

Piezoelectric and Pyroelectric Properties of PZT/P(VDF-TrFE) Composites with Constituent Phases Poled in Parallel or Antiparallel Directions

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Abstract—Composites of lead zirconate titanate (PZT) powder dispersed in a vinylidene fluoride-trifluoroethylene copolymer [P(VDF-TrFE)] matrix have been prepared by compression molding. Three groups of polarized samples have been prepared by poling: only the ceramic phase, the ceramic and polymer phases in parallel directions, and the two phases in antiparallel directions. The measured permittivities of the unpoled composites are consistent with the predictions of the Bruggeman model. The changes in the pyroelectric and piezoelectric coefficients of the poled composites with increasing ceramic volume fraction can be described by modified linear mixture rules. When the ceramic and copolymer phases are poled in the same direction, their pyroelectric activities reinforce while their piezoelectric activities partially cancel. However, when the ceramic and copolymer phases are poled in opposite directions, their piezoelectric activities reinforce while their pyroelectric activities partially cancel.

I. INTRODUCTION

FERROELECTRIC ceramic/polymer composites with various connectivities have attracted considerable research interest [1]–[4] because of their potential in pyroelectric sensor, ultrasonic transducer, and hydrophone applications. The 0-3 composites with ferroelectric ceramic powder embedded in a passive polymer matrix are well developed. Recently, 0-3 composites with ferroelectric polymer matrix also have received increasing attention [5]–[7]. Polyvinylidene fluoride (PVDF) and vinylidene fluoride-trifluoroethylene [P(VDF-TrFE)] copolymer have high permittivities ($\epsilon_r \approx 10 - 14$) compared to other polymers such as epoxy ($\epsilon_r \approx 4$), hence previous work [1]–[4] used PVDF as a high permittivity matrix to facilitate poling of the embedded ceramic particles. The matrix is not expected to be piezoelectrically active as PVDF needs to be mechanically stretched prior to poling to give piezoelectric activity. However, P(VDF-TrFE) with trifluoroethylene (TrFE) content > 20 mol% crystallizes from the melt or from solution in a polar phase (the β

phase) and can be polarized without prior stretching. By using P(VDF-TrFE) as the matrix, both the ceramic phase and the matrix can be piezoelectrically active. The present work reports on the pyroelectric and piezoelectric properties of PZT/P(VDF-TrFE) 0-3 composites as functions of the ceramic volume fraction and compares the results with model predictions. Composites with only the ceramic phase poled, with both phases poled in the same direction and with both phases poled in opposite directions, have been studied. Our aim is to identify the contributions of the individual phases to the overall properties of the composites.

II. SAMPLE PREPARATION

The P(VDF-TrFE) 70/30 copolymer pellets used in the present study were supplied by Piezotech (St-Louis, France). The Curie temperature of the copolymer upon the first heating was $T_{ch} = 102^\circ\text{C}$ and that upon cooling was $T_{cc} = 62^\circ\text{C}$; the melting temperature T_m was 153°C as determined by using a Perkin Elmer DSC7 differential scanning calorimeter. A copolymer disk of 12.8 diameter mm and 0.6 mm thickness was fabricated by a hot pressing method at 200°C under a pressure of 10 MPa for 5 minutes.

The lead zirconate titanate (PZT) ceramic powder, PKI502, with particle size of 1–3 μm was supplied by Piezo Kinetics (Bellefonte, PA). Calcination and sintering were carried out before the fabrication of samples. A ceramic rod of 13 mm diameter and 40 mm length was prepared by pressing at a pressure of 100 MPa at room temperature. After binder burnout and sintering, the ceramic rod was cut into thin disks of 0.5 mm thickness. Some of the sintered disks were crushed and ground into powder to be used in subsequent composite fabrication.

In the fabrication of 0-3 composites, P(VDF-TrFE) copolymer pellets were first dissolved in acetone, then an appropriate amount of the sintered PZT powder was added to the copolymer solution. This composite solution was placed in an ultrasonic bath to ensure that the ceramic powder was distributed evenly in the copolymer solution. The composite solution then was poured onto a clean glass plate to allow complete evaporation of the solvent. The resulting film, approximately 30 mm \times 20 mm in size, has

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a rough top surface. In order to produce smooth samples with uniform thickness, the composite film was cut into small pieces, which were compression-molded at 220°C under a pressure of 30 MPa to form a composite rod with 13 mm diameter and 40 mm length. The composite rod then was cut into disks of about 0.5 mm thickness. The ceramic volume fraction ϕ in the composite disks was calculated using the following equation:

$$\rho = \phi\rho_c + (1 - \phi)\rho_p \quad (1)$$

where ρ , ρ_c and ρ_p are the densities of the composite, ceramic, and copolymer, respectively. For electrical measurements, air-dried silver paint electrodes were applied to both sides of the disk samples.

Because the ceramic particles are dispersed in a dilute copolymer solution during the fabrication process, the particles are coated with thin layers of copolymer as verified by scanning electron microscope (SEM) observations. Because the composite samples are quite thick (≈ 0.5 mm), the ceramic powder does not form a continuous phase in the thickness direction even at the highest ceramic volume fraction ($\phi \approx 0.6$), i.e., all the samples have 0-3 connectivity.

