

Pyroelectric Properties of PZT/P(VDF-TrFE) 0-3 Composites

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Abstract - 0-3 composites of lead zirconate titanate particles dispersed in a polyvinylidene fluoride-trifluoroethylene copolymer matrix may have a good potential for pyroelectric sensor applications. Thermal expansion mismatch together with the piezoelectric activity of the constituents produces a secondary pyroelectric effect in a composite. A model for this secondary effect in 0-3 composites has been developed to extend our previous description of the primary pyroelectric coefficient. The pyroelectric coefficient, dielectric constant, thermal expansion coefficient, shear modulus and bulk modulus of composite samples with different ceramic volume fraction have been investigated experimentally. The pyroelectric coefficient is compared with theoretical predictions.

INTRODUCTION

Ferroelectric ceramic/copolymer composites with different connectivities [1] have attracted much interest because of their particular mechanical, electrical and thermal properties. They have a promising potential for the use in actuators or sensors. Copolymer films in pyroelectric infrared sensors [2] may be replaced by composites [3], as their pyroelectric, dielectric and thermal properties can be varied with the ceramic volume fraction or by poling procedure [4]. One particular feature of ferroelectric composites of ceramic particles like lead titanate (PT) or lead zirconate titanate (PZT) in poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE) copolymer is that the matrix and inclusions can be polarized in parallel or in antiparallel directions [5]. When the matrix and inclusions are polarized in opposite directions, the pyroelectric activity will be reduced but the piezoelectric activity reinforced. On the other hand, if the two phases are polarized in parallel, the pyroelectric response reinforces while the piezoelectric activity partially cancels, thereby reducing vibration-induced electrical noise in pyroelectric sensors [6,7].

THEORY

Pyroelectricity is the appearance of an electric charge at the surface of a polar material when temperature changes the polarization. If the polar material is electroded and connected to an external circuit which

integrates the charge, the pyroelectric coefficient p is calculated by [8]:

$$p = \frac{\Delta(Q/A)}{\Delta T} \approx \frac{1}{A} \frac{\Delta Q}{\Delta T} \quad (1)$$

where A is the electrode area, ΔQ is the change of total charge due to a change in sample temperature ΔT .

Under stress free conditions, the pyroelectric coefficient contains contributions from the temperature variation of the dipolar moments and the variation of the dipolar density by thermal expansion (primary and secondary effects of a homogeneous ferroelectric material). The approximation in Eq. (1) is only valid when the area A of the sample is constant [9]. Thermal expansion, however, changes also the electrode area, and therefore the measured effective pyroelectric coefficient typically is the sum of the primary plus a fraction of the secondary coefficient.

Various models have been proposed to predict the effective piezoelectric and pyroelectric coefficients of composite ferroelectrics. Yamada has described a system of PZT powder embedded in a PVDF matrix [10]. Furukawa has considered 0-3 composites of spherical polar inclusions dispersed in an unpolar matrix [11]. For high volume fraction of inclusions or when the ceramic particles are of a similar size as the thickness of the composites sample, a cube model was proposed by Dias and Das-Gupta [9].

For the case that the difference in the polarization of the two phases is compensated by charges at the interfaces between matrix and inclusions and that mismatch in the thermal expansion of the two constituents can be neglected, we have derived a model for the effective pyroelectric coefficient which is universal for composites of all connectivities [12]:

$$p_f = \frac{\epsilon - \epsilon_m}{\epsilon_i - \epsilon_m} p_i + \frac{\epsilon_i - \epsilon}{\epsilon_i - \epsilon_m} p_m \quad (2)$$

where p_i and p_m are the pyroelectric coefficients of the inclusions and matrix, and ϵ , ϵ_i , ϵ_m are the dielectric permittivities of the composite, inclusions and matrix, respectively. In the sense of Bhalla's definition [13] Eq. (2) represents the "primary pyroelectric effect of a composite", which includes the sum of primary and secondary effects of the pure phases, and is therefore denoted as p_f .

