JOURNAL OF APPLIED PHYSICS

Modeling of poling, piezoelectric, and pyroelectric properties of ferroelectric 0–3 composites

Y. T. Or and C. K. Wong^{a)}

Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China

B. Ploss

Fachhochschule Jena, FB Physikalische Technik, University of Applied Sciences, Carl-Zeiss-Promenade 2, 07745 Jena, Germany

F. G. Shin

Department of Applied Physics, Materials Research Center and Center for Smart Materials, The Hong Kong Polytechnic University, Hong Kong, China

(Received 10 December 2002; accepted 9 June 2003)

A model for the piezoelectric and pyroelectric activities of 0-3 composites of ferroelectric particles in a linear matrix has been developed based on the polarization behavior of the inclusions. The model is applied to simulate the piezoelectric activity of a lead zirconate titanate/epoxy system polarized under different fields and the piezo- and the pyroelectric properties of lead titanate/ polyvinylidene fluoride-trifluoroethylene 70/30 mol%] composites polarized with different poling times. The model predictions show reasonably good agreement with experimental data. The ability to predict the gross properties of 0-3 composites in terms of the poling field and poling time may be especially helpful in the making of practical composites with particular properties. © 2003 American Institute of Physics. [DOI: 10.1063/1.1596718]

I. INTRODUCTION

Composites of ferroelectric polymers and ferroelectric ceramics reveal piezoelectric and pyroelectric activity after being subjected to a high electric field which aligns the spontaneous polarization along the poling direction. These composites are useful for practical applications as they combine the high piezoelectric and pyroelectric activities of ferroelectric ceramic with excellent mechanical properties of a polymer. Applications of such composites include electromechanical transducers, e.g., microphones and hydrophones, as well as pyroelectric detectors in infrared sensors and microcalorimeters.

In our previous papers, we have theoretically studied some polarization switching behavior of multilayered¹ and 0-3 composites.² Effects of the permittivity and electric conductivity of the constituents have been discussed. However, there is still a lack of theoretical models to account for the effect of poling time and field, which predict the macroscopic properties of a ferroelectric composite from the polarization acquired by the constituents. Extensive experimental work is usually required to characterize and optimize composite systems which limit their application, in practice. Piezoelectric and pyroelectric activities of various 0-3 composite systems have been systematically studied and are reported in literature (e.g. see recent reviews by Dias et al.,³ Tressler *et al.*,⁴ and Bhimasankaram *et al.*,⁵ and references therein). Most of these works were focused on technical aspects and applications, while many fundamental aspects were not fully understood. On the other hand, models for piezoelectric and pyroelectric properties of ferroelectric 0–3 composites have also been given recently.^{6,7}

The emphasis of this article is to study the gross properties of such composite systems in terms of the poling field and poling time. This will be useful for the selection of materials and the poling treatment of composite systems for tailored applications. We shall give a theoretical description of the poling process of dilute 0-3 composite systems, built up from consideration of a single-inclusion problem in which a single-ferroelectric sphere is surrounded by a linear matrix medium under the action of a uniform electric field. A modified model of Miller et al.^{8,9} is used for the description of the polarization–electric field (P-E) relation of the ferroelectric constituent. The predictions of the model will be compared to experimental results of the piezoelectric properties of PZT/epoxy 0-3 composites given by Furukawa et al.¹⁰ and to our studies of piezo- and pyroelectric properties of lead titanate (PT)/polyvinylidene fluoride-trifluoroethylene [P(VDF-TrFE)] 0-3 composites.

II. THEORY

 D_m

Consider a ferroelectric ceramic/polymer composite with 0-3 connectivity, i.e., the ferroelectric ceramic particles are not in contact with each other while the polymer phase is self-connected in three dimensions as illustrated schematically in Fig. 1. The particles are assumed to have a spherical shape.