III. PERMITTIVITY MEASUREMENT

The permittivities of the unpoled copolymer, ceramic, and 0-3 composites were measured as functions of temperature at 1 kHz using a HP4194A impedance analyzer. The sample under measurement was heated or cooled at a rate of about 1°C/minute in a temperature-controlled oven until a given temperature was reached, then it was kept at that temperature for 30 minutes before the measurement was made. The permittivities of PZT, P(VDF-TrFE), and two composites with ceramic volume fractions $\phi = 0.3$ and 0.6 upon heating and cooling are shown as functions of temperature in Fig. 1. Abrupt changes in the permittivity occur at different temperatures upon heating and cooling for the copolymer and 0-3 composite samples. The strong thermal hysteresis effect arises from the first order nature of the Curie transition in the copolymer phase, and this feature was observed previously in the pure copolymer [8], [9]. The permittivities of the composites can be understood in terms of the Bruggeman equation [10], [11]:

$$\frac{\varepsilon - \varepsilon_c}{\varepsilon_p - \varepsilon_c} \left(\frac{\varepsilon_p}{\varepsilon} \right)^{\frac{1}{3}} = 1 - \phi \quad (2)$$

where ϕ is the ceramic volume fraction of the composite; and ε_c , ε_p , and ε are the permittivities of the ceramic, copolymer, and composites, respectively. Fig. 2 shows that the experimental data at 25°C agree well with the model prediction.

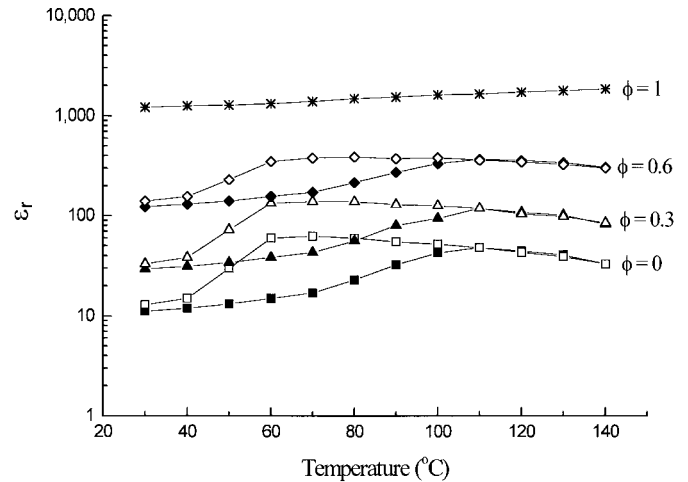


Fig. 1. Relative permittivity ε of PZT, P(VDF-TrFE), and 0-3 composites with ceramic volume fraction $\phi = 0.3$ and 0.6 as functions of temperature. The closed and open symbols represent data in heating and cooling runs, respectively. * = data identical in heating and cooling runs.

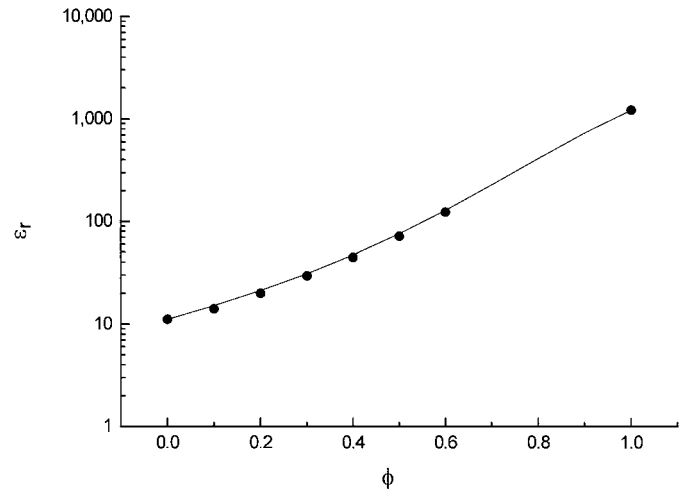


Fig. 2. Relative permittivity ε of PZT/P(VDF-TrFE) 0-3 composites at 25°C as a function of ceramic volume fraction. The symbols and solid line denote experimental data and values calculated according to the Bruggeman model, respectively.

IV. ELECTRIC FIELD EXPERIENCED BY THE CERAMIC PARTICLE INSIDE A COMPOSITE

For a composite containing a spherical particle of permittivity ε_c embedded in a continuous medium of permittivity ε , the local field experienced by the ceramic particle E_c can be estimated from:

$$E_c = \frac{3\varepsilon}{2\varepsilon + \varepsilon_c} E_o \quad (3)$$

where E_o is the applied electric field. Therefore, the electric field ratio is [12]:

$$L_E = \frac{E_c}{E_o} = \frac{3\varepsilon}{2\varepsilon + \varepsilon_c} \quad (4)$$