Thermal expansion mismatch together with the piezoelectric activity of the constituents produces a contribution to the measured pyroelectric coefficient which has been defined as "secondary pyroelectric effect of a composite" (p_2). Bhalla et al. has derived p_2 for series and parallel connections [13]. The secondary effect is usually smaller than the primary pyroelectric activity, but it can become significant in particular arrangements.

To investigate if this secondary effect needs also to be considered in 0-3 composites we have derived p_2 and obtained the following expression for a sample under unclamped condition:

$$p_2 = \phi \frac{4\mu_m}{1 + \frac{4\mu_m}{3k_i}} (\alpha - \alpha_i) \left(\frac{d_i \frac{3\epsilon_m}{\epsilon_i + 2\epsilon_m} - d_m}{1 - \phi \frac{\epsilon_i - \epsilon_m}{\epsilon_i + 2\epsilon_m}} \right) \quad (3)$$

where ϕ is the volume fraction of the inclusion, α and α_i are the thermal volume expansion coefficients of the composite and inclusions, μ_m is the shear modulus of the matrix, k_i is the bulk modulus of the inclusion, and d_i and d_m are the hydrostatic piezoelectric constants of the inclusion and matrix, respectively. The detailed derivation of Eq. (3) will be published elsewhere.

The volume expansion coefficient of a composite has been given by Levin [14]:

$$\alpha - \alpha_i = (\alpha_m - \alpha_i) \frac{1/k_i - 1/k}{1/k_i - 1/k_m} \quad (4)$$

With the bulk modulus k of the composite as given by Hashin [15]:

$$\frac{1}{k} = \frac{\frac{1}{k_i} \frac{\phi}{1 + 4\mu_m/3k_i} + \frac{1}{k_m} \frac{1-\phi}{1 + 4\mu_m/3k_m}}{\frac{\phi}{1 + 4\mu_m/3k_i} + \frac{1-\phi}{1 + 4\mu_m/3k_m}} \quad (5)$$

one obtains:

$$\alpha - \alpha_i = \frac{(\alpha_m - \alpha_i)(1-\phi)(1 + 4\mu_m/3k_i)}{\phi(1 + 4\mu_m/3k_m) + (1-\phi)(1 + 4\mu_m/3k_i)} \quad (6)$$

The shear μ and bulk k modulus were calculated from Young's modulus E and the Poisson's ratio σ by the classical relations:

$$\mu = \frac{E}{2(1+\sigma)} \quad (7)$$

$$k = \frac{E}{3(1-2\sigma)} \quad (8)$$

EXPERIMENTAL

The PVDF-TrFE 70/30 mol % copolymer used in the present study is supplied by Piezotech. The PZT powder PKI 502 (supplied by Ultra-sonic Powders Ltd.) was sintered at 1285 °C and crashed by ball milling and hand

milling. The mean particle size is about 1 μm , as determined with a particle size analyzer. The copolymer pellets were dissolved in methyl-ethyl-ketone and suitable amounts of PZT powder were blended into the PVDF-TrFE solution to form composites with different volume fractions of ceramic. The mixture was stirred by a magnetic stirrer, slowly warmed until it became viscous and agitated in an ultrasonic bath for one hour to ensure that the ceramic powder was distributed evenly in the copolymer solution. After evaporation of the solvent, the composites were compression molded into disk samples 15 mm in diameter and about 0.4 mm thick. 0-3 composites with ceramic volume fractions between 0.1 and 0.6 have been prepared. The samples were annealed at 120 °C, to increase the crystallinity of the copolymer. The pure ceramic sample was prepared by pressing the PZT powder into a disc and sintered at 1285 °C.

Two sets of composite samples were poled under different conditions.

