Longitudinal and transverse piezoelectric coefficients of lead zirconate titanate/vinylidene fluoride-trifluoroethylene composites with different polarization states

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Composite films comprising lead zirconate titanate (PZT) ceramic particles dispersed in a vinylidene fluoride-trifluoroethylene copolymer matrix have been prepared by compression molding. The ceramic and copolymer phases of the composite films are polarized separately, resulting in samples with three different polarization states: only the ceramic phase polarized, both phases polarized in the same direction, and two phases polarized in opposite directions. The effect of polarization state on the longitudinal and transverse piezoelectric coefficients (d_{33} and d_{31}) of the composite film has been investigated as functions of ceramic volume fraction ϕ_c. When the ceramic and copolymer phases of a composite film are polarized in the same direction, their piezoelectric activities partially cancel each other, thereby giving almost zero piezoelectric activity at $\phi_c \sim 0.4$. On the other hand, when the phases of a composite film are polarized in opposite directions, their piezoelectric activities reinforce. However, depolarization of the ceramic phase is observed at high ϕ_c, leading to a decrease in the piezoelectric activity. The observed d_{33} and d_{31} values for the composite films agree well with theoretical predictions. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1497699]

I. INTRODUCTION

Composite materials comprising ferroelectric ceramic particles dispersed in a polymer matrix have attracted considerable research interest because of their mechanical flexibility, low acoustic impedance, low dielectric constant, and high piezoelectric (voltage) coefficient.[1–3] In addition, their properties can be tailored by using different constituent materials and different ceramic contents, giving them additional advantage in applications such as pyroelectric sensors, ultrasonic transducers, and hydrophones. Recently, composite materials with a ferroelectric polymer matrix such as polyvinylidene fluoride (PVDF) and vinylidene fluoride-trifluoroethylene [P(VDF–TrFE)] copolymer, have also attracted increasing research interest.[4–6] Because of the higher permittivity of ferroelectric polymers ($\varepsilon_r \sim 10$–14) as compared to other polymers such as epoxy ($\varepsilon_r \sim 4$), it is easier to polarize the ceramic particles in a ferroelectric polymer matrix. Moreover, the ferroelectric polymer matrix and the ceramic particles can be polarized in the same direction or in opposite directions, giving an additional degree of freedom in tailoring the composite properties.

In the present work, lead zirconate titanate (PZT)/P(VDF–TrFE) composite films have been prepared, and the effects of polarization states of the phases on the piezoelectric properties of the composite film have been studied. The ceramic and copolymer phases of the composite film have been polarized separately using special methods so as to give samples with three different polarization states: only the ceramic phase polarized, the two phases polarized in the same direction, and the two phases polarized in opposite directions. The transverse and longitudinal piezoelectric coefficients of the composite films have been measured as functions of ceramic volume fraction and compared with model predictions.

II. SAMPLE PREPARATION

Modified PZT powder, PKI502, was supplied by Piezo Kinetics, USA. The powder was first sintered at 1260 °C for 90 min; then the resulting ceramic sample was ground into fine particles. The average diameter of the ceramic particles was about 0.5 μm, as determined by using a particle-size analyzer (Horbia CAPA-700). The P(VDF–TrFE) 70/30 mol % copolymer was supplied by Piezotech, France. The Curie temperature upon heating was 103 °C and the melting temperature was about 154 °C, as determined by using a differential scanning calorimeter (Perkin Elmer DSC7).

In the fabrication of PZT/P(VDF–TrFE) composite films, the copolymer pellets were first dissolved in methyl-ethyl-ketone. Various amounts of PZT particles were then added to the copolymer solution and dispersed by ultrasonic agitation. After the solvent had evaporated, the resulting mixture was compression molded into films of thickness 100 μm. A P(VDF–TrFE) film was also prepared in a similar