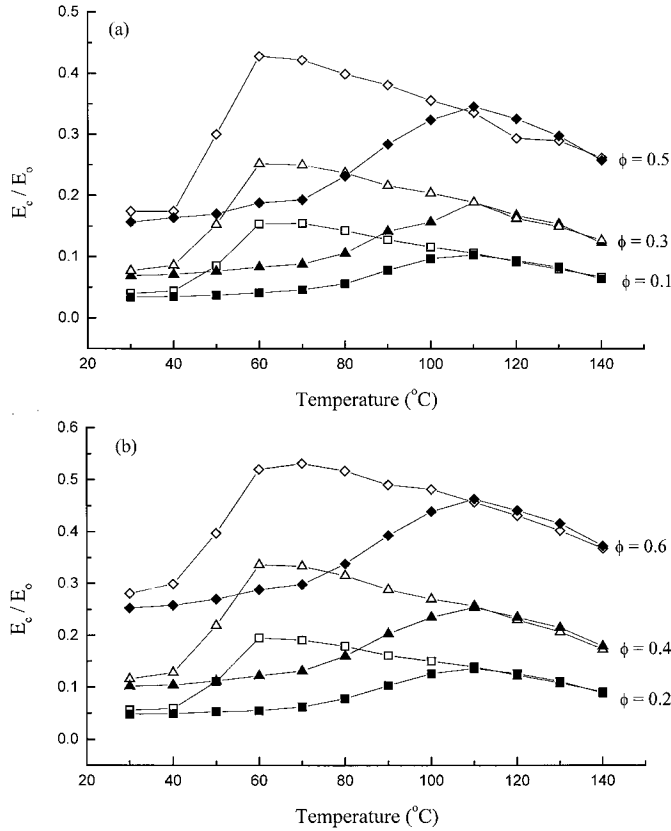


Fig. 3. Local field coefficient E_c/E_o as a function of temperature. (a) $\phi = 0.1, 0.3,$ and 0.5 ; (b) $\phi = 0.2, 0.4,$ and 0.6 . The closed and open symbols represent data in heating and cooling runs, respectively.

The measured ε and ε_c are used to calculate L_E as a function of temperature (Fig. 3). L_E varies from less than 0.1 to more than 0.5, depending on ϕ and on whether the sample is being heated or cooled. For a given ϕ , L_E is higher upon cooling. Because the coercive field of the PKI502 ceramic is less than 1 kV/mm at 70 $^{\circ}\text{C}$ and the applied field E_o is above 30 kV/mm, the field E_c (3 to 15 kV/mm) experienced by the ceramic phase should be high enough to polarize the PZT ceramic particles inside the composites.

V. STEPWISE POLING

To impart piezoelectric activity to the samples, they were subjected to a poling process to orient the dipoles in the ceramic and the copolymer phases. In the present study, three groups of samples were poled in an oil bath. In group 1, only the ceramic phase is poled. In group 2, both phases are poled in the same direction. In group 3, the two phases are poled in opposite directions. The poling procedure is as follows:

1. The composite is heated to 120 $^{\circ}\text{C}$ (above T_{ch}) then cooled naturally to 70 $^{\circ}\text{C}$ to obtain a higher L_E (see Fig. 3). A stepwise poling procedure (described later) is used to maximize the applied field at 70 $^{\circ}\text{C}$. The poling electric field is switched off before cooling. As the copolymer is in a paraelectric state when

the field is applied, only the ceramic phase has been polarized. The copolymer transforms into an unpoled ferroelectric phase when cooling through T_{cc} to room temperature without an applied field.

2. After the ceramic phase has been polarized by the stepwise poling procedure at 70 $^{\circ}\text{C}$, the sample is cooled through T_{cc} to room temperature with the field applied. By this procedure the copolymer phase is polarized in the same direction as that of the ceramic phase.
3. In order to polarize the ceramic phase in a direction opposite to that of the copolymer, samples that have been polarized by step (2) are reheated to 50 $^{\circ}\text{C}$, then a poling field of 10 kV/mm is applied in the reverse direction for half an hour. The sample then was cooled to room temperature with the reverse poling field kept on.

In the stepwise poling procedure, the applied electric field was increased from 0 to E_1 and kept at E_1 for 4 minutes. The field was switched off and the sample was short circuited for about 4 minutes. The applied field was increased after the short-circuit step, and the above procedure was repeated until it was close to the breakdown field of the sample. The current flowing through the sample was monitored. If the current remained below 20 μA , it was a good indication that the field can be increased further.

The maximum field we have been able to apply to some samples using the stepwise process is 70 kV/mm. Hence, with this stepwise process, high poling fields could be applied to samples, and the risk of electric breakdown could be reduced. This may result from the short-circuit period during which the mechanical stress and the injected charges were partially relaxed, thereby leading to a more homogeneous electric field distribution. Limiting the current flow during poling to less than 20 μA has greatly reduced the risk of sample breakdown. After the maximum allowable field E_o has been reached, the field is held for 2 hours, then procedures 1, 2, and 3 are used to produce three groups of samples with different characteristics.

The intensities $I_{(002)}$ and $I_{(200)}$ of the (002) and (200) peaks in the X-ray diffraction pattern are used to evaluate the degree of poling of the PZT ceramic in the composites. The poling ratio α_c is defined as [13]:

$$\alpha_c = 1 - \left(\frac{I_{(002)}}{I_{(200)}} \right) \left(\frac{I'_{(200)}}{I'_{(002)}} \right) \quad (5)$$

where $I'_{(002)}$ and $I'_{(200)}$ are the intensities of the (002) and (200) X-ray diffraction peaks associated with the ceramic after poling, and $I_{(002)}$ and $I_{(200)}$ are the intensities before poling. The α_c values for the three groups of samples are given in Tables I, II, and III. These values indicate that the ceramic particles inside the composites are not fully polarized. Attempts have been made to repolarize the sample, but α_c still cannot be improved significantly.

