

Pyroelectric and Piezoelectric Properties of Lead Titanate/Polyvinylidene Fluoride-Trifluoroethylene 0-3 Composites

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ABSTRACT

Composites of calcium modified lead titanate powder dispersed in a polyvinylidene fluoride/trifluoroethylene copolymer matrix have been prepared using solvent casting followed by compression molding. Two groups of poled samples have been prepared: one with only the ceramic phase polarized and the other with both phases polarized. The observed 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, the piezoelectric activities of the two phases partially cancel each other while the pyroelectric activities reinforce. Hence, at a certain ceramic volume fraction, the composite is pyroelectric but not piezoelectric.

1 INTRODUCTION

FERROELECTRIC ceramic/polymer composites with various connectivities have attracted considerable research interests [1–13] because of their potential in pyroelectric sensor, ultrasonic transducer and underwater hydrophone applications. 0-3 composites with ferroelectric ceramic powder embedded in a passive polymer matrix are well-developed while 0-3 composites with ceramic particles in a ferroelectric polymer matrix have also received increasing attention [13–15]. PVDF and PVDF-TRFE copolymer have high permittivities ($\epsilon \sim 10$ to 14) compared to other polymers such as epoxy (~ 4) hence early work [6, 14, 16] only considered polyvinylidene fluoride (PVDF) as a high permittivity matrix to facilitate poling. The matrix is not expected to be piezoelectrically active because PVDF needs to be mechanically stretched prior to poling to give piezoelectric activity. However, PVDF-TRFE with trifluoroethylene (TRFE) content > 20 mol% crystallizes from the melt or from solution in a polar phase (the β phase) and can thus be poled without prior stretching. Therefore, when the copolymer is used as the matrix, it is possible to produce a composite with both the ceramic phase and the matrix being piezoelectrically active. The present work reports on the pyroelectric and piezoelectric properties of calcium modified lead titanate (PTCA)/PVDF-TRFE 0-3 composites as functions of the volume fraction of the ceramic, and compares the results with model predictions. Composites with only the ceramic phase poled and with both phases poled in the same direction have been studied. It is our aim to identify the contributions from the individual phases to the overall properties of the composites.

2 SAMPLE PREPARATION

The PVDF-TRFE copolymer used in the present study was obtained in pellet form from Piezotech in France. It contains ~ 30 mol% of TRFE as confirmed by differential scanning calorimetry (DSC) measurements. 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 $T_m = 153^\circ\text{C}$. A copolymer disk of diameter 12.8 mm and thickness 0.5 mm was prepared by compression molding in a press at 200°C . A pressure of 8.1 MPa was applied at 200°C for 5 min and then the sample was cooled to room temperature with the pressure kept on.

Calcium modified lead titanate $((\text{Pb}_{0.76}\text{Ca}_{0.24})[(\text{Co}_{0.5}\text{W}_{0.5})_{0.04}\text{Ti}_{0.96}\text{O}_3])$ a ceramic powder with particle size of 1 to 3 μm was supplied by Zhongshan University in China. To prepare the ceramic samples, $\sim 5\%$ wt of a binder (consisting of polyvinyl alcohol (PVA) in deionized water and acetone) was added to the PTCA powder. A ceramic disk of diameter 13 mm diameter and thickness 2 mm was prepared by pressing at room temperature with a pressure of 100 MPa. After binder burnout and sintering, the diameter of the disk decreased to ~ 11 mm and it was then ground to a thickness of ~ 1 mm. In the preparation of 0-3 composites, PVDF-TRFE copolymer was first dissolved in acetone at room temperature and an appropriate amount of PTCA powder was gradually introduced into the solution with constant stirring. The composite was left at room temperature for one day and then heated in an oven at 120°C for 2 h to allow complete evaporation of the solvent. The composite was then crushed into small pieces and compression molded at 210°C under a pressure of 377 MPa. The composite disks have a diameter of 12.5 mm and thicknesses ranging from 0.5 to 0.7 mm. Silver paint was

Table 1. Pyroelectric and piezoelectric properties of the polarized ceramic, copolymer and 0-3 composites with only the ceramic phase poled. Shown are the ceramic volume fraction ϕ , the stepwise poling field at 120°C, E_0 , the relative permittivity before (ϵ') and after (ϵ) poling, the dielectric loss $\tan \delta$, the pyroelectric coefficient p and figure of merit F_p , the ceramic poling ratio α_c , the charge coefficient d_{33} , and the coupling coefficient k_t .