The electric displacement D of the ceramic and polymer phase are given by¹¹

$$D_i = \varepsilon_i E_i + P_i, \tag{1}$$

$$=\varepsilon_m E_m + P_m, \qquad (2)$$

^{a)}Electronic mail: wongck.a@polyu.edu.hk

0021-8979/2003/94(5)/3319/7/\$20.00

3319



FIG. 1. Schematic illustration of a ceramic/polymer 0-3 composite.

where ε , *E*, and *P* represent the permittivity, electric field, and ferroelectric polarization, respectively. We generally use the subscripts *i* and *m* to denote the ceramic inclusion and polymer matrix, while no subscript is used for the composite. In this article, we are more interested, finally, in the case of a linear matrix where $P_m = 0$. For the present discussion, however, there is no harm in considering that the matrix is also ferroelectric. For a composite with a small ceramic volume fraction, the electric field acting on the respective phases satisfies the following relation:

$$E = \phi E_i + (1 - \phi) E_m, \qquad (3)$$

where ϕ is the ceramic volume fraction. We assume that the two constituent materials are uniformly polarized and the homogeneously polarized spheres are covered with surface charge density q_o at the pole along the polarizing direction $(\theta=0)$ with an angular distribution given by¹² (see Fig. 2):

$$q = q_o \cos \theta, \tag{4}$$

where q represents the surface charge density at angle θ .

For a dilute dispersion of spherical inclusions in a matrix medium of permittivity ε_m and electric conductivity σ_m with a uniform electric field applied along (say) the Z direction, Eqs. (5) and (6) are obtained from a consideration of the boundary value problem of a single inclusion in an infinite matrix:²

$$D_i + 2\varepsilon_m (E_i - E_m) = D_m + q_o, \qquad (5)$$

$$j_i + 2\sigma_m(E_i - E_m) = j_m - \partial q_o / \partial t, \qquad (6)$$

where *j* is the conduction current density, which is related to electric field by $j = \sigma E$. Differentiating Eq. (5) with respect to time and adding to Eq. (6) to eliminate q_o , we obtain



FIG. 2. Homogeneously polarized sphere covered with "compensating" charge.

$$\frac{3(\sigma_m E + \varepsilon_m \partial E/\partial t)}{(1 - \phi)(\varepsilon_i + 2\varepsilon_m) + 3\phi\varepsilon_m} = \frac{E_i}{\tau} + \frac{\partial E_i}{\partial t} + \frac{(1 - \phi)\partial(P_i - P_m)/\partial t}{(1 - \phi)(\varepsilon_i + 2\varepsilon_m) + 3\phi\varepsilon_m},$$
(7)

where $\tau = \{3\phi\varepsilon_m + (1-\phi)(\varepsilon_i + 2\varepsilon_m)\}/\{3\phi\sigma_m + (1-\phi)(\sigma_i + 2\sigma_m)\}$. When *E* changes with time, the relation $\partial P/\partial t = [\partial P/\partial E] [\partial E/\partial t]$ may be employed for subsequent calculations.

The P-E relationship of a ferroelectric material is very complex and has been the subject of many investigations. We choose to adopt a convenient mathematical model developed by Miller *et al.*,^{8,9} which may be expressed as

$$\frac{\partial P}{\partial E} = \left(1 - \tanh \sqrt{\frac{P - P_{\text{sat}}}{\xi P_s - P}}\right) \left(\frac{\partial P_{\text{sat}}}{\partial E}\right),\tag{8}$$

where P_{sat} is the polarization on the saturated hysteresis loop at the field of interest, and P and P_s are the magnitudes of the ferroelectric polarization and saturation polarization, respectively. $\xi = +1$ for an increasing field and $\xi = -1$ for a decreasing field. Following Wong *et al.*'s² modification, the polarization of the saturated hysteresis loop is written as a function of the electric field as

$$P_{\text{sat}} = \xi P_s \tanh\left\{\frac{\xi E - E_c}{2E_c} \ln\left[\frac{1 - (-P_r/P_s)^{1/n}}{1 + (-P_r/P_s)^{1/n}}\right]\right\}^n, \qquad (9)$$

where P_r and E_c are taken as positive quantities representing the magnitude of remanent polarization and coercive field, respectively. $n \equiv n_1/n_2$ ranges from 1/3 to 1 with n_1 and n_2 being odd numbers.

Solving Eqs. (7) and (8) for a given poling E(t), the time development of the electric fields and the polarization in the ceramic inclusions (and in the matrix) can be evaluated.

III. THE PIEZOELECTRIC PROPERTIES OF LEAD ZIRCONATE TITANATE/EPOXY 0–3 COMPOSITES

Furukawa *et al.*¹⁰ prepared lead zirconate titanate (PZT)/ epoxy 0–3 composites with ceramic volume fraction ϕ = 0.048, 0.131, and 0.232. The composites were polarized under different dc poling fields at 120 °C for 30 min, then kept at the same temperature for 10 min under short-circuit condition. The piezoelectric coefficients d_{31} were measured at 50 °C.