TABLE I
 PROPERTIES OF UNPOLARIZED COPOLYMER, POLARIZED CERAMIC,
 AND 0-3 COMPOSITES WITH ONLY THE CERAMIC PHASE POLARIZED.¹

ϕ	ρ g/cm ³	E_o kV/mm	Before poling ε	After poling ε	p $\mu\text{C}/\text{m}^2\text{K}$	F_p $\mu\text{C}/\text{m}^2\text{K}$	d_{33} pC/N	α_c^3
0	1.91	—	11.2	—	0	0	0	—
0.1	2.49	33.5	16.4	15.0	1.3	0.09	10	0.64
0.2	3.02	33.0	23.6	21.8	3.4	0.16	12	0.58
0.3	3.57	32.0	34.0	31.2	6.5	0.21	15	0.51
0.4	4.08	32.0	48.8	45.0	12.6	0.28	20	0.56
0.5	4.71	30.5	80.0	73.4	20.4	0.28	26	0.51
0.6	5.24	30.0	136.6	124.2	36.0	0.29	32	0.49
1.0	7.48	5.0	1220	1116	533	0.45	410	0.74

¹The ceramic volume fraction ϕ , density ρ , poling field E_o , relative permittivity ε , pyroelectric coefficient p , pyroelectric figure of merit $F_p(=|p|/\varepsilon)$, piezoelectric coefficient d_{33} , and poling ratio α_c are shown.

²All properties and coefficients are measured at 25°C.

³The α_c values are calculated according to (5).

TABLE II
 PROPERTIES OF POLARIZED COPOLYMER AND CERAMIC, AND 0-3 COMPOSITES WITH
 BOTH THE CERAMIC AND COPOLYMER PHASES POLARIZED IN THE SAME DIRECTION.¹

ϕ	E_o kV/mm	Before poling ε	After poling ε	p $\mu\text{C}/\text{m}^2\text{K}$	F_p $\mu\text{C}/\text{m}^2\text{K}$	d_{33} pC/N	α_c^3	α_p^4
0	40.0	11.2	9.5	25.7	2.71	-37	—	1
0.1	52.0	16.4	12.7	17.7	1.39	-32	0.68	0.71
0.2	70.0	23.6	18.4	20.2	1.10	-31	0.70	0.79
0.3	51.0	34.0	28.6	22.1	0.77	-21	0.64	0.77
0.4	48.0	48.8	42.2	27.4	0.65	-10	0.61	0.80
0.5	42.0	80.0	69.2	33.1	0.48	21	0.56	0.47
0.6	37.0	136.6	121.4	49.9	0.41	32	0.57	-0.36
1.0	5.0	1220	1116	533	0.48	410	0.74	—

¹The ceramic volume fraction ϕ , poling field E_o , relative permittivity ε , pyroelectric coefficient p , pyroelectric figure of merit $F_p(=|p|/\varepsilon)$, piezoelectric coefficient d_{33} and poling ratios α_c, α_p are shown.

²All properties and coefficients are measured at 25°C.

³The α_c values are calculated according to (5).

⁴The α_p values are calculated according to (8).

TABLE III
 PROPERTIES OF POLARIZED COPOLYMER AND CERAMIC, AND 0-3 COMPOSITES WITH
 BOTH THE CERAMIC AND COPOLYMER PHASES POLARIZED IN OPPOSITE DIRECTIONS.¹

ϕ	E_o kV/mm	Before poling ε	After poling ε	p $\mu\text{C}/\text{m}^2\text{K}$	F_p $\mu\text{C}/\text{m}^2\text{K}$	d_{33} pC/N	α_c^3	α_p^4
0	40.0	11.2	9.5	-25.7	2.71	37	—	1.0
0.1	48.0	16.4	12.3	-15.1	1.23	32	0.61	0.70
0.2	40.0	23.6	18.0	-13.4	0.74	28	0.64	0.83
0.3	34.0	34.0	27.6	-9.1	0.33	20	0.52	0.88
0.4	36.0	48.8	42.8	-2.2	0.05	27	0.44	0.85
0.5	32.0	80.0	70.2	7.7	0.11	21	0.53	1.40
0.6	32.0	136.6	124.2	22.2	0.18	42	0.49	2.32
1.0	5.0	1220	1116	533	0.48	410	0.74	—

¹The ceramic volume fraction ϕ , poling field E_o , relative permittivity ε , pyroelectric coefficient p , pyroelectric figure of merit $F_p(=|p|/\varepsilon)$, piezoelectric coefficient d_{33} and poling ratios α_c, α_p are shown.

²All properties and coefficients are measured at 25°C.

³The α_c values are calculated according to (5).

⁴The α_p values are calculated according to (9).

VI. PYROELECTRIC COEFFICIENTS

The pyroelectric coefficient p of the sample under constant field and constant stress is determined from the change of the total charge ΔQ at the electrode due to a change in temperature $\Delta\Theta$:

$$p = \frac{1}{A} \left(\frac{\Delta Q}{\Delta\Theta} \right) \quad (6)$$

where A is the area of the electrode. In the present study, p was measured using the digital integration method [14]. Prior to measurement, the poled samples were annealed in a short-circuit condition for 12 hours at a temperature (70°C) above the highest temperature used in the measurement. This eliminates the contribution of thermally stimulated current in subsequent measurements.

The pyroelectric coefficients p of the annealed samples were measured by heating at a rate of about 1°C/min from 25°C to 45°C, and the values of p and the pyroelectric figure of merit $F_p (= |p|/\epsilon)$ are given in Tables I, II, and III. Among the three groups, the group 2 composites have the highest figure of merit.