ϕ	E_0 MV/m	ϵ'	ϵ	$\tan \delta$	p	F_p $\mu\text{C}/\text{m}^2\text{K}$	α_c	d_{33} pC/N	k_t
0	32.1	11.2	9.5	0.015	—	—	—	—	—
0.09	32.9	17.2	14.3	0.020	2.3	0.16	0.67	5.1	—
0.19	30.7	20.3	18.4	0.025	5.4	0.29	0.69	8.3	—
0.28	28.5	26.2	24.2	0.036	11.5	0.48	0.70	11.7	0.14
0.39	30.4	32.6	30.3	0.049	20.9	0.69	0.67	13.5	0.16
0.48	28.5	45.6	42.4	0.032	39.1	0.92	0.68	20.8	0.14
0.54	20.3	59.5	57.3	0.037	40.7	0.71	0.65	22.8	0.15
1	4.9	251.5	245.0	0.018	295.6	1.21	0.91	72.8	0.51

applied to both sides of the copolymer, ceramic and composite samples, to serve as electrodes.

The volume fraction of ceramic ϕ in a composite was calculated using the relation

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

where ρ , ρ_c and ρ_p are the densities of the composite, ceramic and copolymer, respectively. Because the ceramic particles are dispersed in a dilute copolymer solution in the first step of the fabrication process, the particles are coated with thin layers of copolymer as verified by scanning electron microscope (SEM) observations. Since the composite samples are quite thick (~ 0.5 mm), the ceramic does not form a continuous phase in the thickness direction even at the highest volume fraction of ceramic $\phi \sim 0.54$, i.e. the connectivity in the sample has not changed from 0-3 to a partially 1-3.

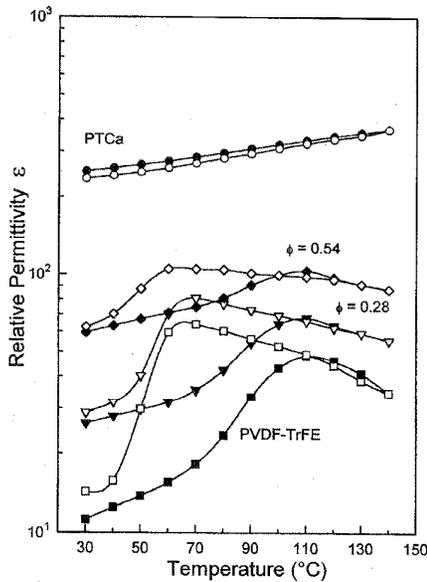


Figure 1. Thermal hysteresis in the permittivities of PVDF-TRFE and PTCA/PVDF-TRFE 0-3 composites with $\phi = 0.28$ and $\phi = 0.54$. The filled and open symbols correspond to data in heating and cooling runs, respectively.

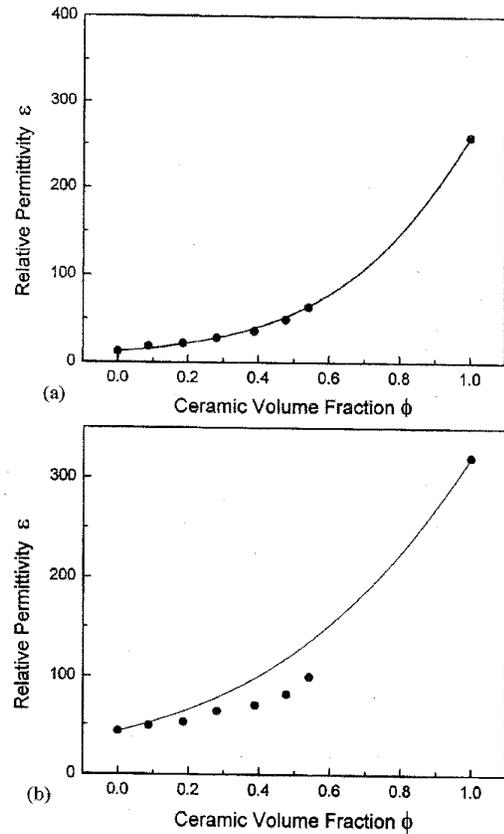


Figure 2. Permittivity of PTCA/PVDF-TRFE 0-3 composites as a function of the volume fraction of ceramic ϕ , upon heating (a) at 40°C and (b) at 80°C. The filled circles and the solid curve represent experimental data and theoretical prediction according to the Bruggeman model (Equation (2)), respectively.

