

Polarization behavior of ferroelectric multilayered composite structures

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(Received 16 September 2002; accepted 10 January 2003)

We model the polarization behavior of ferroelectric multilayered composite structures including the double layer and the triple layer under the action of variable fields. The model takes into consideration the ceramic/polymer interfacial charge and the nonlinear hysteresis nature of the ferroelectric constituent materials to study the poling process of multilayered structures. The results obtained are compared with available experimental results on double-layer lead zirconate titanate/polyvinylidene fluoride-trifluoroethylene and triple-layered triglycine sulphate/polyvinylidene fluoride-trifluoroethylene/triglycine sulphate systems. In general the broad features of the experimental results were reproduced, and fairly good agreement between the predictions and the experimental results was found. The work also demonstrates that electrical conductivity in the ferroelectric materials is an important factor controlling the poling process. © 2003 American Institute of Physics. [DOI: 10.1063/1.1558961]

I. INTRODUCTION

Composite systems of ferroelectric ceramics and ferroelectric polymers combine the high pyroelectric and piezoelectric activities of the ceramic with the excellent mechanical properties of the polymer, thus deriving tailor-made advantages for sensor and transducer applications. Ferroelectric materials possess spontaneous polarization but usually show no net macroscopic polarization due to the different orientations of the individual domains. In order to impart piezoelectric and pyroelectric activities, they must be subjected to a poling process, to align the spontaneous polarization in the material(s). In a ferroelectric ceramic/polymer composite, the permittivity of the ferroelectric ceramic is normally much higher than that of the polymer, thus the electric field acting on the ceramic phase would be much lower than the applied electric field.¹ In this context, it seems impossible to pole the ceramic in the composite. However, successful thermal poling of various composite systems like lead titanate, lead zirconate titanate (PZT), and lanthanum modified lead zirconate titanate with polymer have been reported in the literature.²⁻⁴ However, the poling recipes/techniques are still quite empirical because a firm understanding of the physical processes involved in poling has not been fully established.

The present work aims to systematically analyze the physical process(es) pertaining to the poling of the multilayered composite. Understanding of the physical process behind poling will give an idea on the materials selection and

the poling parameters for particular applications. In this article, we shall first give a theoretical description on poling of multilayered composite systems by considering the continuity of the total current density going through each ferroelectric layer along the poling direction. A modified model of Miller *et al.*⁵⁻⁷ is used for the description of the P - E relation of each ferroelectric layer. The modeling will be applied to study the switching of the bilayer PZT/polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE) composite investigated by Furukawa *et al.*¹ and the poling of P(VDF-TrFE) with ferroelectric triglycine sulphate (TGS) electrodes investigated by Ploss *et al.*⁸ Then we shall show the comparison between the experimental results with the theoretical predictions.

II. THEORY

Consider a multilayered composite consisting of n ferroelectric layers connected in series along the thickness direction (see Fig. 1). The constitutive equation of the i th layer is given by

$$D_i = \epsilon_i E_i + P_i, \quad (1)$$

where i is an integer between 1 to n . D , ϵ , E , and P represent the dielectric displacement, permittivity, electric field, and ferroelectric polarization, respectively. P_i generally depends on E_i in a complicated manner and a model for describing P - E relations must be used, as will be explained later. In contrast, when some layer, say j th layer, is nonferroelectric, then $P_j = 0$.

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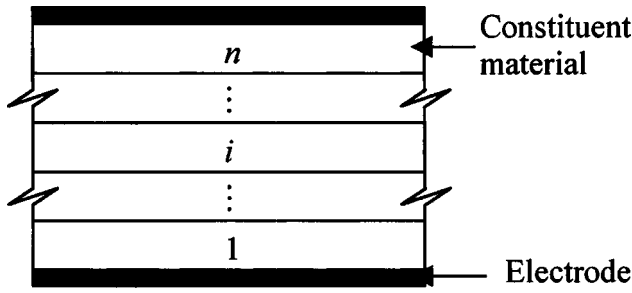


FIG. 1. Schematic for the multilayered composite.

In the measurement of dielectric displacement of a ferroelectric sample, the Sawyer–Tower circuit is usually adopted, which is merely a capacitor divider where the sample is in series with a standard reference capacitor. Assuming the reference capacitor is a perfect insulator, the measured dielectric displacement of the ferroelectric sample at a certain time t_0 is given by the integration of current density across the reference capacitor

$$D(t_0) = \int_0^{t_0} J_r dt. \tag{2}$$

J denotes current density and the subscript r represents the reference capacitor.