The pyroelectric coefficients for the three groups of composites at 25°C are shown as functions of ϕ in Fig. 4. For group 1 composites (with only the ceramic phase poled), p increases monotonically from 0 to 36 $\mu\text{C}/\text{m}^2\text{K}$ as ϕ increases from 0 to 0.6, simply reflecting the contribution of the polarized ceramic phase. For group 2 composites (with both phases poled in parallel directions), p first decreases slightly and then increases significantly with increasing ϕ . The composites at $\phi < 0.4$ have smaller p values than that of the copolymer because ceramic particles of the same volume fraction as the copolymer phase give a smaller contribution. The contribution of the ceramic phase becomes increasingly important at higher ϕ and, at $\phi = 0.6$, p is higher than that of the copolymer by a factor of 2. For group 3 composites (with the two phases poled in antiparallel directions), the pyroelectric activity in the copolymer phase is increasingly compensated by the pyroelectric activity in the ceramic phase as ϕ increases. At $\phi \cong 0.4$ the pyroelectric coefficient changes sign; at higher ϕ , p has a positive sign, indicating that the contribution of the ceramic phase is now dominant.

For the group 1 composites, if we make the reasonable assumption that p is proportional to the ceramic poling ratio α_c , the local field coefficient L_E (4) and the ceramic volume fraction ϕ , then [13]

$$p = \alpha_c \phi L_E p_c \quad (7)$$

where p_c is the pyroelectric coefficient of PZT at full poling. It is seen from Fig. 4 that there is reasonably good agreement between experimental data and theoretical predictions. However, at $\phi > 0.4$, the calculated values are higher than the experimental data, implying that this simple linear mixture rule is not valid at high ϕ . For group 2 and group 3 samples, p also contains the contribution of

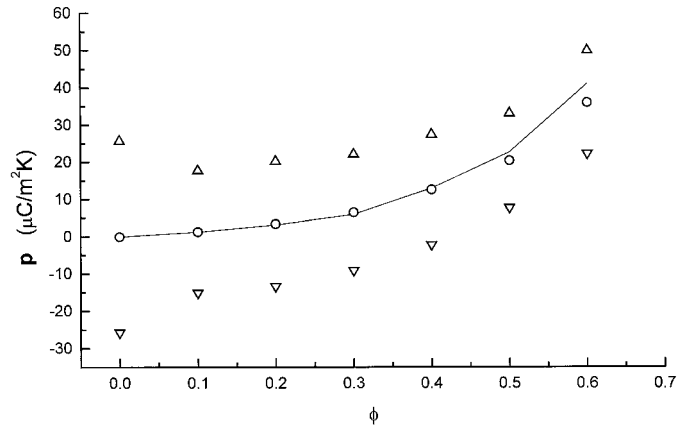


Fig. 4. Pyroelectric coefficient p of composites at 25°C as a function of ceramic volume fraction ϕ . ○ = Data for group 1 samples (with only the ceramic phase poled). The symbols denote data, and the solid line denotes theoretical values calculated according to (7). △ = Data for group 2 samples (with the ceramic and copolymer phases poled in the same direction). ▽ = Data for group 3 samples (with the ceramic and copolymer phases poled in opposite directions).

the copolymer phase, so for group 2 samples

$$p = \alpha_c \phi L_E p_c + \alpha_p (1 - \phi) p_p \quad (8)$$

and for group 3 samples

$$p = \alpha_c \phi L_E p_c - \alpha_p (1 - \phi) p_p \quad (9)$$

where α_p and p_p represent the poling ratio and the pyroelectric coefficient at full poling of the copolymer phase, respectively. Assuming that the pure copolymer sample is fully poled ($\alpha_p = 1$) and $p_p = 25.7 \mu\text{C}/\text{m}^2$, α_p for the composites are calculated and given in Tables II and III. For $\phi = 0.1 - 0.4$, α_p varies from 0.70 to 0.88, indicating that the copolymer matrix is not fully poled. At $\phi > 0.5$, the calculated α_p values are unreasonable (being negative or higher than 1), showing again that the simple linear mixture rule is not valid at such high ceramic volume fraction.

VII. PIEZOELECTRIC COEFFICIENTS

The piezoelectric charge coefficient d_{33} (strain/electric field at constant stress or charge density/stress at constant electric field) was measured at 60 Hz using a Pennebaker model 8000 piezo d_{33} tester (American Piezo-Ceramics, Inc., Mackeyville, PA). As seen from Fig. 5, group 1 and 3 composites have positive d_{33} values, and group 2 composites have negative d_{33} values up to $\phi = 0.4$ and positive values at higher ϕ . The explanation for the ϕ dependence and sign of d_{33} is similar to those for p once we recognize that the piezoelectric coefficients of the ceramic and copolymer phases have opposite signs. The observed d_{33} values at $\phi < 0.5$ are compared with those calculated ac-