The first set of samples was heated to 120 °C, i.e. a temperature where the copolymer is in the paraelectric state, and an electric field of 35 kV was applied for one hour. The field is then switched off before cooling to room temperature. As the field is released above the Curie transition temperature of the copolymer, only the ceramic phase is polarized. To verify this, the same procedure has been applied to a copolymer sample. This copolymer sample has no detectable piezoelectric and pyroelectric activities, thus showing that it is not polarized.

The poling procedure applied to the second set of samples is similar to that applied to the first set except that the field is maintained while cooling to room temperature. As the sample cools through the Curie transition temperature with the electric field still applied, the copolymer phase is poled in the same direction as the ceramic phase.

The poled samples were then short circuited for one day at 40 °C to release the charge injected into the copolymer during the poling process.

The pyroelectric coefficient of the samples was measured using the digital integration technique [16]. The dielectric constant has been determined with a spectrum analyzer. To obtain additional information on the polarization state of the ceramic inclusions, the intensities $I_{(002)}$ and $I_{(200)}$ of the (002) and (200) X-ray diffraction peaks of PZT have been measured before and after poling the samples. The poling ratios of the inclusions have been calculated from the ratios of the peak intensities [17] and is also included in Tables I and II.

The hydrostatic piezoelectric coefficient was measured in a hydrostatic chamber filled with air [18]. Acoustic pressure was generated by two loudspeakers mounted on opposite sides and vibrating in phase to minimize vibrations of the chamber itself. The drive frequency (25 Hz) is low enough to ensure uniform pressure. Under the adiabatic conditions of the experiment, the temperature of the air in the chamber is also modulated with the pressure. To avoid a pyroelectric contribution to the measured current signal, the sample

has been thermally insulated from the air by placing it inside a beaker filled with silicone oil.

Thermal expansion measurements were conducted with a computer controlled thermal mechanical analyzer (TMA). The samples were positioned under a linear variable differential transformer (LVDT) inside a temperature chamber heated at a rate of 5 °C/min. The temperature and the displacement were recorded and the linear thermal expansion coefficient calculated as $\alpha = \Delta t / t \Delta T$ where t is the thickness of the sample and T the temperature. The Young's modulus E of the copolymer was determined with a dynamic mechanical thermal analyzer (DMTA). A sample of 14 mm length, 2 mm width and 0.099 mm thickness was tested at a frequency of 10 Hz and a strain of 5 μ m.

RESULTS

The results of pyroelectric coefficient, dielectric constant and the ceramic poling ratio of samples with different ceramic volume fractions are summarized in Tables I and II.

Table I Composites with only the ceramic phase

ϕ	$-p$ [μ C/m ² K]	Ceramic poling ratio	ϵ
0	0	-	11.2
0.1	1.3	0.64	15
0.2	3.4	0.58	21.8
0.3	6.5	0.51	31.2
0.4	12.6	0.56	45
0.5	20.4	0.51	73.4
0.6	36	0.49	124
1	533	0.74	1116

Table II Composites with the ceramic and copolymer phases poled in the same direction.

ϕ	$-p$ [μ C/m ² K]	Ceramic poling ratio	ϵ
0	25.7	-	9.5
0.1	17.7	0.68	12.7
0.2	20.2	0.7	18.4
0.3	22.1	0.64	28.6
0.4	27.4	0.61	42.2
0.5	33.1	0.56	69.2
0.6	49.9	0.57	121
1	533	0.74	1116

The hydrostatic piezoelectric coefficient of the ceramic d_i and the copolymer d_m have been measured as $d_i=34$ pC/N and $d_m=-9.3$ pC/N. The expansion coefficients of the copolymer, ceramic and composites with volume fractions between 0.2 and 0.6 are given in Table III.

The Young's modulus E and the Poisson's ratio σ of the ceramic are 71 GPa and 0.31 as given by the supplier. Following Eqs. (4) and (5), the bulk modulus k_i is found to be 62.3 GPa, the shear modulus μ_i is 27.1 GPa.