The overall electric field of the composite is given by¹

$$E = \sum_{i=1}^n \nu_i E_i, \tag{3}$$

where $\nu_i = d_i / \sum_{j=1}^n d_j$ is the volume fraction of the i th layer. The interfacial charge density between the k th and $(k + 1)$ th layer can be written as

$$q_k = D_{k+1} - D_k, \tag{4}$$

where k is an integer between 1 and $n - 1$. Continuity of current requires

$$J_r = J_k = J_{k+1} = \sigma_k E_k + \frac{\partial D_k}{\partial t} = \sigma_{k+1} E_{k+1} + \frac{\partial D_{k+1}}{\partial t}, \tag{5}$$

where σ represents the electric conductivity. Equations (1) and (5) yield

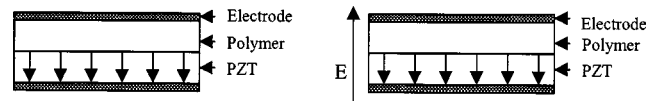


FIG. 2. (a) The composite is prepolarized to $-P_r$. (b) The composite is poled by applying an electric field opposite to the prepolarized direction.

$$\sigma_k E_k + \epsilon_k \frac{\partial E_k}{\partial t} + \frac{\partial P_k}{\partial t} = \sigma_{k+1} E_{k+1} + \epsilon_{k+1} \frac{\partial E_{k+1}}{\partial t} + \frac{\partial P_{k+1}}{\partial t} \tag{6}$$

and the relation $\partial P / \partial t = (\partial P / \partial E)(\partial E / \partial t)$ may be employed for subsequent calculations.

In the absence of a simple fundamental physical theory that can accurately predict the ferroelectric polarization as a function of applied electric field, we here make use of a convenient mathematical model developed by Miller *et al.*^{5,6}

$$\frac{\partial P}{\partial E} = \left(1 - \tanh \sqrt{\frac{P - P_{\text{sat}}}{\xi P_s - P}} \right) \left(\frac{\partial P_{\text{sat}}}{\partial E} \right), \tag{7}$$

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 spontaneous polarization, respectively. $\xi = +1$ for an increasing field and $\xi = -1$ for a decreasing field. The saturated polarization of the hysteresis loop is written as a function of the electric field as

$$P_{\text{sat}} = \xi P_s \tanh \left[\frac{\xi E - E_c}{2E_c} \ln \left(\frac{1 + P_r / P_s}{1 - P_r / P_s} \right) \right], \tag{8}$$

where P_r and E_c are taken as positive quantities in Eq. (8). They represent the remanent polarization and coercive field, respectively.

Solving Eqs. (3), (6), and (7) with known applied electric field profile will give the electric field and the ferroelectric polarization in both phases as a function of time, thereby the time development of the dielectric displacement and the current density of the composite can be evaluated by Eqs. (2) and (5) accordingly. The interfacial charge density at each interface can be calculated by Eq. (4). In this article, all these equations were solved by Wolfram Mathematica 4.0.

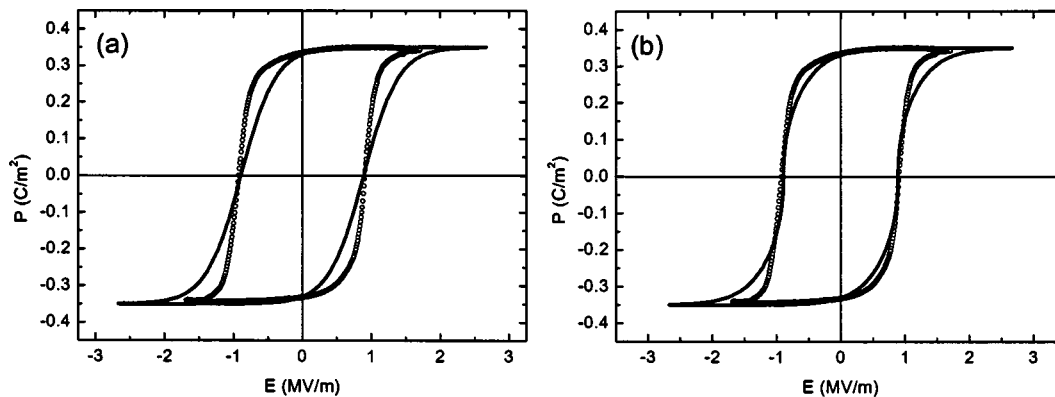


FIG. 3. (a) P – E hysteresis loop of PZT ceramic predicted by Miller's model (solid line) with the experimental result (circles). (b) P – E hysteresis loop of PZT ceramic predicted by Miller's model with $n = 5/11$ (solid line) and the experimental result (circles).

TABLE I. Properties of constituents for PZT ceramic and P(VDF-TrFE) copolymer.

	P_s (C/m ²)	P_r (C/m ²)	E_c (MV/m)	n	$\varepsilon/\varepsilon_0^a$	σ ($\Omega^{-1} \text{m}^{-1}$)	ν^a
PZT	0.35 ^a	0.33 ^a	0.89 ^a	5/11	1900 ^a	10 ⁻¹¹ ^b	0.75
P(VDF-TrFE) 52/48 mol %	40	1.8 × 10 ⁻⁸	0.25

^aReference 1.^bReference 11.

III. APPLICATION TO SWITCHING OF BILAYER PZT/P(VDF-TrFE) COMPOSITE

Furukawa *et al.*¹ have studied the switching characteristics of a bilayer PZT/P(VDF-TrFE) composite with 75%

ceramic volume fraction. The composite was first prepolarized in the reverse direction [see Fig. 2(a)] and the field was released. A dc electric field of 1.25 MV/m was then applied on the sample at 100 °C in the forward direction [see Fig.