The resulting or "remanent" polarization in the ceramic inclusion as a function of the applied electric field can be calculated by solving Eq. (7) together with an appropriate simulation of the P-E hysteresis of the PZT ceramic involved. Here, the P-E hysteresis loop of the PZT ceramic is simulated by Miller *et al.*'s^{8,9} model with the materials parameters of PZT and epoxy as listed in Table I. Furukawa *et al.*¹⁰ have reported that the PZT ceramic has been fully polarized under a field of 0.7 MV/m. Therefore, we have assumed an E_c which is one-third of this value, i.e., 0.233 MV/m. Figure 3 shows the simulated P-E hysteresis loop

TABLE I. Material parameters of PZT and epoxy at 120 °C.

	$P_s (C/m^2)$	$P_r~({\rm C/m^2})$	E_c (MV/m)	$\epsilon/\epsilon_{o \text{ (unpoled)}}^{a}$	$\sigma \; (\Omega^{-1} \mathrm{m}^{-1})$
PZT	0.35	0.33	0.233	1750	$1.5 \times 10^{-10 \text{ b}}$
Epoxy		••••	••••	4.6	0.65×10^{-11} c

^aSee Ref. 10. ^bSee Ref. 13.

^cSee Ref. 14.

for PZT ceramic from the modified Miller *et al.*'s^{8,9} model [Eqs. (8) and (9)] with n=5/11. $P_m=0$ because epoxy is nonferroelectric.

The development of the polarization in the PZT inclusions has been simulated under the experimental conditions just given, and the result is shown in Fig. 4(a). It is seen that, under the poling field of 5 MV/m, the ceramic polarization basically increases with poling time, and it relaxes slightly after the release of the field. The final remanent polarization attained in the total process is denoted by P_{ri} . Figure 4(b) shows the simulated results for the remanent polarization in the ceramic inclusion P_{ri} as a function of poling field. Generally speaking, a higher poling field results in a higher P_{ri} . It is seen that P_{ri} increases quite linearly with the poling field. Saturation in P_{ri} can be obtained when poling fields of about 10 MV/m and 12 MV/m are applied for 1800 s to the composites with $\phi = 0.232$ and 0.048, respectively. In addition, the relation between the poling field and poling time required to obtain 95% of the maximum achievable P_{ri} has been calculated and is shown in Fig. 4(c). It is evident that under a higher poling field, a high P_{ri} is obtained in a shorter poling time. Moreover, under the same poling field, the composites with higher ϕ become polarized faster.

A further discussion of the gross piezoelectric properties of the poled composites based on our simulation results requires one to know the relationship between P_{ri} and the piezoelectric properties of the ceramic material. As this relation is not well known, we make the reasonable assumption that the piezoelectric coefficient of the inclusion is directly proportional to its P_{ri} and can, therefore, be written as

$$d_{3ki} = (P_{ri} / P_{ri}^{f}) d_{3k}^{f} \quad k = 1, 2, 3,$$
(10)



FIG. 3. Simulated P-E hysteresis loop of PZT ceramic [from Eqs. (8) and (9) with $n_1/n_2 = 5/11$].



FIG. 4. The simulated (a) polarization and (b) remanent polarization in PZT inclusions of PZT/epoxy 0–3 composites with ϕ =0.048 (circle), 0.131 (square), and 0.232 (triangle) as a function of (a) time (The final remanent polarization is denoted by P_{ri}), (b) poling field after a poling time of 1800 s. (c) The simulated poling time required to obtain 95% of the maximum achievable remanent polarization in PZT inclusions of PZT/epoxy 0–3 composites with ϕ =0.048 (circle), 0.131 (square), and 0.232 (triangle) as a function of poling field.

where P_{ri}^{f} and d_{3k}^{f} denote the remanent polarization and the piezoelectric coefficient of a fully polarized ceramic at the temperature of the experiment.