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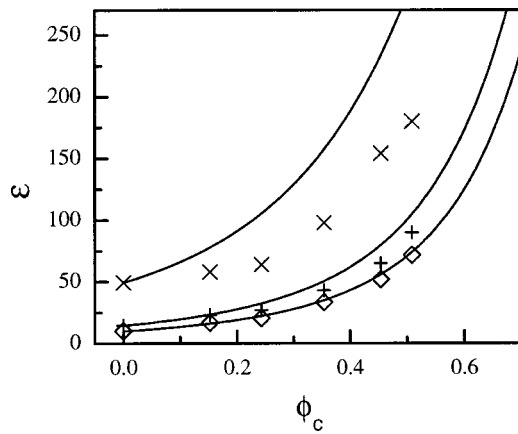
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FIG. 1. Permittivity ε of PZT/P(VDF–TrFE) composite films as a function of ceramic volume fraction ϕ_c at various temperatures: 23 °C, $\diamond$; 60 °C, $+$; and 120 °C, $\times$. The solid line denotes the values calculated according to the Bruggeman model [Eq. (2)].
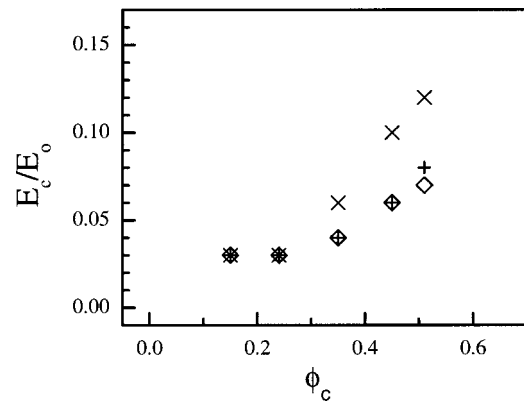

FIG. 2. Ratio of the local electric field to the applied electric field E_c/E_0 as a function of ceramic volume fraction ϕ_c at various temperatures: 23 °C, $\diamond$; 60 °C, $+$; and 120 °C, $\times$.

way. The ceramic volume fraction was calculated using the density of PZT ($=7600$ kg/cm^3, provided by the manufacturer) and the observed densities of the polymer and composite films. Gold electrodes were thermally evaporated on the top and bottom surfaces of the films for the subsequent poling and measurements.

III. SAMPLE POLING

To impart piezoelectricity to a PZT/P(VDF–TrFE) composite, a high electric field is applied to the sample to orient the dipoles in each phase. However, since PZT has a much larger permittivity than P(VDF–TrFE), the electric field is greatly reduced in the ceramic phase. The local electric field experienced by the ceramic particle E_c can be approximated by[7]

$$E_c = \frac{1}{\phi_c} \frac{\varepsilon - \varepsilon_p}{\varepsilon_c - \varepsilon_p} E_0, \tag{1}$$

where ε, ε_c, and ε_p are the permittivities of the composite, ceramic and copolymer, respectively, ϕ_c is the ceramic volume fraction, and E_0 is the applied electric field. Therefore, before poling, the permittivity of the composite films is measured using an impedance analyzer (HP 4194A) so as to determine the field required for poling the samples.

The observed ε values of the composite films at various temperatures are shown in Fig. 1. It is seen that ε increases with increasing ϕ_c. At a given ϕ_c, ε increases slightly as the temperature increases from 25 to 60 °C; it increases considerably as the temperature increases to 120 °C, which is associated with the Curie transition in the copolymer phase at 103 °C.[5] The permittivity of a composite can be understood in terms of the Bruggmenn equation[8]

$$\frac{\varepsilon - \varepsilon_c}{\varepsilon_p - \varepsilon_c} \left(\frac{\varepsilon_p}{\varepsilon} \right)^{1/3} = 1 - \phi_c. \tag{2}$$

In the present study, the observed ε_p value and $\varepsilon_c = 1700$ (provided by the manufacturer) are used to calculate ε as a function of ϕ_c, giving the results shown in Fig. 1. It can be seen that the calculated values of ε at 25 and 60 °C agree

well with the observed values; but the discrepancy becomes large at 120 °C. This may be due to the influence of the copolymer phase transition at 103 °C and further investigation is needed.

The ratio E_c/E_0 is calculated using Eq. (1), the observed ε and ε_p values and $\varepsilon_c = 1700$, and the results are shown in Fig. 2. The E_c/E_0 ratio exhibits similar variations with ϕ_c and temperature as those of ε.