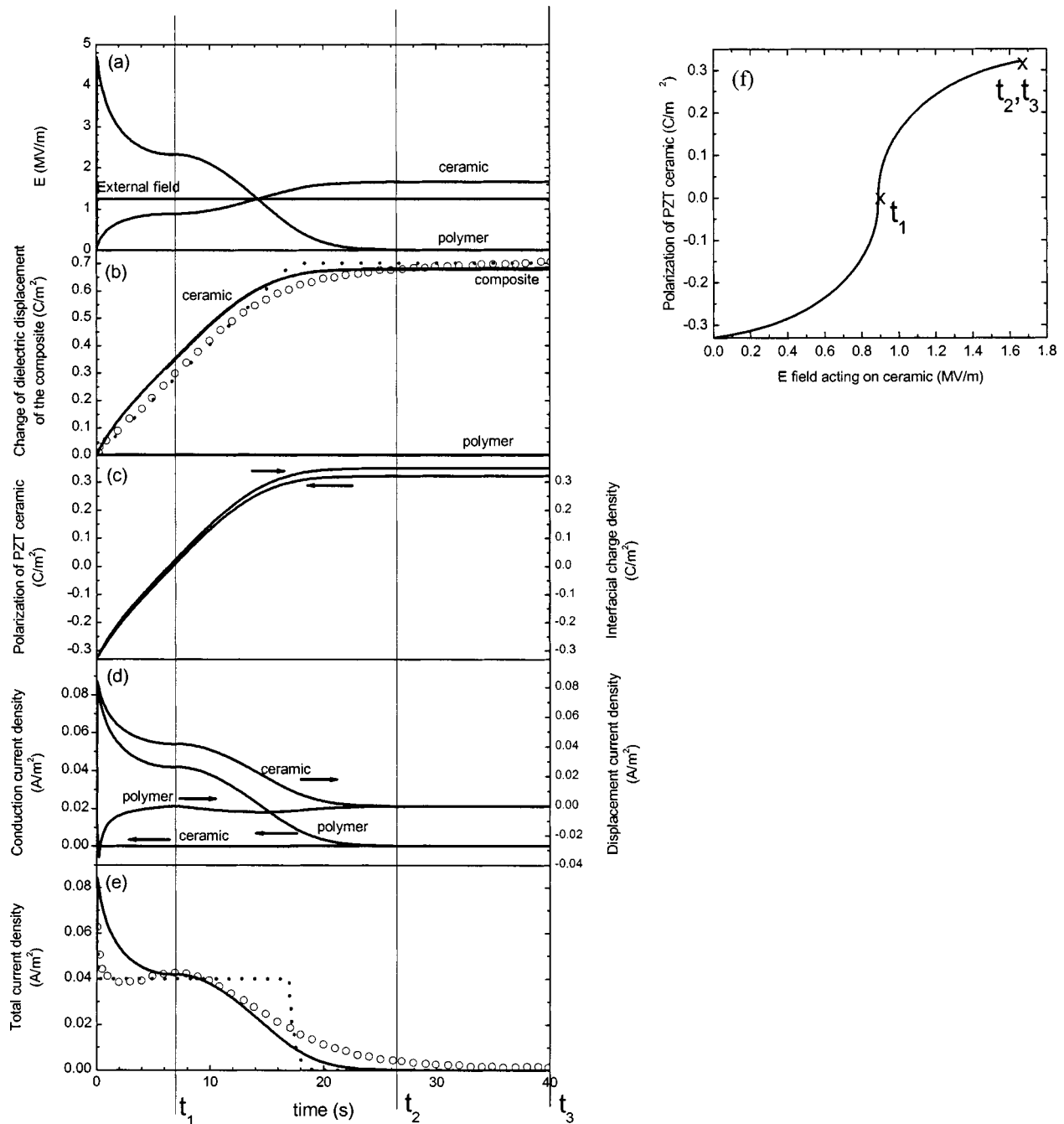


FIG. 4. Comparison of observed (circles), prediction by Furukawa *et al.* (dotted lines) and our calculated (solid lines) switching characteristics in a PZT/polymer composite.