Many theoretical works have been carried out to express the gross piezoelectric properties of the 0-3 composite system in terms of the piezoelectric properties of the constituents. For the present work, we adopt the expressions for the

Downloaded 01 Apr 2011 to 158.132.161.9. Redistribution subject to AIP license or copyright; see http://jap.aip.org/about/rights_and_permissions

piezoelectric constant as developed by Wong *et al.*⁶ and given as

$$d_{33} = \phi L_E \{ 2L_T^{\perp} d_{31i} + L_T^{\parallel} d_{33i} \},$$
(12)

$$d_{31} = \phi L_E \{ (L_T^{\perp} + L_T^{\parallel}) d_{31i} + L_T^{\perp} d_{33i} \},$$
(11)

$$\begin{cases} L_{E} = \frac{1}{\phi} \frac{\varepsilon - \varepsilon_{m}}{\varepsilon_{i} - \varepsilon_{m}} \\ L_{T}^{\perp} = \frac{1}{\phi} \left\{ \frac{1}{3} \frac{k^{-1} - k_{m}^{-1}}{k_{i}^{-1} - k_{m}^{-1}} - \frac{1}{3} \frac{\mu^{-1} - \mu_{m}^{-1}}{\mu_{i}^{-1} - \mu_{m}^{-1}} \right\} \\ L_{T}^{\parallel} = \frac{1}{\phi} \left\{ \frac{1}{3} \frac{k^{-1} - k_{m}^{-1}}{k_{i}^{-1} - k_{m}^{-1}} + \frac{2}{3} \frac{\mu^{-1} - \mu_{m}^{-1}}{\mu_{i}^{-1} - \mu_{m}^{-1}} \right\} \end{cases}$$
(13)

For 0–3 composites with spherical inclusion, ε may be calculated from the Bruggeman formula¹⁵

$$\frac{\varepsilon_i - \varepsilon}{\varepsilon^{1/3}} = (1 - \phi) \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_m^{1/3}}.$$
(14)

The bulk modulus k and the shear modulus μ of the composite are calculated by

$$k = k_m + \frac{\phi(k_i - k_m)}{1 + (1 - \phi)(k_i - k_m)/(k_m + 4\mu_m/3)},$$
(15)

$$\mu_{l} = \mu_{m} \left\{ 1 + \frac{15(1 - \nu_{m})(\mu_{i}/\mu_{m} - 1)\phi}{7 - 5\nu_{m} + 2(4 - 5\nu_{m})[\mu_{i}/\mu_{m} - (\mu_{i}/\mu_{m} - 1)\phi]} \right\},\tag{16}$$

$$\mu_{u} = \mu_{m} \bigg[1 + \bigg(\frac{\mu_{i}}{\mu_{m}} - 1 \bigg) \frac{\beta}{\alpha + \beta \gamma} \phi \bigg], \tag{17}$$

where

$$\begin{cases} \alpha = \frac{42}{5\mu_m} \frac{\mu_m - \mu_i}{1 - \nu_m} \phi(\phi^{2/3} - 1)^2 \\ \beta = [(7 - 10\nu_i) - (7 - 10\nu_m) \vartheta] 4\phi^{7/3} + 4(7 - 10\nu_m) \vartheta \\ \gamma = \frac{\mu_i}{\mu_m} + \frac{7 - 5\nu_m}{15(1 - \nu_m)} \left(1 - \frac{\mu_i}{\mu_m}\right) + \frac{2(4 - 5\nu_m)}{15(1 - \nu_m)} \left(1 - \frac{\mu_i}{\mu_m}\right) \phi^{\prime} \\ \vartheta = \frac{(7 + 5\nu_i)\mu_i + 4(7 - 10\nu_i)\mu_m}{35(1 - \nu_m)\mu_m} \end{cases}$$

$$(18)$$

Subscripts u and l for the effective shear modulus denote the upper and lower bound, respectively. v represents Poisson's ratio.

By using Eqs. (10) and (11) with our simulated P_{ri} as shown in Fig. 4(b), the d_{31} coefficients of the PZT/epoxy composites as a function of poling field have been evaluated using the materials data listed in Table II. Figure 5 shows our predictions, together with the experimental results reported by Furukawa *et al.*¹⁰ Apart from the sample with ϕ =0.232, it is seen that fairly good agreement is achieved, with most of the experimental data points falling within our predicted bounds. For the sample with ϕ =0.232, a fairly good agreement is obtained at poling fields smaller than 4 MV/m, but not for larger fields. The discrepancy may come from the assumed simple proportionality of d_{31} and P_{ri} , which may become inadequate at large values of P_{ri} .

