] C. K. Wong, Y. W. Wong, and F. G. Shin, J. Appl. Phys. **92**, 3974 (2002).
[10] J. N. Goodier, Trans. ASME **55**, 39 (1933).
[11] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, New York, 1960), pp. 43–44.
[12] C. K. Wong, Y. M. Poon, and F. G. Shin, J. Appl. Phys. **90**, 4690 (2001).
[13] K. H. Chew, F. G. Shin, B. Ploss, H. L. W. Chan, and C. L. Choy, J. Appl. Phys. **94**, 1134 (2003).
[14] R. M. Christensen, *Mechanics of Composite Materials* (Krieger Publishing Company, Malabar, FL, 1979), pp. 41–44.
[15] T. Furukawa, K. Fujino, and E. Fukada, Jpn. J. Appl. Phys. **15**, 2119 (1976).
[16] S. L. Miller, J. R. Schwank, R. D. Nasby, and M. S. Rodgers, J. Appl. Phys. **70**, 2849 (1991).