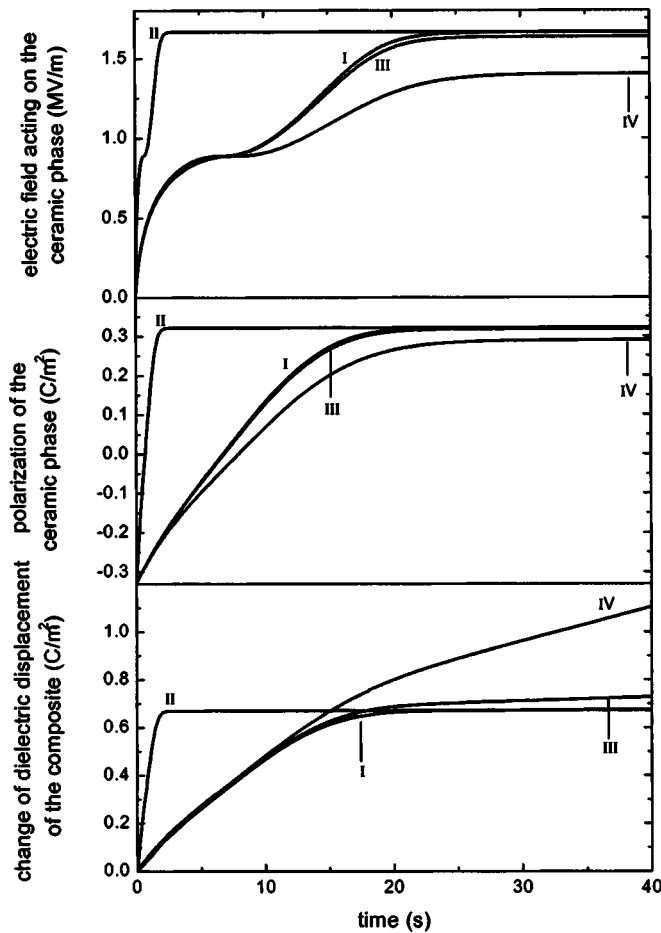


FIG. 5. Predictions of switching characteristics of PZT/polymer composite with parameters using (i) original value, (ii) one higher order of magnitude in conductivity of polymer, (iii) one higher order of magnitude in conductivity of ceramic, and (iv) two higher order of magnitude in conductivity of ceramic.

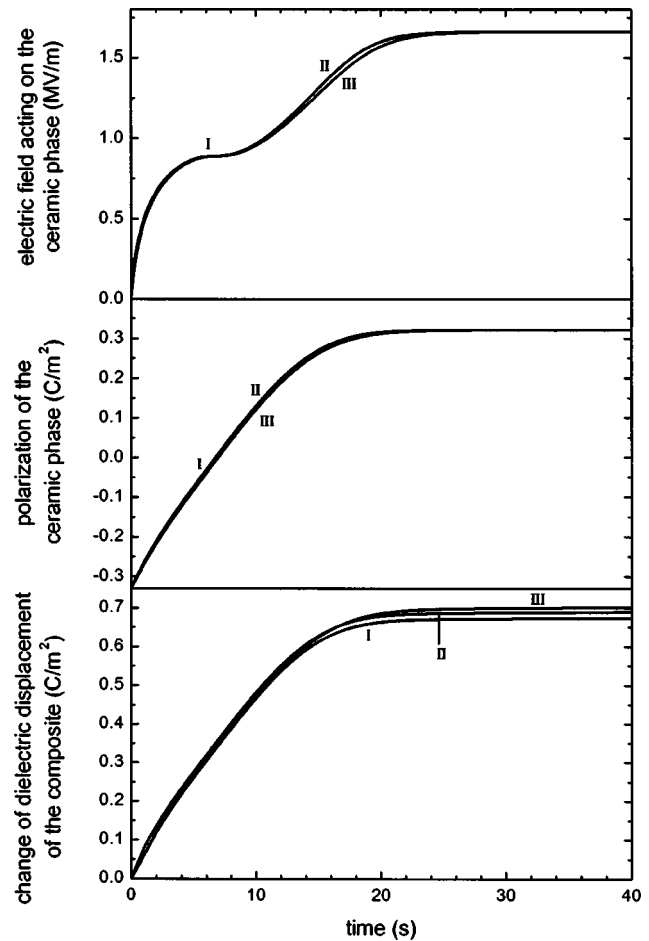


FIG. 6. Predictions of switching characteristics of PZT/polymer composite with parameters using (i) original value, (ii) two times higher in the permittivity of polymer, and (iii) two times higher in the permittivity of ceramic.

2(b)]; the dielectric displacement and the current density were measured with time. Assuming $P-E$ hysteresis behavior for the PZT ceramic phase is a perfect square loop and the dielectric displacement is continuous across constituents, Furukawa *et al.* have modeled the switching processes for their bilayer composite system. Our modeling takes into consideration the ceramic/polymer interfacial charge and more realistic hysteresis behavior of the ferroelectric constituent.

The $P-E$ relationship of PZT ceramic can be simulated by Eqs. (7) and (8), in which three parameters (P_s , P_r , and E_c) are necessary for the prediction. We converted the $D-E$ graph of PZT ceramic shown in Ref. 1 into a $P-E$ graph by use of Eq. (1). Therefore P_s , P_r , and E_c can be identified to be 0.35, 0.33 C/m², and 0.89 MV/m, respectively. Figure 3(a) shows the calculated [Eqs. (7) and (8)] $P-E$ saturated hysteresis loop of PZT ceramic and the “experimental” loop from Furukawa *et al.*’s $D-E$ measurements. It is found that the two do not fit well. It is noted that the $P-E$ loop shape can be quite different even when the material parameters P_s , P_r , and E_c are similar. Following Wong *et al.*,⁷ we make a numerical modification to Miller *et al.*’s model to adjust the $P-E$ loop shape. Equation (8) is modified as

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

where $n \equiv n_1/n_2$ ranges from 1/3 to 1 with n_1 and n_2 being odd numbers. Figure 3(b) shows the experimental loop and the fitting given by Eqs. (7) and (9) with n equal to 5/11. Better agreement is observed between the two loop shapes.

On the other hand, P(VDF-TrFE) 52/48 mol % copolymer used in Ref. 1 is known to be a ferroelectric copolymer having a Curie temperature near 70 °C. Since the experiment was carried out at 100 °C, the copolymer was in its paraelectric phase. We thus treat it as a linear material.

The material parameters used for the calculations are listed in Table I.