IV. PIEZOELECTRIC AND PYROELECTRIC PROPERTIES OF LEAD TITANATE/POLYVINYLIDENE FLUORIDE-TRIFLUOROETHYLENE 0-3 COMPOSITES

PT powder with 300 nm particle diameter was prepared by a sol-gel method and dispersed in a solution of P(VDF– TrFE) 70/30 mol% copolymer in methylethylketone, followed by solution casting and compression molding to form 30 μ m thick PT/P(VDF–TrFE) 0–3 composite films with ϕ =0.1, 0.2, and 0.3. The samples were annealed at 120 °C for 2 h. A dc electric field of 50 MV/m with 3 ms ramp time was applied to the composites at 120 °C, which is above the Curie temperature of the P(VDF–TrFE), for different poling times. The poled samples were then annealed under shortcircuit conditions for 18 h at 60 °C. The piezoelectric coefficients d₃₃ of the composites were measured at room temperature using a piezo d₃₃ meter (ZJ-3D type, Institute of

TABLE II. Dielectric, elastic, and piezoelectric constants of PZT and epoxy at 50 $^\circ\text{C}.$

	${m \epsilon}/{m arepsilon_{\it o\ (poled)}}^{ m a}$	Y (GPa) ^a	$ u^{\mathrm{b}}$	$-d_{31}^{f} (pC/N)^{a}$	$d_{33}^f (\text{pC/N})^b$
PZT	1700	36	0.3	177	400
Epoxy	4.2	1.8	0.35		•••

^aSee Ref. 10.

^bSee Ref. 6.

Acoustics, Academica Sinica). Mechanical stress with an ac force of $0.250 N_{\rm rms}$ and a frequency of 110 Hz was applied to the sample along the thickness direction and the current signal was measured. To measure the pyroelectric coefficients at room temperature, the sample temperature was sinusoidally modulated with frequency 5 mHz and amplitude 1 K using a Peltier element. The pyroelectric current signals were recorded with an electrometer and measured with a lock-in amplifier.

In this section, we report on the simulation of the gross piezo- and pyroelectric properties of these composites based on the calculated polarization behavior of the ceramic inclusion, in a manner similar to Sec. III. Tables III and IV show the materials parameters for the constituents which have been used. The P-E hysteresis loop of PT ceramic has also been simulated by the modified Miller *et al.*'s^{8,9} model with Eqs. (8) and (9), and is shown in Fig. 6. The remanent polarization P_{ri} of the PT inclusions has been calculated with Eqs. (7) and (8) as a function of poling time under the poling procedure described herein and is shown in Fig. 7.

It is found that the remanent polarization of the inclusions in the composites increases quite linearly with poling time between 0 and 1.5 s. The ceramic inclusions in the composites with higher ϕ can be polarized more rapidly than in composites with lower ϕ , because of a shorter τ of the former. The maximum value of P_{ri} in the composites with ϕ =0.3 and 0.1 is reached after poling times of 1.1 s and 1.5 s, respectively. These simulated results reveal that the time scale for fully polarizing a 0–3 PT/P(VDF–TrFE) composite



FIG. 5. Measured piezoelectric coefficients d_{31} of PZT/epoxy composites with $\phi = 0.048$ (circle), 0.131 (square), and 0.232 (triangle) as a function of poling field (from Ref. 3) together with the simulated curves. The solid and the dashed lines denote the calculated lower and upper bound, respectively.

TABLE III. Material parameters of PT and P(VDF-TrFE) at 120 °C.

	P_s (C/m ²) ^a	P_r (C/m ²) ^b	E_c (MV/m) ^c	$\boldsymbol{\varepsilon}/\boldsymbol{\varepsilon}_o$	$\sigma \ (\Omega^{-1} \ \mathrm{m}^{-1})$
PT	0.57	0.50	5	200	10^{-10}
P(VDF–TrFE)				50 ^d	2.5×10 ^{-9e}

^aSee Ref. 16. ^bSee Ref. 12.

^cSee Ref. 17.

^dMeasured in the present study.

^eSee Ref. 18.

is at least three orders of magnitude shorter than the poling times used in many experimental investigations.

The piezoelectric coefficients d_{33} of the composites have been calculated by using Eqs. (10) and (12) together with the simulated P_{ri} from Fig. 7, and the results are shown in Fig. 8. Good agreement with the experimental results is achieved. The composites with higher ϕ attain a larger d_{33} under the same poling condition. Apart from the samples with ϕ =0.1, all of the experimental data fall within the theoretically predicted bounds. Due to the small signals in the measurement of d_{33} for the composite with ϕ =0.1, the experimental accuracy of these data might be smaller.