Table 2. Pyroelectric and piezoelectric properties of the polarized ceramic, copolymer and 0-3 composites with both the ceramic and copolymer phases poled in the same direction. The density ρ , for other symbols, see Table 1.

ϕ	ρ kg/m^3	ϵ	$\tan \delta$	p $\mu\text{C}/\text{m}^2\text{K}$	F_p $\mu\text{C}/\text{m}^2\text{K}$	α_p	α_c	d_{33} pC/N	k_t
0	1930	9.5	0.015	25.7	2.71	1.00	—	-37.2	0.29
0.09	2360	12.2	0.020	33.5	2.75	1.01	0.78	-32.5	0.25
0.19	2850	15.9	0.023	35.2	2.21	1.07	0.73	-23.1	0.26
0.28	3320	20.2	0.026	35.8	1.77	1.04	0.77	-16.0	0.12
0.39	4290	29.5	0.031	53.4	1.81	1.13	0.73	-11.0	—
0.48	4610	40.0	0.035	48.7	1.22	0.95	0.74	12.6	0.12
0.54	4840	55.0	0.038	68.2	1.24	0.75	0.73	18.7	0.16
1	6870	245.0	0.018	295.6	1.21	—	0.91	72.8	0.51

3 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 was heated or cooled at a rate of ~ 1 °C/min in a temperature controlled oven, until a given temperature was reached, and then kept at that temperature for 30 min before the measurement was made. The permittivities of PTCA, PVDF-TRFE

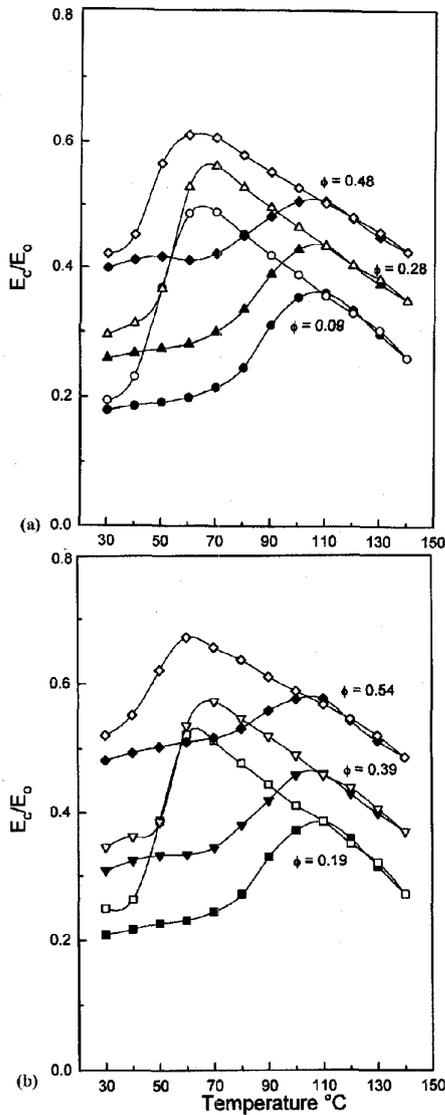


Figure 3. Calculated local field coefficient (E_c/E_o) as a function of temperature using Equation (4). (a) $\phi = 0.09, 0.28$ and 0.48 , (b) $\phi = 0.19, 0.39$ and 0.54 . The filled and open symbols correspond to heating and cooling, respectively.

and two composites with volume fractions of ceramic $\phi = 0.28$ and 0.54 upon heating and cooling are shown as functions of temperature in Figure 1. Abrupt changes in the permittivities occur at different temperatures upon heating and cooling [17] for the copolymer and 0-3 composites, thereby revealing a thermal hysteresis effect. The permittivities of the composites can be understood in terms of the Bruggeman equation [18, 19]

$$\frac{\epsilon_c - \epsilon}{\epsilon^{1/3}} = \frac{(1 - \phi)(\epsilon_c - \epsilon_p)}{\epsilon_p^{1/3}} \quad (2)$$

where ϵ_c, ϵ_p and ϵ are the permittivities of the ceramic, copolymer and composite, respectively. Figure 2 shows that the experimental data agree quite well with the model prediction.