A. Poling of the ceramic phase

To polarize the ceramic phase in the composite film, the sample is heated to 120 °C and subjected to a dc electric field of 40 MV/m for 2 h. The field is then switched off and the sample is cooled to room temperature. At 120 °C, the copolymer phase is in the paraelectric state; so if an electric field is applied to the sample, only the ceramic phase is polarized. As shown in Fig. 2, as ϕ_c increases from 0.15 to 0.51 the E_c/E_0 ratio at 120 °C increases from 0.03 to 0.12, thus the electric field experienced by the ceramic particle (E_c) ranges from 1.2 to 4.8 MV/m if $E_0 = 40$ MV/m. Electric breakdown occurs in the composite film when $E_0 > 40$ MV/m. Since the coercive field of PZT is about 1 MV/m, an applied electric field of 40 MV/m should be high enough to polarize the ceramic phase in a composite with high ϕ_c. For low ϕ_c, the poling efficiency is low owing to the small E_c. However, it is noted that, even for high ϕ_c, the ceramic phase cannot be well polarized under the described condition (i.e., 40 MV/m at 120 °C) unless the poling time is long enough (e.g., 2 h). This is because when the dipoles in the ceramic phase align towards the applied field, severe discontinuity of the electric displacement occurs at the interface of the ceramic and copolymer phases. When the field is removed, this discontinuity will make the aligned dipoles relax back to random orientation. If the field is kept for longer time, space charges in the copolymer phase can drift and accumulate at the interface, the discontinuity is thus removed and the dipole orientation is stabilized.[9] The local electric field in the ceramic phase also increases, thus the poling efficiency is enhanced for a composite with low ϕ_c.

B. Poling of the copolymer phase

After the ceramic phase has been polarized, the copolymer phase in the composite film is polarized at 60 °C under an ac field at frequency 10 Hz. At 60 °C (below the Curie temperature), the coercive field of P(VDF–TrFE) is smaller than that at room temperature, so it is easier to polarize the copolymer phase. As discussed in the previous section, the aligned dipoles in the ceramic phase are stabilized by the charges accumulated at the interface. If an electric field is applied to the sample for a duration substantially shorter than the dielectric relaxation time of the charges in the copolymer phase, the polarization state of the ceramic phase will remain essentially unchanged when the copolymer phase is being polarized.[10] Since the dielectric relaxation time of P(VDF–TrFE) is much longer than 1 s, we have used an ac field at frequency 10 Hz to polarize the copolymer phase. The direction of the resulting polarization (remanent polarization) in the copolymer phase is determined by the electric field direction in the last half cycle of the ac voltage. A Sawyer–Tower circuit, which is designed for the measurement of polarization hysteresis loop, is used to apply several cycles of an ac field to the sample and to measure the remanent polarization P_r of the sample at the same time. By using an ac field ranged from 70 MV/m for $\phi_c=0$ to 26 MV/m for $\phi_c=0.51$, P_r has almost the same value (~ 40 mC/m^2) for all the samples.

In the present study, PZT/P(VDF–TrFE) composite films with three different polarization states are prepared: group A (only the ceramic phase polarized), group B (the two phases polarized in the same direction), and group C (the two phases polarized in opposite directions).

IV. PIEZOELECTRIC COEFFICIENTS

The piezoelectric coefficient d_{ij} is defined as the electric displacement induced by a unit of applied stress. When both the stress and electric displacement are along the poling direction (i.e., thickness direction in the present work), the coefficient is called longitudinal piezoelectric coefficient d_{33}. If the stress is applied along the length of the sample and the electric displacement is induced in the thickness direction, the coefficient is called transverse piezoelectric coefficient d_{31}. Because of Poisson effect, d_{33} and d_{31} have opposite signs. On the other hand, it has been shown that the piezo-
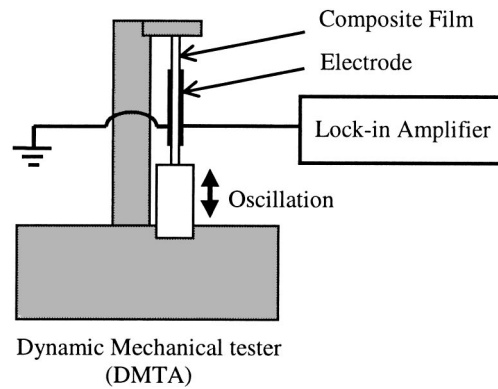

FIG. 3. Experimental setup for the measurement of the transverse piezoelectric coefficient d_{31}.

electric coefficients of PZT and P(VDF–TrFE) have opposite signs; that is, the values of d_{33} and $-d_{31}$ for PZT are positive while those for P(VDF–TrFE) are negative.