The experimental results, as well as our predicted d_{33} of the composites as a function of poling time, reveal that these composites can be fully polarized quite rapidly under the poling conditions just mentioned, i.e., within less than 10 s.

The present model calculates the time dependence and, consequently, the time scale of the poling process based on the 0-3 composite arrangement. In literature, a longer poling time is normally used. For a pure ceramic, a longer poling time tends to increase the remanent polarization and decrease relaxation effects after poling, which is not discussed here. Also, the hysteresis loop of a pure ceramic is, to some degree, time dependent. However, our model for the hysteresis loops themselves [i.e., the modified Miller *et al.*'s^{8,9} model, Eqs. (8) and (9) is a static one, with no explicit or implicit time dependence introduced. Thus, in addition, the interplay between the polarization of the inclusion and the electric conductivity of the matrix considered by our model and the time dependent effects of the hysteresis loops of the constituents, should also affect the poling time scale of a ferroelectric composite. Our comparisons between the calculated and measured values seem to suggest that the effects of relaxation after poling and time dependent hysteresis loops might not be significant considerations for the development of a sufficiently high P_{ri} in PT 0-3 composites. A shorter poling time is also effected by the small permittivity of PT which is substantially lower than that of ceramics like PZT, hence a smaller τ .

TABLE IV. Dielectric, elastic, piezoelectric, and pyroelectric constants of PZT and P(VDF–TrFE) at room temperature.

	ϵ/ϵ_o	Y ^c (GPa)	ν^{c}	$-d_{31}^f$ (pC/N)	d ^f ₃₃ (pC/N)	p^{fa} (μ C/cm ² K)
PT	200 ^a	126.7	0.22	12.5	100	300
P(VDF–TrFE)	11.6 ^b	2.32	0.39			

^aSee Ref. 19.

^bMeasured in the present study.

^cSee Ref. 10.

Downloaded 01 Apr 2011 to 158.132.161.9. Redistribution subject to AIP license or copyright; see http://jap.aip.org/about/rights_and_permissions



FIG. 6. Simulated P-E hysteresis loop of PT ceramic [from Eqs. (8) and (9) with $n_1/n_2 = 5/11$].

The experimental observations are consistent with the assumption of a complete compensation of the polarization of the inclusions by charge at the inclusion-matrix interfaces, i.e., $P_{ri} = q_o$. Under this condition, the electric fields in the matrix and inclusions are zero, and the pyroelectric coefficient *p* of the composite is given by⁷

$$p = \phi L_E p_i \,. \tag{19}$$

The pyroelectric coefficient of the matrix $p_m = 0$ as the P(VDF–TrFE) 70/30 mol% copolymer cannot be polarized at a temperature above its Curie transition temperature (106 °C). Following the idea of Sec. III, we take

$$p_i = (P_{ri}/P_{ri}^f)p^f,$$
 (20)

where p^f refers to the pyroelectric coefficient of a fully polarized ceramic. L_E has been defined in Eq. (13).

Ì

The pyroelectric coefficients p of the PT/P(VDF-TrFE) 0-3 composites as a function of poling time can, therefore, be evaluated by using Eqs. (19) and (20) together with the simulated P_{ri} from Fig. 7. The results in Fig. 9 show that the predictions and the experimental data agree well. Similar to d_{33} , it is seen that both the predicted and the experimental p



FIG. 7. The simulated "remanent" polarization in PT inclusions of PT/ P(VDF–TrFE) 0–3 composites with ϕ =0.1 (circle), 0.2 (square), and 0.3 (triangle) as a function of poling time.





FIG. 8. The measured piezoelectric coefficients d_{33} of PT/P(VDF–TrFE) 0–3 composites with ϕ =0.1 (circle), 0.2 (square), and 0.3 (triangle) as a function of poling time together with the simulated curves. The solid and the dashed lines denote the calculated lower and upper bound, respectively.

increase rapidly within the first second of poling. Composites with higher ϕ attain a higher p under the same poling condition. The experimental results and the predictions reveal that the composites attain a maximum pyroelectric coefficient at poling times of less than 10 s, consistent with the time scale of the development of the simulated P_{ri} and d_{33} .