Figure 4 shows the experimental results, the predictions given by Furukawa *et al.* [Figs. 4(b) and 4(e)] together with predictions based on our model. According to the latter, the electric field acting on the two phases follows very different trends once the external electric field is applied on the composite. At $t \leq t_1$ (labeled in Fig. 4), the electric field acting in the ceramic phase would increase but that in the polymer phase would decrease with time. The electric field acting on the ceramic phase would tend to remain constant when it approaches the coercive field of the ceramic. The polarization and the interfacial charge density increase from their

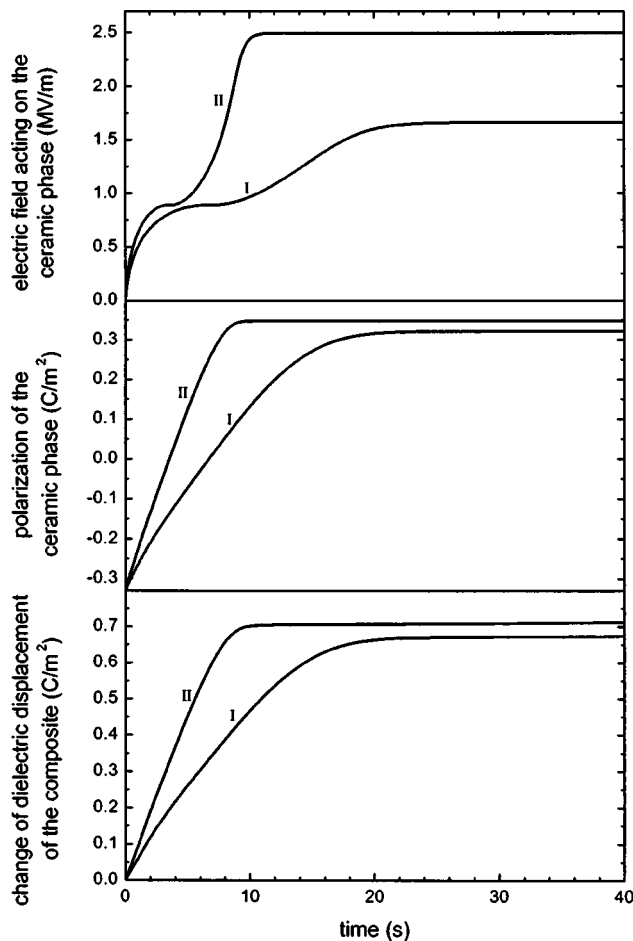


FIG. 7. Predictions of switching characteristics of PZT/polymer composite with parameters using (i) original value and (ii) 50% higher external electric field.

initial negative values of $-P_r$ to zero. At the same time, a linear change of dielectric displacement of the composite with time can be observed. Here the change of dielectric displacement refers to the difference of the dielectric displacement between time t and the initial time $t=0$ at which the external field is applied. On the other hand, the total current density follows closely the conduction current of the polymer phase, which is governed by the conductivity of the polymer phase and the electric field acting on it. At $t_1 < t < t_2$, the electric field acting on the ceramic phase further increases. The polarization of the ceramic phase and the interfacial charge density increase from zero to positive values

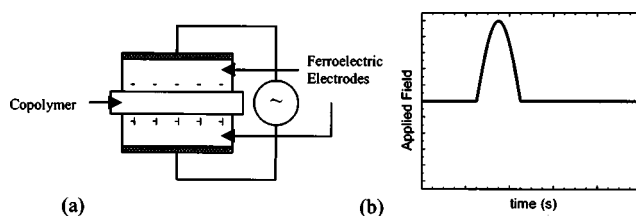


FIG. 8. Two identical ferroelectric electrodes are first prepolarized to $-P_r$ and are separated. The unpoled copolymer is inserted between the electrodes shown in (a), to form a triple-layered composite. The composite is poled by applying an external field, shown in (b).

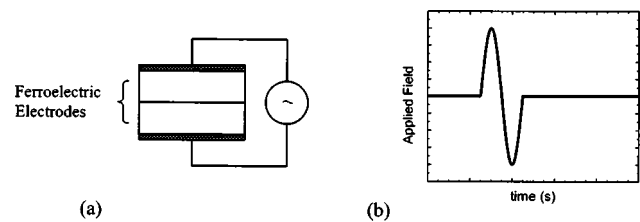


FIG. 9. After poling, the copolymer is removed and the ferroelectric electrodes are stacked together, as shown in (a). A field, shown in (b), is applied to the stack.

quite gradually because the slope of the ceramic $P-E$ curve would decrease after the coercive field is reached [see Fig. 4(f)]. At the same time, the electric field acting on the polymer phase and the total current density gradually decrease. At t equals to t_2 , our prediction on the electric field acting on the ceramic reaches a maximum; therefore, the polarization of the ceramic phase, the interfacial charge density and the change of dielectric displacement of the composite attain maximum and keep constant thereafter. At the same time, the electric field acting on the polymer phase reaches a minimum and the total current density drops to nearly zero. At t_3 , the switching process is said to be finished.

Furukawa *et al.* have shown an agreement in the change of electric displacement of the composite between their predictions with the experimental result. Due to the assumption of the perfect square loop nature in PZT made by Furukawa *et al.*, their predictions show discontinuity in the change of dielectric displacement and the current density at particular times [see Figs. 4(b) and 4(e)]. Significant improvement is obtained in our predicted dielectric displacement and the current density, which follows quite well the observed result. The improvement is due to the more realistic description of the nonlinear hysteresis nature in PZT by Miller *et al.*'s model. It confirms that consideration of a realistic hysteresis loop is beneficial to the study of the switching characteristics of the ferroelectric composite structures. Qualitative agreement seems to affirm the validity of the basic mechanism we presented for the switching process.