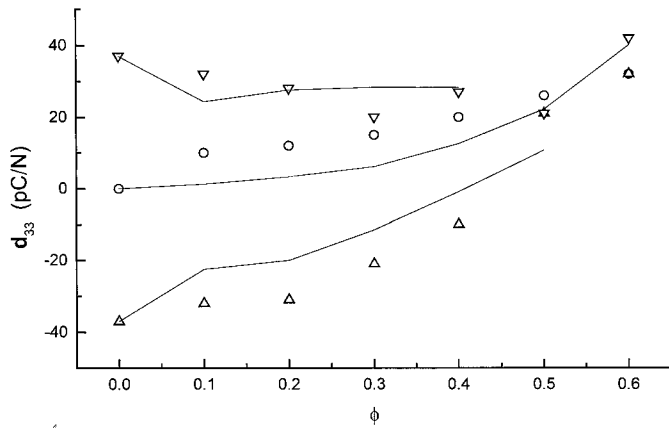


Fig. 5. Piezoelectric coefficient d_{33} of composites at 25°C as a function of ceramic volume fraction ϕ . The symbols and solid lines denote data and theoretical values calculated according to (10)–(12), respectively. O = Data for group 1 samples (with only the ceramic phase poled). Δ = Data for group 2 samples (with the ceramic and copolymer phases poled in the same direction). ∇ = Data for group 3 samples (with the ceramic and copolymer phases poled in opposite directions).

according to the following modified linear mixture rules:

$$d_{33} = \alpha_c \phi L_E d_{33c} \quad (\text{group 1}) \quad (10)$$

$$d_{33} = \alpha_c \phi L_E d_{33c} - \alpha_p (1 - \phi) d_{33p} \quad (\text{group 2}) \quad (11)$$

$$d_{33} = \alpha_c \phi L_E d_{33c} + \alpha_p (1 - \phi) d_{33p} \quad (\text{group 3}) \quad (12)$$

where the α_p values used in the calculation were estimated from the pyroelectric data and shown in Tables II and III. It is noted that the negative sign in the second term of (11) and the positive sign in the second term of (12) result from the fact that the piezoelectric coefficients of the ceramic and copolymer phases have opposite signs [15]. Fig. 5 shows that (10)–(12) can correctly predict the trends, although the agreement between theory and experiment is only fair.

VIII. POLARIZATION IN 0-3 COMPOSITES

The laser-induced pressure pulse (LIPP) method [16]–[18] for studying polarization distribution is well established. The experimental setup was described previously [18]. The measurements are performed using a Quantel Nd:YAG laser, which emits pulses of energy 50 mJ and width 7 ns at a wavelength of 532 nm. The laser beam of 8 mm diameter impinges on the surface of a composite sample enclosed in an electrically shielded sample holder. It is absorbed by a black target painted on the electrode (air-dried silver paint) using a black marker pen. Due to ablation and localized heating, a pressure pulse that propagates along the z axis (sample thickness direction) at the velocity of sound v is generated. For short pressure pulses, the voltage (into a 50Ω load) measured during the penetration of the pulse into the sample or its exit is proportional to the piezoelectric coefficient e_{33} (defined

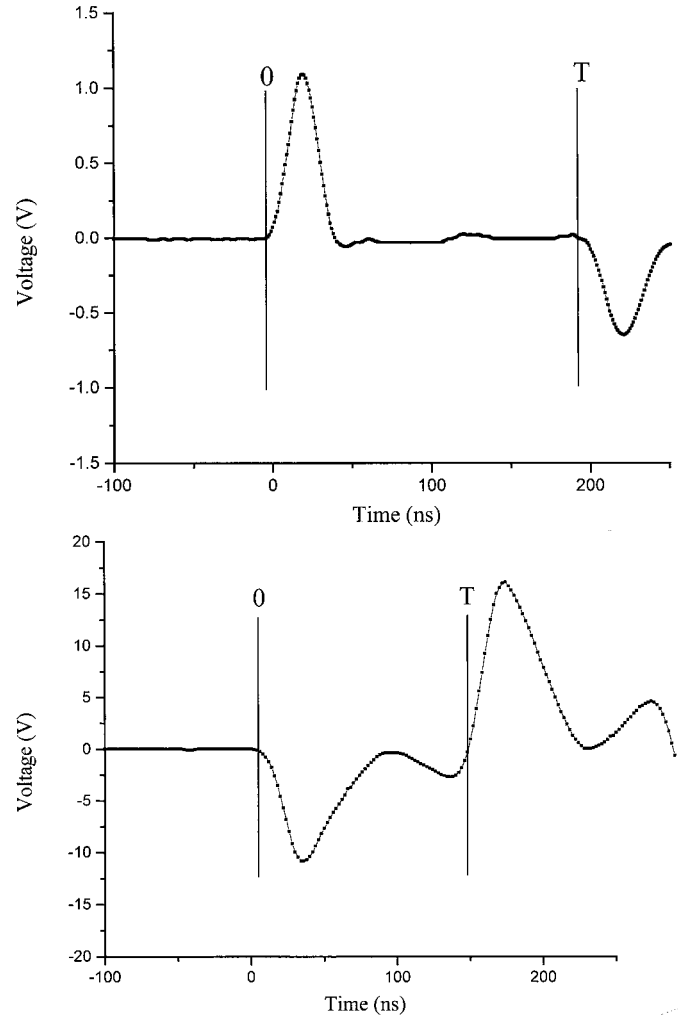


Fig. 6. LIPP signal during the propagation of a pressure pulse in (top) a P(VDF-TrFE) sample and (bottom) a PZT sample. The pressure pulse enters the sample at $t = 0$ and leaves the sample at $t = T$.

as stress/electric field at constant strain or charge density/strain at constant electric field) near the sample surface [16].