In the present study, d_{33} is measured at 60 Hz using a piezo tester (2J-3D, Institute of Acoustics Academica Sinica). In the measurement of d_{31} (Fig. 3), a composite film is stretched along the length direction sinusoidally at a frequency f of 10 Hz in a dynamic mechanical tester (DMTA MK-III, Rheometric Scientific). The applied stress σ is measured from the tester and the current I induced on the film surface is measured using a lock-in amplifier. d_{31} is then calculated as

$$d_{31}=\frac{I}{2\pi fA\sigma},\tag{3}$$

where A is the area of the electrode.

The observed d_{33} and $-d_{31}$ values for the three groups of composite films are given in Table I and are plotted as functions of ϕ_c in Figs. 4–6. As shown in Fig. 4, the observed d_{33} and $-d_{31}$ values for group A samples (with only the ceramic phase polarized) increase slowly as ϕ_c increases from 0 to 0.25 and then faster at $\phi_c>0.3$, showing that the piezoelectric activity of the ceramic phase is more significant at high ϕ_c.

As shown in Fig. 5, for the group B samples (with the two phases polarized in the same direction) d_{33} has a value of -22 pC/N at $\phi_c=0$, changes sign at $\phi_c\sim0.42$ and reaches a value of 17 pC/N at $\phi_c=0.51$. Similarly, as ϕ_c

TABLE I. Ceramic volume fraction ϕ, density ρ, permittivity ε, longitudinal and transverse piezoelectric coefficients (d_{33} and d_{31}) of the three groups PZT/P(VDF–TrFE) composite films: group A (only the ceramic phase polarized), group B (the two phases polarized in the same direction), and group C (the two phases polarized in opposite directions).

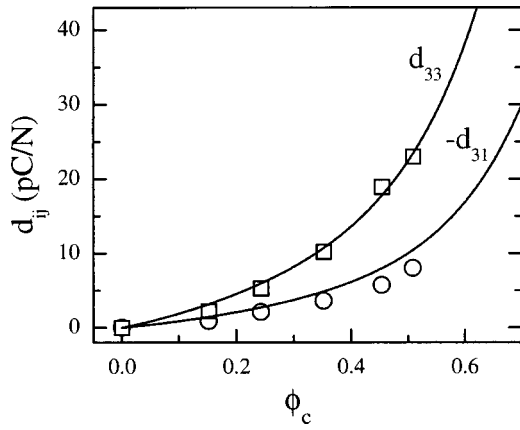| ϕ	ρ (g/cm^3)	ε	d_{33} (pC/N)			$-d_{31}$ (pC/N)		
			Group A	Group B	Group C	Group A	Group B	Group C
0	1.90	9.9	0	−22.1	22.1	0	−6.2	6.2
0.15	2.21	16.8	2.2	−21.3	22.7	0.9	−5.5	2.9
0.24	3.27	20.5	5.3	−14.7	20.2	2.1	−1.7	4.0
0.35	3.88	33.4	10.2	−5.4	18.6	3.6	0.4	4.1
0.45	4.45	52	18.9	6.6	22.2	5.7	3.7	4.3
0.51	5.2	72	23	16.8	10.8	8.0	4.6	2.7

FIG. 4. Longitudinal and transverse piezoelectric coefficients (d_{33} and d_{31}) of the PZT/P(VDF–TrFE) composite films as functions of ceramic volume fraction ϕ_c. Only the ceramic phase of the composite films is polarized (group A).

FIG. 6. Longitudinal and transverse piezoelectric coefficients (d_{33} and d_{31}) of the PZT/P(VDF–TrFE) composite films as functions of ceramic volume fraction ϕ_c. The ceramic and copolymer phases of the composite films are polarized in opposite directions (group C).

increases from 0 to 0.51, the observed $-d_{31}$ value changes from -6.2 to 4.6 pC/N, with the sign change occurring at $\phi_c \sim 0.35$. Since the piezoelectric coefficients of the ceramic and copolymer phases have opposite signs, the piezoelectric activities of the two phases partially cancel each other when they are polarized in the same direction. At low ϕ_c, the piezoelectric activity of the copolymer phase is stronger than that of the ceramic phase, hence, the piezoelectric coefficients of the composite film have the same sign as those of P(VDF–TrFE). As ϕ_c increases, the piezoelectric activity of the copolymer phase is increasingly compensated by the piezoelectric activity of the ceramic phase, leading to a decrease in magnitude of the piezoelectric coefficient. At high ϕ_c, the piezoelectric activity of the PZT phase becomes dominant, causing a change of sign of the piezoelectric coefficient.