In addition, we have tried different poling parameters in the calculations to find out the dependencies of the poling process. First, we use different conductivity values (1–2 orders of magnitude higher than the original values given in Table I) of either phase and recalculate the switching process under identical driving conditions. Figure 5 shows that a higher conductivity of the polymer phase can effectively shorten the buildup time of the electric field acting on the ceramic phase, therefore faster polarization development and change of dielectric displacement can be obtained. It is suggested that higher conductivity of the polymer phase can be achieved either by raising the sample temperature or by doping a small amount of a highly conductive third phase such as carbon, germanium, silver, or silicon into the polymer phase.⁹ On the contrary, a higher conductivity of the ceramic phase results in slower development and lower electric field acting on the ceramic phase, therefore lower polarization of the ceramic phase and lower change of dielectric displacement are expected.

TABLE II. Properties of constituents for TGS crystals and P(VDF-TrFE) copolymer.

	P_s^a (C/m ²)	P_r^a (C/m ²)	E_c^a (MV/m)	ϵ/ϵ_0^a	σ ($\Omega^{-1} \text{m}^{-1}$)	n	d (μm) ^a
TGS	0.028 65	0.028	0.212	40.67	10^{-10b}	11/19	1000
P(VDF-TrFE) 70/30 mol %	0.0572	0.054	43.5	12.3	5×10^{-13c}	13/19	4

^aReference 8.
^bReference 12.
^cReference 13.

It is expected that the permittivity of both phases would not vary by an order of magnitude. We double the original permittivity value of either phase to study the switching process. The predictions shown in Fig. 6 show that a variation in the permittivity of both phases do not have much effect.

On the other hand, Fig. 7 shows the effect of a higher external field (50% higher than the experimental condition): a faster development and higher electric field acting on the ceramic phase. A higher polarization and higher dielectric displacement can be achieved.

Here we conclude that high applied electric field, high conductivity of polymer but low conductivity of ceramic are desirable for fast and high polarization buildup in the ceramic phase of the bilayer ceramic/polymer composite.

IV. APPLICATION TO POLING OF P(VDF-TrFE) WITH FERROELECTRIC TGS ELECTRODES

A poling technique was proposed by Ploss *et al.*,⁸ in which an unmetallized polymer film was poled in a sandwich between ferroelectric crystals. If a high electrical voltage/field is applied to the stack, the polarization of the ferroelectric crystals is saturated, and the interfaces to the polymer film form well defined sources for a high dielectric displacement. Here we are going to extend our previous discussion to study the polarization of such a triple-layered composite in a similar manner.

Ploss *et al.*⁸ prepared the 1000- μm -thick TGS crystals as ferroelectric electrodes. The ferroelectric TGS crystals were first prepolarized to $-P_r$. The 4- μm -thick ferroelectric P(VDF-TrFE) 70/30 mol % copolymer was then stacked between two identical TGS electrodes. One half cycle of a sinusoidal voltage of 1000 V with duration of 2 s was applied to the triple-layered composite at room temperature (see Fig. 8). The applied voltage and the dielectric displacement were recorded as a function of time using a Sawyer-Tower circuit. The copolymer was then removed and the crystals were brought into contact and a full cycle of a sinusoidal voltage of 1000 V with duration of 2 s was applied to the crystal sandwich (see Fig. 9), and the applied voltage and the dielectric displacement were recorded with time. After the negative half cycle, the crystals were allegedly in the initial state ($-P_r$) again.

The parameters used in our calculations are listed in Table II. The electric field acting on the two phases, the polarization, the change of electric polarization of the two phases, and the change of dielectric displacement of the composite as a function of time are calculated as in the last section and shown in Figs. 10(a)–10(d), respectively. It is found that for the first 1 s, i.e., when the first half cycle of the electric field is applied on the composite, the electric fields acting on both phases increase with time. The maximum electric field acting on the TGS crystals and the copolymer are about 0.35 and 70 MV/m, respectively. During the first 1 s, the polarization of the prepolarized TGS crystals increases from $-P_r$ (-0.028 C/m^2) to a maximum about 0.025 C/m^2 while that of copolymer increases from 0 to a maximum about 0.047 C/m^2 . During the time between 1 and 2 s, when the applied electric field gradually returns to zero, the electric fields acting on both phases decrease with time. The polarization of the TGS crystals drops slightly from 0.025 to 0.0238 C/m^2 while that of the copolymer is nearly unchanged. At time $t=2 \text{ s}$, i.e., when the applied electric field