Figs. 6 and 7 show the voltages produced when the pressure wave enters the samples from the anode (the side connected to positive voltage during ceramic poling). The piezoelectric coefficient e_{33} of the PZT ceramic and P(VDF-TrFE) copolymer have opposite signs, hence the LIPP signals from the two samples have opposite polarities (Fig. 6). For group 1 samples, in which the piezoelectric activity arises only from the ceramic phase, the voltage generated has the same polarity as that of the PZT ceramic. For group 2 samples, the copolymer phase also contributes to the piezoelectric activity. Between for $\phi \leq 0.4$, the LIPP signals have the same polarity as the copolymer (Fig. 7). For $\phi > 0.4$, however, the contribution of the ceramic overcompensates that of the copolymer, hence the LIPP signals have the same polarity as that of the ceramic. Like the group 2 samples, the copolymer phase in the group 3 samples also contributes to the piezoelectric activity, but the piezoelectric activities of both phases reinforce so that

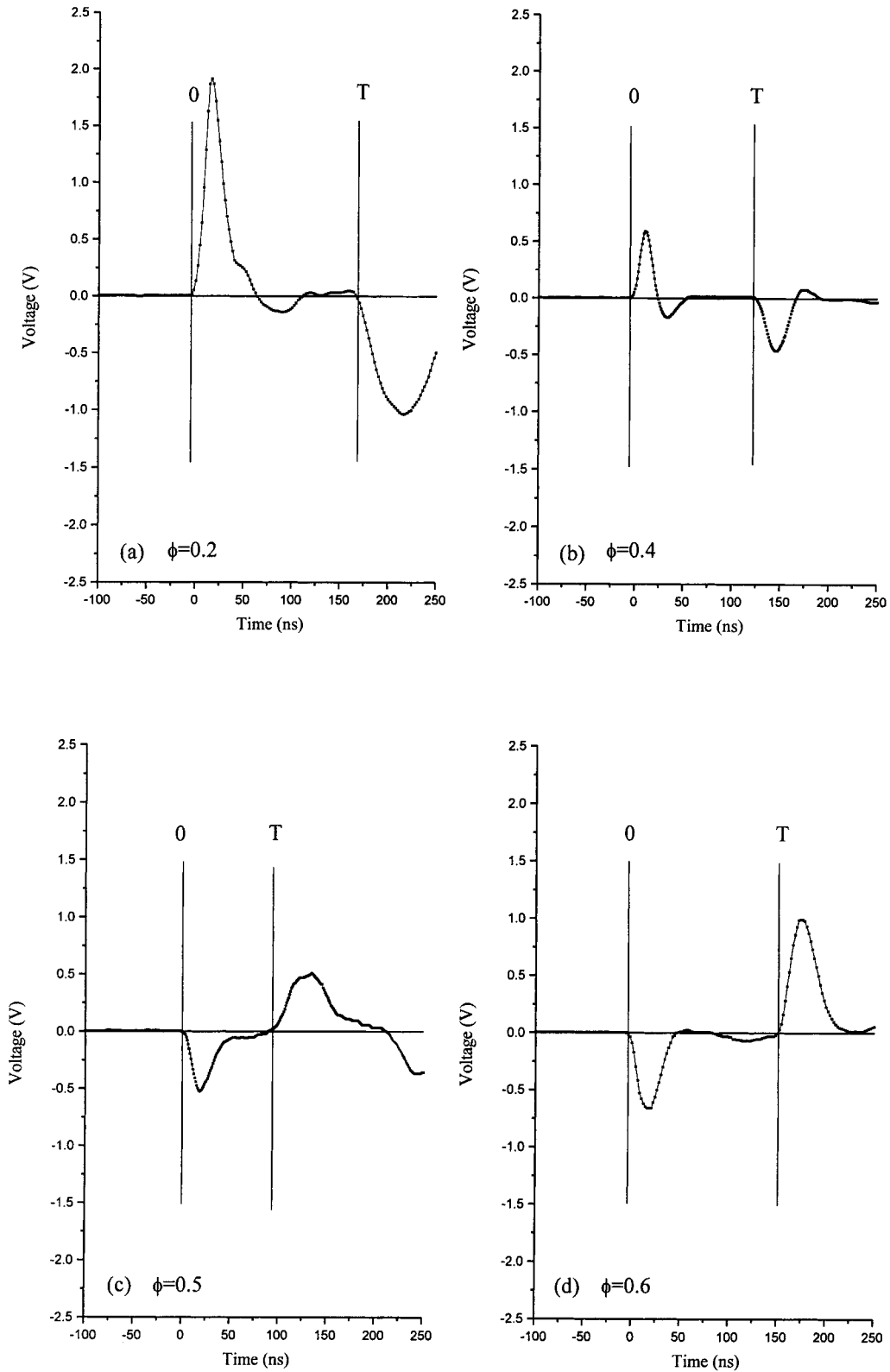


Fig. 7. LIPP signal during the propagation of a pressure pulse in group 2 composite samples with various ϕ . The pressure pulse enters the sample at $t = 0$ and leaves the sample at $t = T$. (a) $\phi = 0.2$, (b) $\phi = 0.4$, (c) $\phi = 0.5$, (d) $\phi = 0.6$.

all the LIPP signals have the same polarity as that of the ceramic (not shown).