Unlike group B samples, the observed d_{33} value for group C samples remains roughly unchanged as ϕ_c increases from 0 to 0.45 and then decreases by about 50% as ϕ_c further increases to 0.51, while the observed $-d_{31}$ value decreases slightly with increasing ϕ_c (Fig. 6). The ceramic and
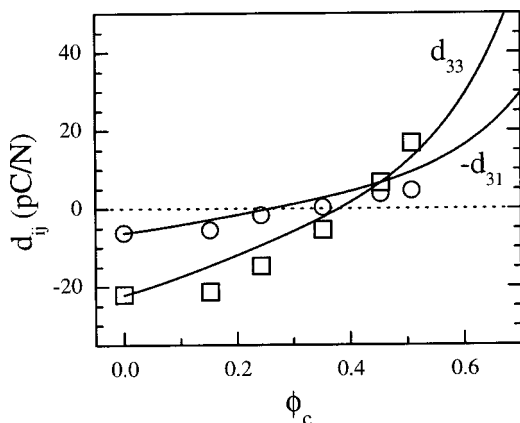
copolymer phases of group C samples are polarized in opposite directions, so their piezoelectric activities reinforce each other. At low ϕ_c, the piezoelectric activity of the ceramic phase is not very large (Fig. 4) and is about the same as that of the copolymer phase of the same volume fraction. Therefore, the piezoelectric coefficients of the composite film are almost the same as those of (PVDF–TrFE). The decrease in the piezoelectric coefficient at high ϕ_c indicates that the ceramic phase is depolarized to some extent after the poling process of the copolymer phase. This may arise from the redistribution of the space charges at the interface of the ceramic and copolymer phases activated by the antiparallel polarized copolymer phase.

It has been observed using a scanning electron microscope that the PZT particles are quite spherical and are uniformly dispersed in the composite. For a ferroelectric composite with uniformly dispersed spherical ceramic particles, the piezoelectric coefficients d_{33} and d_{31} can be calculated as[11]

$$d_{33} = \phi_c F_{E,c}\{2F_{T,c}^{\perp} d_{31c} + F_{T,c}^{\parallel} d_{33c}\}$$
$$+ \phi_p F_{E,p}\{2F_{T,p}^{\perp} d_{31p} + F_{T,p}^{\parallel} d_{33p}\}, \qquad (4)$$

$$d_{31} = \phi_c F_{E,c}\{(F_{T,c}^{\perp} + F_{T,c}^{\parallel}) d_{31c} + F_{T,c}^{\perp} d_{33c}\}$$
$$+ \phi_p F_{E,p}\{(F_{T,p}^{\perp} + F_{T,p}^{\parallel}) d_{31p} + F_{T,p}^{\perp} d_{33p}\}, \qquad (5)$$

where ϕ is the volume fraction, F is a field factor representing the fraction of an applied field distributed to the constituent phase, the subscripts c, p, E, and T denote ceramic, copolymer, electric field, and stress field, respectively, and the superscripts $\perp$ and $\parallel$ denote directions normal to and parallel to the applied field, respectively. F is given by

$$F_{E,c} = \frac{1}{\phi_c} \frac{\varepsilon - \varepsilon_p}{\varepsilon_c - \varepsilon_p}, \qquad (6)$$

$$F_{E,p} = \frac{1}{\phi_p} \frac{\varepsilon_c - \varepsilon}{\varepsilon_c - \varepsilon_p}, \qquad (7)$$