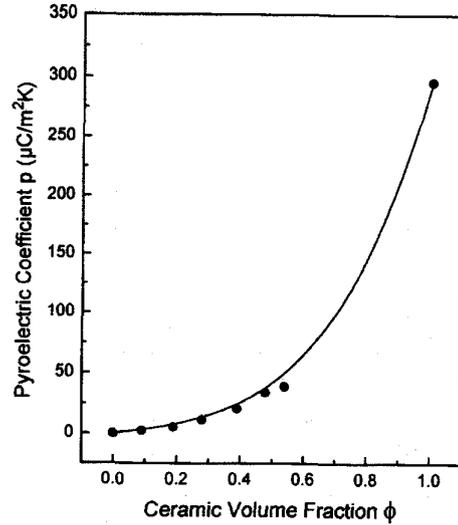


Figure 4. Pyroelectric coefficient p of group 1 PTCA/PVDF-TRFE 0-3 composites as a function of the volume fraction of ceramic ϕ at 25°C . The filled circles and the curve represent experimental data and theoretical prediction according to Equation (7), respectively.

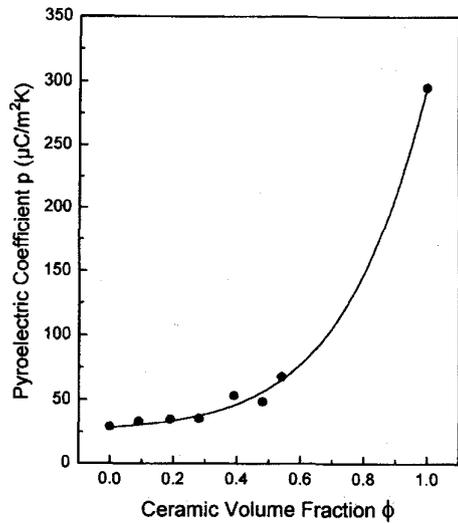


Figure 5. Pyroelectric coefficient p of group 2 PTCA/PVDF-TRFE 0-3 composites as a function of the volume fraction of ceramic ϕ at 25°C . The filled circles represent experimental data. The curve is the least-square fit of the data.

4 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 particle is given by [20]

$$E_c = \frac{3\epsilon E_o}{2\epsilon + \epsilon_c} \quad (3)$$

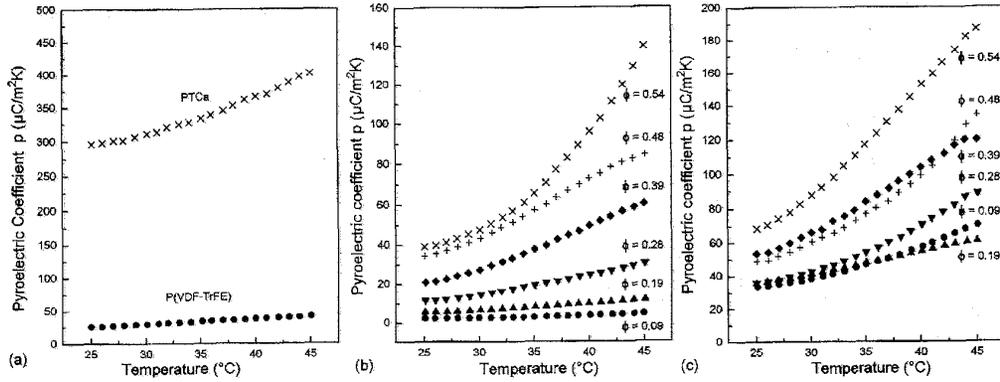


Figure 6. Pyroelectric coefficient p as a function of temperature. (a) PTCA ceramic and PVDF-TRFE copolymer, (b) composites in which only the ceramic phase is poled, (c) composites in which both phases are poled in the same direction.

where E_c is the applied electric field. Therefore the electric field ratio (or local field coefficient) is

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

The measured ε and ε_c are used to calculate L_E as a function of temperature (Figure 3). L_E varies from 0.2 to 0.7 depending on ϕ and on whether the sample is being heated or cooled. For a given ϕ , L_E is higher upon cooling. Since the coercive field of the ceramic is not high (~ 5 kV/mm at 100°C), the field $E_c = 6$ to 10 kV/mm, experienced by the ceramic should be high enough to pole the PTCA ceramic particles inside the composites.

5 SAMPLE POLING

To impart piezoelectric activity to the samples, they were subjected to a poling process so as to orient the dipoles in the ceramic and the copolymer phases [13, 16, 21–23]. In the present study, two groups of samples were poled in an oil bath. In group 1, only the ceramic phase is poled and in group 2 both phases are poled. The poling procedure is as follows:

Group 1. Samples are heated to 120°C (above T_{ch}) and a stepwise poling method is used. The applied field E_o is increased from 0 to E_1 and kept at E_1 for 4 min. The field is switched off and the sample is short-circuited for ~ 8 min. The applied field E_o is increased after the short-circuit step and the above procedure is repeated until E_o is close to the breakdown field of the sample. The field is then switched off before cooling the sample to room temperature. Since E_o is switched off above T_{ch} , only the ceramic phase is poled. To verify this, the same procedure is applied to a copolymer sample. The copolymer has no detectable piezoelectric and pyroelectric activities, thus showing that it is not polarized.