Young's modulus of the copolymer has been

measured as 2.05 GPa and the Poisson's ratio is assumed to be 0.4. Following Eqs. (4) and (5) the shear modulus μ_m and bulk modulus k_m are calculated as 0.73 GPa and 3.42 GPa, respectively.

Table III Thermal expansion coefficients of composites with different ceramic volume fractions

Ceramic vol. fraction	Expansion coeff. α [$\times 10^{-6}/K$]
0	74.5
0.2	70.7
0.3	52.0
0.4	44.8
0.5	35.1
0.6	24.5
1	3.9

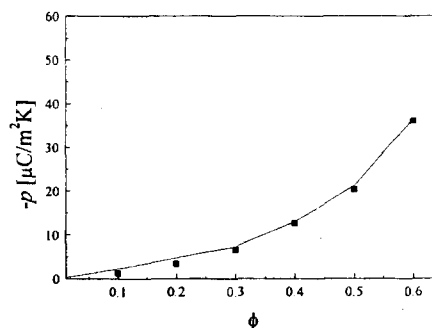


Fig. 1 p vs ϕ for composites with only the ceramic poled

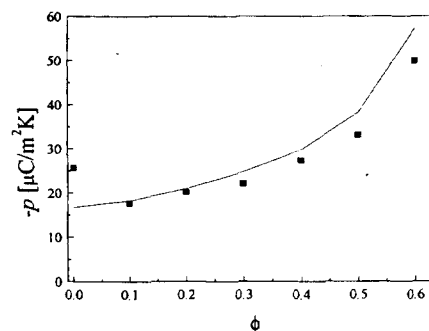


Fig. 2 p vs ϕ for composites with the ceramic and copolymer phases poled in same direction

The measured pyroelectric coefficients for the two sets of samples are shown in Figs. 1 and 2 (symbols). The experimental data allow also to calculate the predictions of Eqs. (2) and (3) for p_1 and p_2 . The pyroelectric coefficient of the inclusions has been calculated from the value of the ceramic bulk sample under consideration of the poling ratios determined from the X-ray diffraction measurements. A good fit to the experimental data is

obtained by assuming the poling ratio of the copolymer matrix to be 0.65. The theoretical curves for the total pyroelectric coefficient $p=p_1+p_2$ are also included in Figs. 1 and 2.

The secondary pyroelectric coefficient has been calculated with Eq. (3) for three cases: only the ceramic phase polarized, both phases are poled in parallel direction, and the two phases polarized in antiparallel directions. The results are shown in Fig. 3. The symbols represent values based on the measured expansion coefficients of the composites while the lines are obtained with Eq. (6). The good match supports Levin's model for the expansion coefficient of a 0-3 composite.

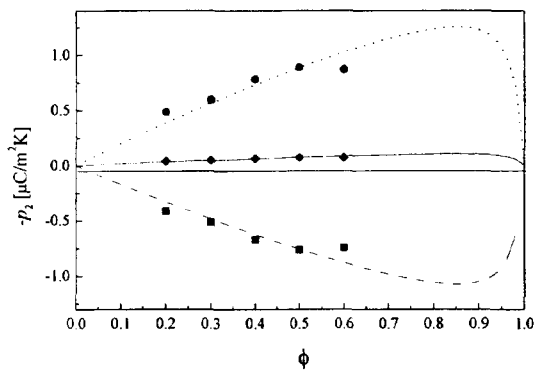


Fig. 3 Secondary pyroelectric coefficient of unclamped 0-3 PZT/P(VDF-TrFE) composites.

• : the two phase polarized in parallel, ■ : in antiparallel directions, ◆ : only the ceramic phase polarized.

CONCLUSION

The total pyroelectric coefficient of 0-3 PZT/P(VDF-TrFE) composites with various ceramic volume fractions agrees well with the experimental results. A model for the secondary pyroelectric coefficient has been developed and may be used to develop composites optimized for a high p_2 .

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