FIG. 5. Longitudinal and transverse piezoelectric coefficients (d_{33} and d_{31}) of the PZT/P(VDF–TrFE) composite films as functions of ceramic volume fraction ϕ_c. The ceramic and copolymer phases of the composite films are polarized in the same direction (group B).
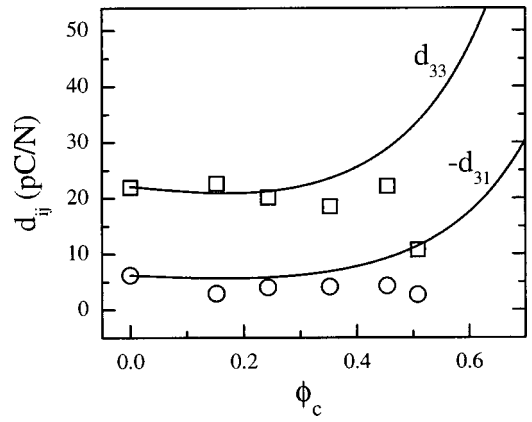
$$F_{T,c}^{\perp}=\frac{1}{\phi_c \alpha}\left[\left(\frac{\nu_c}{Y_c}-\frac{\nu_p}{Y_p}\right)\left(\frac{1}{Y}-\frac{1}{Y_p}\right)-\left(\frac{\nu}{Y}-\frac{\nu_p}{Y_p}\right)\right.$$

$$\left.\times\left(\frac{1}{Y_c}-\frac{1}{Y_p}\right)\right], \tag{8}$$

$$F_{T,c}^{\parallel}=\frac{1}{\phi_c \alpha}\left[\left(\frac{1-\nu_c}{Y_c}-\frac{1-\nu_p}{Y_p}\right)\left(\frac{1}{Y}-\frac{1}{Y_p}\right)-2\left(\frac{\nu}{Y}-\frac{\nu_p}{Y_p}\right)\right.$$

$$\left.\times\left(\frac{\nu_c}{Y_c}-\frac{\nu_p}{Y_p}\right)\right], \tag{9}$$

$$F_{T,p}^{\perp}=\frac{1}{\phi_p \alpha}\left[\left(\frac{\nu_c}{Y_c}-\frac{\nu_p}{Y_p}\right)\left(\frac{1}{Y_c}-\frac{1}{Y}\right)-\left(\frac{\nu_c}{Y_c}-\frac{\nu}{Y}\right)\right.$$

$$\left.\times\left(\frac{1}{Y_c}-\frac{1}{Y_p}\right)\right], \tag{10}$$

$$F_{T,p}^{\parallel}=\frac{1}{\phi_p \alpha}\left[\left(\frac{1-\nu_c}{Y_c}-\frac{1-\nu_p}{Y_p}\right)\left(\frac{1}{Y_c}-\frac{1}{Y}\right)-2\left(\frac{\nu_c}{Y_c}-\frac{\nu_p}{Y_p}\right)\right.$$

$$\left.\times\left(\frac{\nu_c}{Y_c}-\frac{\nu_p}{Y_p}\right)\right], \tag{11}$$

where ε is the permittivity, Y is the Young's modulus, ν is the Poisson's ratio, and

$$\alpha=\left[\left(\frac{1-\nu_c}{Y_c}-\frac{1-\nu_p}{Y_p}\right)\left(\frac{1}{Y_c}-\frac{1}{Y_p}\right)-2\left(\frac{\nu_c}{Y_c}-\frac{\nu_p}{Y_p}\right)^2\right]. \tag{12}$$

Y and ν of the composite are calculated using the bulk modulus k and shear modulus μ:

$$Y=\frac{9k\mu}{3k+\mu}, \tag{13}$$

$$\nu=\frac{Y}{2\mu}-1, \tag{14}$$

where

$$k=k_p+\phi_c(k_c-k_p)\left[1+\phi_p\frac{k_c-k_p}{k_p+4\mu_p/3}\right]^{-1}, \tag{15}$$

$$\mu=\mu_m\left[1+\left(\frac{\mu_c}{\mu_p-1}\right)\frac{\chi}{\beta+\chi\delta}\phi_c\right], \tag{16}$$

$$\beta=\frac{42}{5\mu_p}\frac{\mu_p-\mu_c}{1-\nu_p}\phi_c(\phi_c^{2/3}-1)^2\vartheta, \tag{17}$$

$$\chi=4\phi_c^{7/3}[(7-10\nu_c)-(7-10\nu_p)\vartheta]+4(7-10\nu_p)\vartheta, \tag{18}$$

TABLE II. Properties of PZT particle and P(VDF–TrFE) matrix used in the calculation of the piezoelectric coefficients for the PZT/P(VDF–TrFE) composite films.