Group 2. The poling procedure is similar to that applied to group 1 samples but E_o is maintained while cooling to room temperature. As the sample cools through T_{ch} and T_{cc} with E_o still applied, the copolymer is poled in the same direction as the ceramic.

With this stepwise process, higher poling field could be applied to the samples since the risk of electric breakdown was reduced. This may result from the short-circuited periods during which the mechanical stress

and the injected charges were partially relaxed, thereby leading to a more homogeneous electric field distribution.

The intensities $I_{(002)}$ and $I_{(200)}$ of the (002) and (200) peaks in the X-ray diffraction pattern were used to evaluate the degree of poling of the PTCA ceramic in the composites. The poling ratio α_c is defined as [24]

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

$$= 1 - \frac{I_{(002)} I'_{(200)}}{I_{(200)} I'_{(002)}}$$

where $I'_{(002)}$ and $I'_{(200)}$ are the intensities after poling and $I_{(002)}$ and $I_{(200)}$ are the intensities before poling. The α_c values for the group 1 and 2 samples, given in Tables 1 and 2, respectively, indicate that the ceramic particles inside the composites are not fully polarized. Attempts have been made to repole the sample but α_c cannot be improved significantly.

6 PYROELECTRIC COEFFICIENTS

The pyroelectric coefficient p of the sample [13], 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 ΔT

$$p = \frac{\Delta Q/A}{\Delta T} \approx \frac{\Delta Q}{A\Delta T} \quad (6)$$

where A is the electrode area. In the present study, p was measured using the digital integration method [25]. Prior to measurement, the poled samples were annealed in a shortcircuited condition for 12 h at a temperature (70°C) above the highest temperature of the measurement. This eliminates the contribution of thermally stimulated current in subsequent measurements.

The pyroelectric coefficients of the annealed samples p were measured by heating at a rate of $\sim 1^{\circ}\text{C}/\text{min}$ from 25 to 45°C and the values of p and the pyroelectric figure of merit F_p , defined as $F_p = p/\varepsilon$ are given in Tables 1 and 2. The figures of merit F_p are higher for the composites with both phases polarized. For these group 2 composites, F_p is higher at lower volume fraction of ceramic (Table 2).

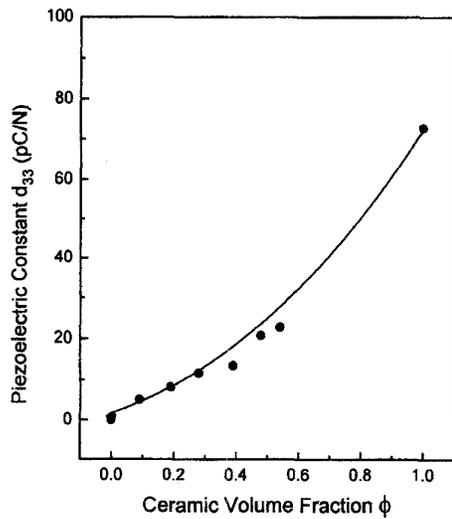


Figure 7. Piezoelectric coefficient d_{33} of group 1 PTCA/PVDF-TRFE 0-3 composites as a function of the volume fraction of ceramic ϕ at 25°C. The filled circle and the curve represent experimental data and theoretical prediction according to Equation (10), respectively.

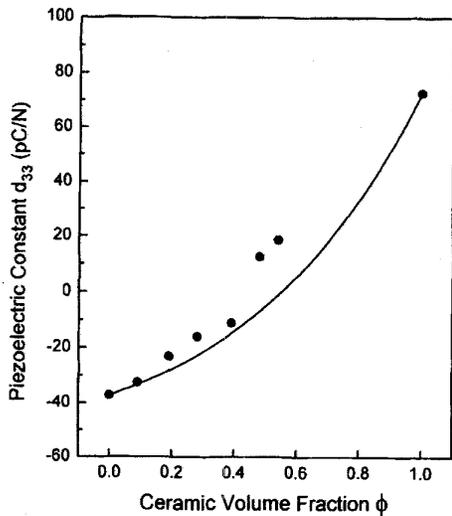


Figure 8. Piezoelectric coefficient d_{33} of group 2 PTCA/PVDF-TRFE 0-3 composites as a function of the volume fraction of ceramic ϕ at 25°C. The filled circle and the curve represent experimental data and theoretical prediction according to Equation (11), respectively.