V. CONCLUSIONS

The effective d_{31} , d_{33} , and p for 0–3 composites of ferroelectric particles in a linear matrix have been studied in terms of the dielectric, elastic, piezoelectric, and pyroelectric properties of the constituents as well as the polarization state of the dispersed particles. The time development and the final polarization of the ceramic inclusions have been computed for a variety of poling schedules. The comparison with experimental data from literature shows that the predictions of the piezoelectric coefficient d_{31} of PZT/epoxy 0–3 composites are fairly realistic at low poling fields. The simulated



FIG. 9. The measured pyroelectric coefficients p of PT/P(VDF-TrFE) 0-3 composites with $\phi = 0.1$ (circle), 0.2 (square), and 0.3 (triangle) as a function of poling time together with the simulated curve (line).

Downloaded 01 Apr 2011 to 158.132.161.9. Redistribution subject to AIP license or copyright; see http://jap.aip.org/about/rights_and_permissions

piezoelectric and pyroelectric properties of PT/P(VDF– TrFE) 0–3 composites agree well with experimental results. The time scale for fully polarizing the PT composites is found to be on the order of 10 s, which is much shorter than for other composite systems reported in the literature. Qualitative agreement affirms that our modeling technique is useful for the prediction of the piezoelectric and pyroelectric properties of 0–3 composites. This may be especially helpful in the selection of materials and the design of poling parameters for ceramic/polymer composites.

ACKNOWLEDGMENT

This work was partially supported by the Center for Smart Materials of The Hong Kong Polytechnic University.

- ¹Y. T. Or, C. K. Wong, B. Ploss, and F. G. Shin, J. Appl. Phys. **93**, 4112 (2003).
- ²C. K. Wong, Y. W. Wong, and F. G. Shin, J. Appl. Phys. **92**, 3974 (2002).
 ³C. J. Dias and D. K. Das-Gupta, IEEE Trans. Dielectr. Electr. Insul. **3**, 706 (1996).
- ⁴J. F. Tressler, S. Alkoy, and R. E. Newnham, J. Electroceram. 2, 257 (1998).

- ⁵T. Bhimasankaram, S. V. Suryanarayana, and G. Prasad, Curr. Sci. **74**, 967 (1998).
- ⁶C. K. Wong, Y. M. Poon, and F. G. Shin, J. Appl. Phys. 90, 4690 (2001).
- ⁷B. Ploss, W. Y. Ng, H. L. W. Chan, B. Ploss, and C. L. Choy, Compos. Sci. Technol. **61**, 957 (2001).
- ⁸S. L. Miller, R. D. Nasby, J. R. Schwank, M. S. Rodgers, and P. V. Dressendorfer, J. Appl. Phys. 68, 6463 (1990).
- ⁹S. L. Miller, J. R. Schwank, R. D. Nasby, and M. S. Rodgers, J. Appl. Phys. **70**, 2849 (1991).
- ¹⁰T. Furukawa, K. Fujino, and E. Fukada, Jpn. J. Appl. Phys., Part 1 15, 2119 (1976).
- ¹¹T. Furukawa, K. Suzuki, and M. Date, Ferroelectrics 68, 33 (1986).
- ¹²B. Ploss, B. Ploss, F. G. Shin, H. L. W. Chan, and C. L. Choy, *Proceedings of the 12th IEEE International Symposium on Applications of Ferroelectrics*, (ISAF 2000) (IEEE, New York, 2000), Vol. 1, p. 301.
- ¹³L. Wu, T. S. Wu, C. C. Wei, and H. C. Liu, J. Phys. C 16, 2823 (1983).
- ¹⁴C. A. May, *Epoxy Resins: Chemistry and Technology*, 2nd ed. (Marcel Dekker, New York, 1988).
- ¹⁵D. A. Bruggeman, Ann. Phys. (Leipzig) 24, 636 (1935).
- ¹⁶M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelec*trics and Related Materials (Oxford, New York, 1977), p. 249.
- ¹⁷H. L. W. Chan, W. K. Chan, Y. Chen, and C. L. Choy, Ferroelectrics **196**, 141 (1997).
- ¹⁸ H. L. W. Chan, Y. Chen, and C. L. Choy, Integr. Ferroelectr. **9**, 207 (1995).
- ¹⁹ M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelec*trics and Related Materials (Oxford, New York, 1977), p. 250.