	ε	μ (GPa)	ν	d_{33} (pC/N)	$-d_{31}$ (pC/N)
PZT particle	1700[a]	27[a]	0.3[b]	400[a]	175[a]
P(VDF–TrFE) matrix	9.9	0.8[b]	0.4[b]	−22.1	−6.2

[a]Manufacturer's data sheet.
[b]Reference 11.

$$\delta=\frac{\mu_c}{\mu_p}+\frac{7-5\nu_p}{15(1-\nu_p)}\left(1-\frac{\mu_c}{\mu_p}\right)+\frac{2(4-5\nu_p)}{15(1-\nu_p)}$$

$$\times\left(1-\frac{\mu_c}{\mu_p}\right)\phi_c, \tag{19}$$

$$\vartheta=\frac{(7+5\nu_c)\mu_c+4(7-10\nu_c)\mu_p}{35(1-\nu_p)\mu_p}. \tag{20}$$

Equations (4) and (5) imply that the piezoelectric coefficient of a composite equals to the sum of the contributions of each phase, including those arising from the difference in compressibility (Poisson's ratio) between the phases. When a unit of stress is applied to a composite, a fraction of the stress $(=F_T)$ is distributed to each phase. Due to the piezoelectric effect, an electric displacement $(=F_T d_{ij})$ is induced; and a fraction of it $(=\phi F_E F_T d_{ij})$ contributes to the apparent electric displacement of the composite.[9] Since PZT has a smaller Poisson's ratio than P(VDF–TrFE), additional stresses normal to the applied stress are induced, giving rise to additional contributions to the piezoelectric coefficient of the composite [e.g., $2\phi_c F_{E,c}F_{T,c}^{\perp}d_{31c}$ in Eq. (4)].

By using Eqs. (4) and (5) and the material parameters listed in Table II, the values of d_{33} and $-d_{31}$ for the three groups of composite films are calculated and compared with the experimental values in Figs. 4–6. It is noted that the theoretical calculations do not depend too much on the input values of the shear moduli and Poisson's ratios of the constituents. This suggests that the theoretical expressions [Eqs. (4)–(20)] can be used for our composites although they are based on an assumption that both inclusion and matrix materials are elastically isotropic.[11] As shown in Fig. 4, very good agreement between the calculated and observed values is obtained for group A samples, implying that the PZT particles are well polarized. Good agreement is also obtained for group B samples (Fig. 5). However, for group C samples, the calculated values agree only with the observed values at low ϕ_c; but there is a large discrepancy above $\phi_c=0.4$ (Fig. 6). As discussed in the previous section, after the copolymer phase has been polarized in opposite direction, the charges accumulated at the interface for stabilizing the dipole orientation in the ceramic phase may redistribute, leading to some degree of depolarization and thus a decrease in the piezoelectric activity of the composite.

V. CONCLUSION

In the present study, PZT/P(VDF–TrFE) composite films with three different polarization states have been prepared by polarizing the phases separately. First, the ceramic phase is well polarized under a dc field at 120 °C. Then the copolymer phase is polarized under an ac field at 60 °C, without altering the polarization state of the ceramic phase significantly. The effect of polarization state on the longitudinal and transverse piezoelectric coefficients (d_{33} and d_{31}) of the composite film with ϕ_c ranging from 0 to 0.51 has been investigated. Since the piezoelectric coefficients of PZT and P(VDF–TrFE) have opposite signs, the piezoelectric activities of the two phases partially cancel each other when they are polarized in the same direction. At $\phi_c \sim 0.4$, the piezoelectric activity of the composite become almost zero. On the other hand, when the phases of a composite film are polarized in opposite directions, their piezoelectric activities reinforce. However, depolarization of the ceramic phase and thus a decrease in the piezoelectric activity of the composite film are observed at high ϕ_c. This may be due to the redistribution of the charges accumulated at the interface of the ceramic and copolymer phases after the poling process of the copolymer phase in opposite direction. The observed d_{33} and d_{31} values for the composite films agree well with predictions of a model.

ACKNOWLEDGMENTS

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