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 (Equation (4)) and the ceramic volume fraction ϕ , then [24]

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

where p_c is the pyroelectric coefficient of PTCA. It is seen from Figure 4 that there is good agreement between experimental data and theoretical predictions, confirming the validity of Equation (7). For group 2 samples, p also contains the contribution of the copolymer phase, so the equation becomes

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

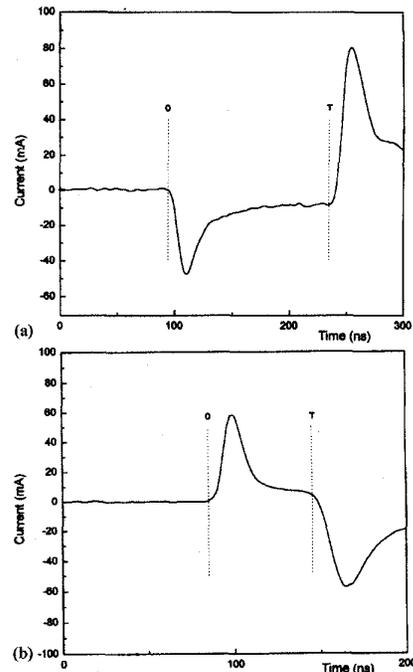


Figure 9. Shortcircuit current during the propagation of a pressure pulse in (a) a 0.71 mm thick PTCA sample and (b) a 0.17 mm thick PVDF-TRFE sample. The pressure pulse enters the sample at $t = 0$ from the anode (the side connected to positive poling voltage) and leaves the sample at $t = T$.

where p_p is the pyroelectric coefficient of the copolymer and α_p is the poling ratio of the copolymer matrix. Since all the parameters except α_p are known, Equation (8) can be used to calculate α_p . To reduce the error arising from data fluctuation, the data points were fitted to a smooth curve (see Figure 5) and then the smoothed p values were used to calculate α_p . As shown in Table 2, α_p is close to 1, indicating that the copolymer matrix is fully polarized. Some of the α_p values are > 1 which reflects the crudeness of the modified linear mixture rule and the error in the observed p . It should be noted that for $\phi > 0.35$, the α_p values may have an error $> 30\%$ because of the increasingly smaller contribution of the copolymer matrix to p .

The p values for PTCA/PVDF-TRFE composites reported by Dias and Das-Gupta [13, 14] are higher than those for group 1 samples but smaller than those for group 2 samples, indicating that the copolymer matrix in their samples may be partially poled. As shown in Figure 6, p increases as the temperature increases, rising by a factor of 2 as the sample is heated from 25 to 40°C.

7 ELECTROMECHANICAL PARAMETERS

The impedance *vs.* frequency curves around the thickness resonance of the composite samples were obtained using an impedance analyzer (HP 4194A). The electromechanical coupling coefficient k_t were evaluated using the IEEE standard formula [26]

$$k_t^2 = \frac{\pi f_s}{2f_p} \tan \left[\frac{\pi(f_p - f_s)}{2f_p} \right] \quad (9)$$