IX. CONCLUSIONS

In the present study, the PZT ceramic particles and the P(VDF-TrFE) matrix in the composite are both ferroelectric. In order to estimate the contribution from each phase, 0-3 composites were fabricated with only the ceramic phase poled or with the two phases poled in the same direction or in opposite directions. For the composites with both phases poled in the same direction, the piezoelectric activities of the two phases reinforce. Because the piezoelectric coefficients of the ceramic and copolymer phases have opposite signs, the piezoelectric activities of the two phases in these composites partially cancel. Consequently, at $\phi \approx 0.45$, the composite is pyroelectric but not piezoelectric. This material may be useful as pyroelectric sensors in situations in which the vibration induced electrical noise needs to be reduced. However, the piezoelectric activities of the two phases reinforce while the pyroelectric activities partially cancel when the two phases are poled in opposite directions. This results in a composite ($\phi \approx 0.45$), which is piezoelectric but not pyroelectric.

The results in the present work show that the ceramic and copolymer phases are not fully poled. We are now attempting to optimize the poling conditions and to understand the underlying mechanisms behind the poling process.

REFERENCES

- [1] T. Furukawa, K. Ishida, and E. Fukada, "Piezoelectric properties in the composite systems of polymers and PZT ceramics," *J. Appl. Phys.*, vol. 50, pp. 4904–4912, 1979.
- [2] R. E. Newnham, D. P. Skinner, K. A. Klicker, A. S. Bhalla, B. Hardiman, and T. R. Gururaja, "Ferroelectric ceramic-plastic composites for piezoelectric and pyroelectric applications," *Ferroelectrics*, vol. 27, pp. 49–55, 1980.
- [3] D. K. Das-Gupta and M. J. Abdullah, "Dielectric and pyroelectric properties of polymer/ceramic composites," *J. Mater. Sci. Lett.*, vol. 7, pp. 167–170, 1988.
- [4] A. Safari, Y. H. Lee, A. Halliyal, and R. E. Newnham, "0-3 piezoelectric composites prepared by coprecipitated PbTiO₃ powder," *Amer. Ceram. Soc. Bull.*, vol. 66, pp. 668–670, 1987.
- [5] C. J. Dias and D. K. Das-Gupta, "Inorganic ceramic/polymer ferroelectric composite electrets," *IEEE Trans. Dielect. Elect. Insulation*, vol. 3, pp. 706–734, 1996.
- [6] H.L.W. Chan, Y. Chen, and C. L. Choy, "Thermal hysteresis in the permittivity and polarization of lead zirconate titanate/vinylidene fluoride-trifluoroethylene 0-3 composites," *IEEE Trans. Dielect. Elect. Insulation*, vol. 3, pp. 800–805, 1996.
- [7] H.L.W. Chan, W. K. Chan, Y. Zhang, and C. L. Choy, "Pyroelectric and piezoelectric parameters of lead titanate/vinylidene fluoride-trifluoroethylene copolymer 0-3 composites," *IEEE Trans. Dielect. Elect. Insulation*, vol. 5, no. 4, pp. 505–512, 1998.
- [8] T. Furukawa and G. E. Johnson, "Dielectric relaxations in a copolymer of vinylidene fluoride and trifluoroethylene," *J. Appl. Phys.*, vol. 52, pp. 940–943, 1981.
- [9] N. Koizumi, N. Haikawa, and H. Habuka, "Dielectric behaviour and ferroelectric transition of copolymers of vinylidene fluoride and trifluoroethylene," *Ferroelectrics*, vol. 57, pp. 99–119, 1984.
- [10] L.K.H. van Beek, "Dielectric behaviour of heterogeneous systems," in *Progress in Dielectrics*. London: Heywood, 1967, pp. 69–114.
- [11] D.A.G. Bruggeman, "Berechnung verschiedener physikalischer Konstanten von heterogenen substanzen," *Annalen Physik*, vol. 24, pp. 636–679, 1935.
- [12] L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics, vol. 8, Electrodynamics of Continuous Media*. U.K.: Pergamon Press, 1960, ch. II.
- [13] H. Yamazaki and T. Kitayama, "Pyroelectric properties of polymer-ferroelectric composites," *Ferroelectrics*, vol. 33, pp. 147–153, 1981.
- [14] Y. Xu, *Ferroelectric Materials and Their Applications*. New York: Elsevier, 1991, p. 68.
- [15] H.L.W. Chan, P.K.L. Ng, and C. L. Choy, "Effect of poling procedure on the properties of lead zirconate titanate/vinylidene fluoride-trifluoroethylene composites," *Appl. Phys. Lett.*, vol. 74, no. 20, pp. 3029–3031, 1999.
- [16] C. Alque and J. Lewiner, "A new method for studying piezoelectric materials," *Rev. Phys. Appl.*, vol. 20, pp. 395–402, 1985.
- [17] R. Gerhard-Multhaupt, G. M. Sessler, J. E. West, K. Holdik, M. Haardt, and W. Eisenmenger, "Investigation of piezoelectric distributions in poly (vinylidene fluoride) by means of quartz- or laser-generated pulses," *J. Appl. Phys.*, vol. 55, pp. 2769–2775, 1984.
- [18] H. L. W. Chan, Z. Zhao, K. W. Kwok, C. L. Choy, C. Boue, C. Alique, and J. Lewiner, "Polarization in thick P(VDF-TrFE) copolymer films," *J. Appl. Phys.*, vol. 80, no. 7, pp. 3982–3991, 1996.

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