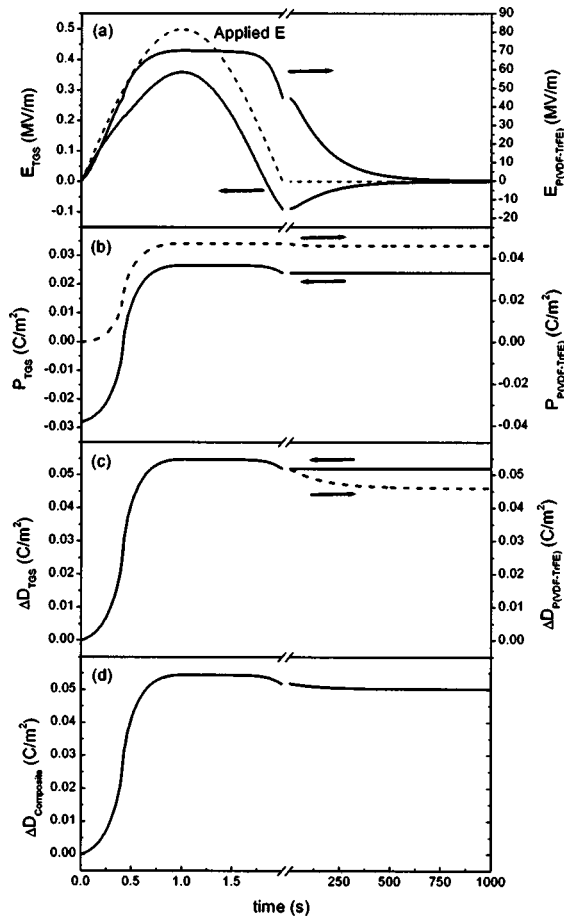


FIG. 10. The simulated results for the (a) electric field, (b) polarization, (c) change of dielectric displacement of the TGS crystals and P(VDF-TrFE) copolymer, and (d) the change of dielectric displacement of the composite as a function of time under the poling procedure shown in Fig. 8.

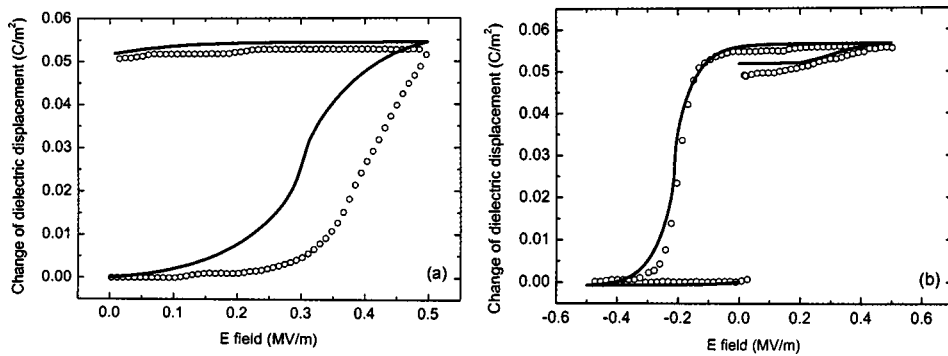


FIG. 11. The simulated results (solid line) are compared with experimental results (circles). (a) Change of D in the TGS/P(VDF-TrFE)/TGS composite during poling under condition shown in Fig. 8. (b) Change of D in the TGS-TGS stack after removing the copolymer, i.e., under condition shown in Fig. 9.

is at zero, the simulated electric field acting on the TGS crystals undershoots to below zero, i.e., -0.1 MV/m, while the electric field acting on the copolymer lags behind the applied electric field and retains a high value of 45 MV/m. Our calculations are extended to $t=1000$ s with the applied field kept at zero. The simulated electric fields acting on both phases are found to approach zero quite gradually. During the time between 2 and 1000 s, the polarization of the copolymer drops slowly with the diminishing electric field acting on it, while the polarization of the TGS crystals is nearly unchanged at all due to the fact that the field acting on the TGS crystals is now well below the coercive field. The change of the dielectric displacements of the TGS crystals and the copolymer roughly follow the polarization development of the constituents, and are almost identical at the first 2 s. The simulated result for the change of dielectric displacement of the TGS/P(VDF-TrFE)/TGS composite is shown in Fig. 10(d), which follows that of the TGS crystals, providing evidence that the dielectric displacement of the TGS/P(VDF-TrFE)/TGS composite is somewhat limited by the TGS crystals, as noted by Ploss *et al.*⁸

The simulated $D-E$ curve for the poling of P(VDF-TrFE) with TGS electrodes is compared with the experimental results,⁸ shown in Fig. 11(a). The $D-E$ curve of the TGS electrode stack, i.e., TGS/TGS, after removing the copolymer film, is also simulated and compared with the experimental result in Fig. 11(b).

In Fig. 11(a), we find that the change of dielectric displacement of the TGS/P(VDF-TrFE)/TGS composite is slightly narrower than the experimental curve, possibly due to some inadequacies in the prediction of the polarization response of the constituent materials by Miller *et al.*'s model. Moreover, Furukawa *et al.* has noted that a virgin copolymer sample when first ramped by an electric field can support a slightly higher field before noticeable switching is observed.¹⁰ After removing of the film, a full sinusoidal voltage is applied on the electrode stack. Only a small increase of dielectric displacement occurs during the positive half cycle [see Fig. 11(b)]. This shows that the polarization of the TGS crystals has been nearly completely switched to P_r which confirms that the change of the dielectric displacement of the TGS/P(VDF-TrFE)/TGS sandwich has been somewhat limited by the TGS crystals. After the negative half cycle the TGS crystals are switched to the initial state, i.e., $-P_r$, therefore the change of dielectric displacement of the TGS crystal returns to zero. We see that all the general fea-

tures of the experimental results are reproduced in our calculations. It seems to confirm the validity of our model for studying the poling of multilayered composite structures.