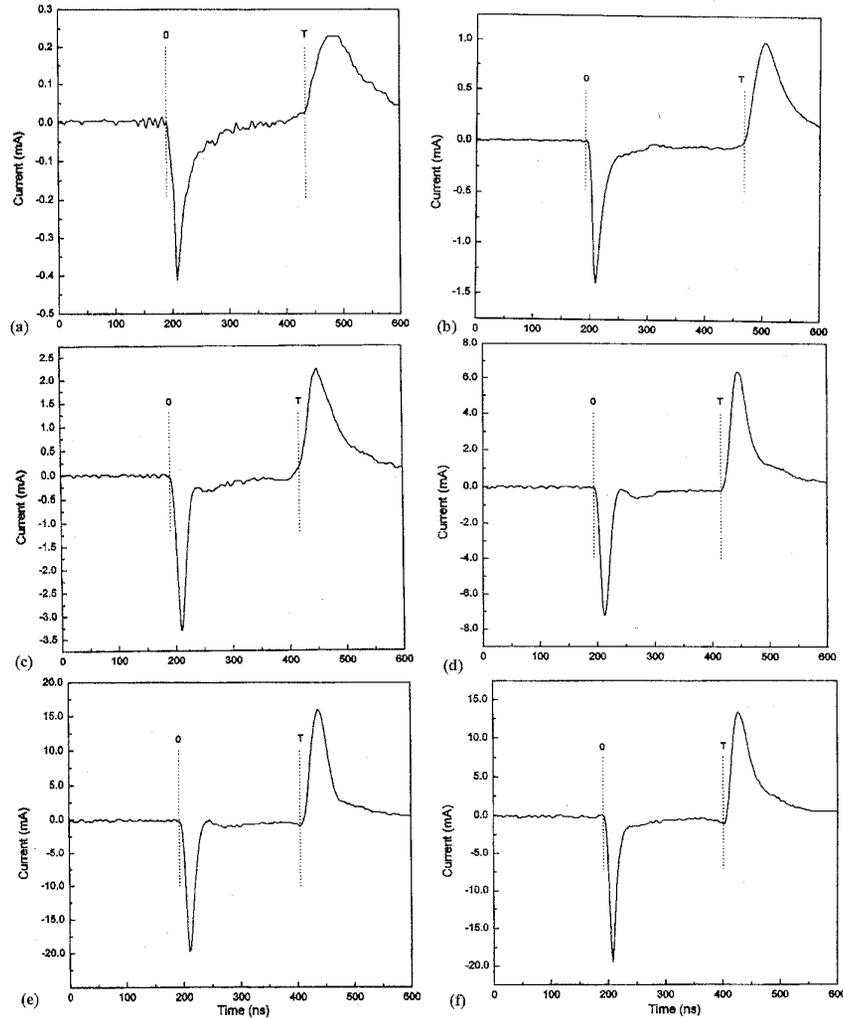


Figure 10. Shortcircuit current during the propagation of a pressure pulses in group 1 composites (a) $\phi = 0.09$, (b) $\phi = 0.19$, (c) $\phi = 0.28$, (d) $\phi = 0.39$, (e) $\phi = 0.48$ and (f) $\phi = 0.54$. The pressure pulse enters the sample at $t = 0$ from the anode (the side connected to positive poling voltage) and leaves the sample at $t = T$.

where f_s and f_p are the series resonance frequency (frequency at maximum conductance) and the parallel resonance frequency (frequency at maximum resistance) of the thickness mode resonance, respectively. The k_t values (Tables 1 and 2) for both groups of composites are rather small. In fact, thickness mode resonance peaks for these samples are very weak, indicating that PTCA/PVDF-TRFE 0-3 composites are not efficient in converting electrical into mechanical energy and *vice versa*.

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.). As seen from Figures 7 and 8, group 1 composites have positive d_{33} values while group 2 composites have positive or negative values depending on ϕ . The observed d_{33} are compared with the values calculated according to the following modified linear mixture rules

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

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

where the α_p values for the group 2 composites have previously been estimated from the pyroelectric data (Table 2). It is clear that there is reasonably good agreement between theoretical predictions and experimental data for both groups of samples. However for $\phi > 0.4$, the observed d_{33} for group 2 composites is significantly higher than the predicted value. This probably indicates that at high ϕ the electromechanical coupling between the two phases may no longer be neglected and more refined models have to be used [10, 13, 14].

8 POLARIZATION IN 0-3 COMPOSITES

The laser induced pressure pulse (LIPP) method, also known as the pressure wave propagation (PWP) method [27-30] for studying polarization distribution is well established. The experimental setup has been

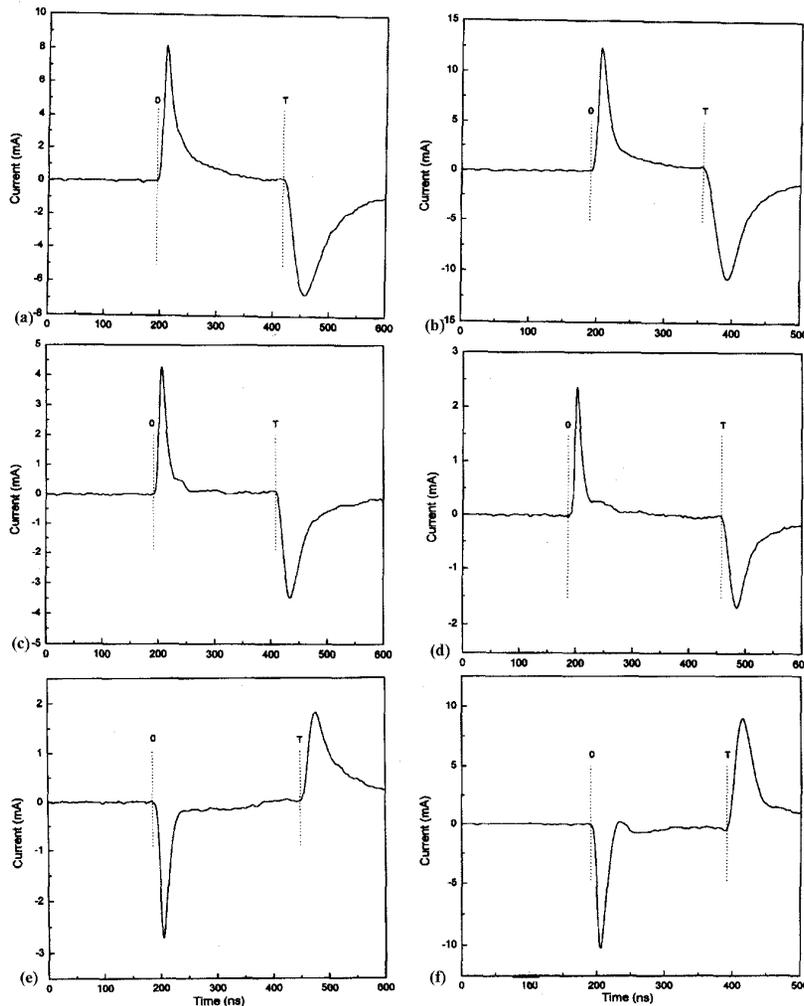


Figure 11. Shortcircuit current during the propagation of a pressure pulses in group 2 composites (a) $\phi = 0.09$, (b) $\phi = 0.19$, (c) $\phi = 0.28$, (d) $\phi = 0.39$, (e) $\phi = 0.48$ and (f) $\phi = 0.54$. The pressure pulse enters the sample at $t = 0$ from the anode (the side connected to positive poling voltage) and leaves the sample at $t = T$.

described previously [28]. 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 diameter 8 mm impinges on the surface of a composite sample enclosed in an electrically shielded sample holder, and 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 is generated which propagates along the z axis (sample thickness direction) at the velocity of sound v . For short pressure pulses, the current measured during the penetration of the pulse into the sample or its exit is proportional to the piezoelectric coefficient e_{33} (defined as stress/electric field at constant strain or charge density/strain at constant electric field) near the sample surface.

Figures 9 to 11 show the currents produced when the pressure wave enters the sample from the anode (the side connected to positive voltage during poling). The piezoelectric coefficient e_{33} of the PTCA ceramic and PVDF-TRFE copolymer have opposite signs, hence the LIPP signals

from the two samples have opposite polarities (Figure 9). When compressed by a pressure wave, positive charges are produced at the anode of the PTCA ceramic while negative charges are generated at the anode of the PVDF-TRFE copolymer. In group 1 samples, where the piezoelectric activity arises only from the ceramic phase, the current generated has the same direction as that in the PTCA ceramic (Figures 9(a) and 10).

For group 2 samples, the copolymer phase also contributes to the piezoelectric activity. It is seen that between $\phi = 0.09$ and 0.39, the LIPP signals have the same polarity as the copolymer (Figures 9(b) and 11). For $\phi = 0.48$ to 0.54, however, the contribution of the ceramic overcompensates that of the copolymer, so the LIPP signals have the same polarity as the ceramic.

9 DISCUSSION AND CONCLUSION

IN the present study, the PTCA ceramic and the PVDF-TRFE matrix in the composite are both ferroelectric. In order to estimate the con-

tribution from each phase, 0-3 composites are prepared with only the ceramic poled or with both phases poled in the same direction. The d_{33} data indicate that the piezoelectric activities of the ceramic and the copolymer phase tend to cancel each other. For the composites with both phases poled in the same direction, d_{33} and k_t of the composite are close to zero at $\phi \sim 0.45$.

On the other hand, the pyroelectric coefficients p of the two phases are additive and increases as ϕ increases. Therefore, at $\phi \sim 0.45$, the composite has the interesting property that it is pyroelectric but nonpiezoelectric. This may be useful in certain applications, e.g. in integrated pyroelectric sensors and array fabrications, where the sensing materials are deposited on very delicate membrane structures, so that the strain resulting from piezoelectric effect may damage the structure. The damage may be avoided by using lead titanate (PT)/PVDF-TRFE. We have recently succeeded in preparing thin PT/PVDF-TRFE films containing nanometer size PT particles [31]. The applications of these films in integrated pyroelectric sensors will be reported in the future.

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