The $D-E$ behavior calculated for each constituent material in the poling process with the experimental $D-E$ loop and the simulated $D-E$ loop by Miller's model are shown in Fig. 12.

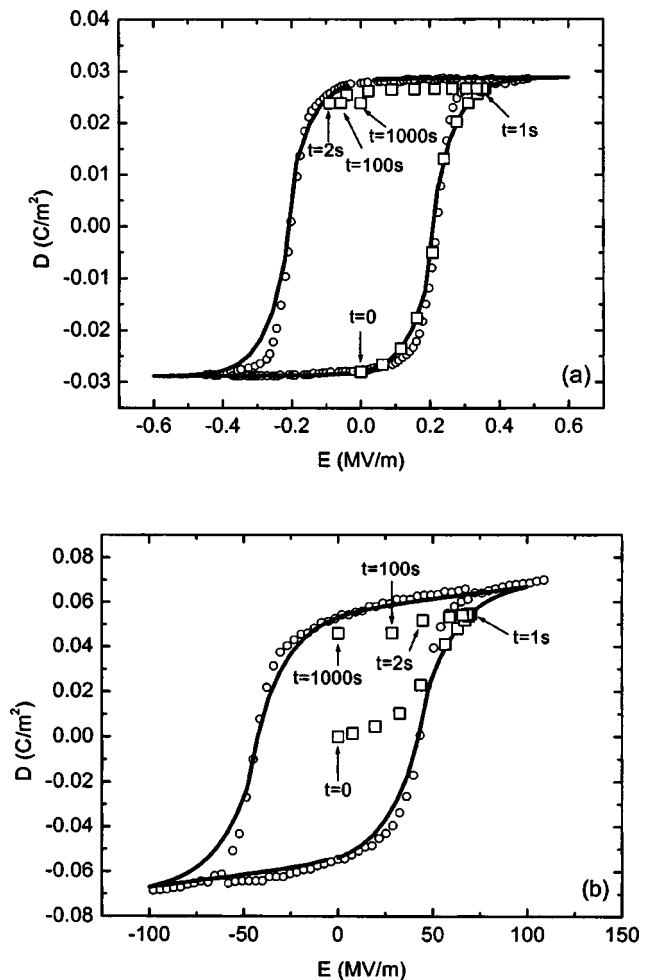


FIG. 12. The squares denote the simulated $D-E$ history in a constituent material during poling of TGS/P(VDF-TrFE)/TGS composite. Corresponding time is labeled in the diagram. The circle and the solid line denote the experimental $D-E$ loop and the loop fitted by Miller *et al.*'s model respectively of the constituent materials. (a) TGS and (b) P(VDF-TrFE).

In addition, it is found that the remanent polarization of the copolymer is about 0.046 C/m^2 , which is only 83% of the maximum remanent polarization of the copolymer. It is calculated that the remanent polarization of the copolymer will increase to about 88.8% and 89.7% of the maximum if the applied voltage of 1200 V and 1500 V instead of 1000 V is applied on the composite sample. In contrast, the remanent polarization of the copolymer will decrease to about 70% of the maximum if only 800 V is adopted. Suppose the composite sample can withstand the electric field twice the electric field that we used in the present study without dielectric breakdown, i.e., 0.998 MV/m, the remanent polarization of the copolymer will become 89.96% of the maximum. Therefore, we expect that P(VDF-TrFE) copolymer can be polarized to not more than 90% of its maximum remanent polarization in a stack with TGS crystals, even when the electric field applied to the stack would be doubled.

V. CONCLUSIONS

A model for studying the poling of ferroelectric multilayered composite systems is discussed by considering the continuity of the total current density going through the layers along the poling direction. The model is applied to study the switching of a bilayer PZT/polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE) composite and the poling of a triple-layered TGS/P(VDF-TrFE)/TGS composite system reported in literature. The P - E relation of each ferroelectric layer is described by using a modified Miller *et al.*'s model. All the experimental main features are reproduced by the simulations and fairly good qualitative agreement is observed. The study of the bilayer PZT/P(VDF-TrFE) reveals the finite conductivity in the polymer phase is justified to be playing an important role in the poling of such composite. The polarization behavior of the triple-layered TGS/P(VDF-TrFE)/TGS composite is also discussed. A higher conductivity of the polymer phase and higher applied electric field are

favorable for speeding up the time development of the electric field acting on the ceramic phase, therefore poling of the ceramic phase in such composite system can be more efficient. It is seen that the change of electric displacement in TGS is somewhat limiting the change of the displacement of the TGS/P(VDF-TrFE)/TGS composite. Our calculation reveals the P(VDF-TrFE) copolymer can be polarized to not more than 90% of its maximum remanent polarization in a stack with TGS crystals, even when the electric field applied to the stack would be doubled. Comparison is made between the experimental results and the predictions, fairly good agreement is also achieved.

ACKNOWLEDGMENTS

This work was partially supported by the Center for Smart Materials of The Hong Kong Polytechnic University. The authors wish to thank the referee for suggesting the use of Eq. (2) in evaluating the measured dielectric displacement.

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