

## Pyroelectric or piezoelectric compensated ferroelectric composites

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The matrix and inclusions of 0–3 composites of lead titanate (PT) in polyvinylidene fluoride trifluoroethylene (P(VDF–TrFE)) have been independently poled by a special poling method. The polarization states of both constituents are investigated by the measurement of the dynamic pyroelectric coefficients of the composites in the temperature range of 20–90 °C, within which the copolymer matrix undergoes a ferroelectric–paraelectric phase change. The pyroelectric coefficients of PT and P(VDF–TrFE) have the same sign, while their piezoelectric coefficients have opposite signs. This allows the preparation of composites with enhanced pyroelectric but reduced piezoelectric activity when the matrix and inclusions are polarized in the same direction, or vice versa if the constituents are oppositely polarized. For a PT volume fraction of 27% it was possible to prepare a pyroelectric composite with vanishing piezoelectric activity or a piezoelectric composite with vanishing pyroelectric activity by poling the matrix and inclusions in parallel or antiparallel directions. © 2000 American Institute of Physics. [S0003-6951(00)04719-7]

Composites of ferroelectric ceramic inclusions embedded in a polymer matrix have a promising potential for applications as they combine the high pyroelectric and piezoelectric coefficients of the ceramic with the good mechanical properties of the polymer. The selection of the components and of the volume ratio allows the fabrication of new materials with tailored properties. If not only the inclusions but also the matrix is ferroelectric [e.g., a polyvinylidene fluoride (PVDF) matrix<sup>1</sup>] the poling state of the matrix provides an additional degree of freedom. For our investigations we choose PVDF trifluoroethylene (P(VDF–TrFE)) of VDF to TrFE molar ratio 56/44 as the matrix material. This material can be easily depolarized by heating it to above the transition temperature at 65 °C (i.e., from the ferroelectric to the paraelectric state). This allows the option of polarizing only the inclusions,<sup>2,3</sup> as well as a direct investigation of their contribution to the effective pyroelectric and piezoelectric coefficients of the composite after depolarizing the copolymer matrix. Investigations on 2.5 μm thick spin-coated PT/P(VDF–TrFE) 0–3 composites with 8 vol% lead titanate (PT) had shown that by using a special poling procedure the matrix and inclusions can be polarized independently of each other.<sup>4</sup> In particular, it is possible to polarize the matrix and inclusions either in the same direction or in opposite directions. However, due to the low ceramic volume fraction, the pyroelectric response from the ceramic particles was small compared to the contribution of the copolymer matrix.

For the studies reported in this sequel, PT ceramic powder<sup>5</sup> of about 100 nm particle size has been embedded in P(VDF–TrFE) 56/44 mol% copolymer to form a 0–3 composite with a ceramic fraction of 27 vol%. The copolymer was first dissolved in methylethylketone. Then the ceramic powder was added to the copolymer solution and dispersed by ultrasonic agitation. After the solvent had evaporated, the

composite was placed between two stainless steel plates covered with aluminum foil and a 30 μm thick film was prepared by compression molding at 220 °C. Gold electrodes were deposited on the top and bottom surfaces of the film.

The poling procedure which has been developed is based on the following considerations: (1) When an electric field is applied to the 0–3 composite for a duration which is substantially shorter than the dielectric relaxation time of charge in both components, then the divergence of the electric displacement is zero. The maximum achievable polarization of P(VDF–TrFE) is substantially lower than the remanent polarization of PT. Therefore, it can be expected that under this condition the polarization state of the inclusions remains essentially unchanged while the matrix is fully poled if the field is of an appropriate magnitude. At room temperature the dielectric relaxation time in P(VDF–TrFE) is typically longer than 1000 s. Therefore, poling durations below 1 s should fulfill this condition, even when the injection of charge from the electrodes is taken into account. (2) On the other hand, the ceramic particles can only be poled efficiently under conditions which allow a substantial transport of charge within the material, i.e., at high temperatures and for a long poling time.

In the experiments the following poling conditions were selected: (i) At room temperature several cycles of a sinusoidal electric field with frequency  $f = 10$  Hz and amplitude  $E_{\text{rms}} = 80$  V/μm are applied to the sample. (ii) At 100 °C, i.e., when the copolymer matrix is in the paraelectric phase, a dc electric field of 55 V/μm is applied for 1 h.

The polarization state of the matrix and inclusions was characterized by the measurement of the pyroelectric coefficient of the composite as a function of temperature between 20 and 90 °C, covering the ferroelectric as well as the paraelectric phase of the copolymer matrix. The Curie temperature of PT is substantially higher, i.e., the inclusions remain ferroelectric over the entire investigated temperature range. A comparison of the pyroelectric coefficient before

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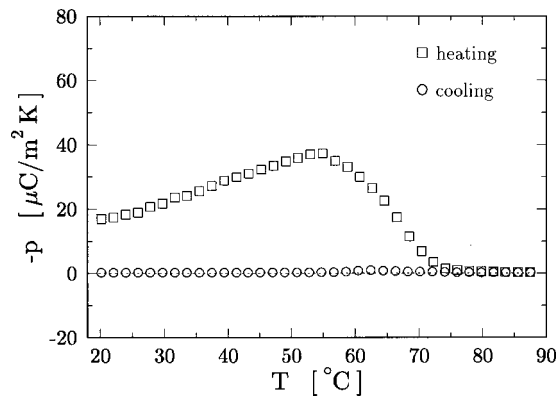


FIG. 1. Pyroelectric coefficient of PT/P(VDF-TrFE) with 27 vol % PT as a function of temperature with only the copolymer matrix polarized.

and after the thermal depolarization of the matrix allows the characterization of the polarization states of both the ceramic inclusions and the copolymer matrix.

An ac method was used to measure the pyroelectric coefficient. At a certain temperature  $T_0$  the sample temperature was sinusoidally modulated [ $T(t) = T_0 + T_{\sim} \sin 2\pi ft$ ] with frequency  $f = 5$  mHz and amplitude  $T_{\sim} = 1$  K using a Peltier element.<sup>6,7</sup> The pyroelectric current signal was amplified with an electrometer and the 90° out of phase component of the current with respect to the temperature modulation was measured with a lock-in amplifier. After setting to a new temperature  $T_0$  the sample was kept at  $T_0$  for 15 min for the signal to become stable before the pyroelectric measurement was performed.

The piezoelectric coefficient  $d_{33}$  of the composites at room temperature was measured using a piezo tester. Sinusoidal mechanical stress with a frequency of 60 Hz was applied to the sample while the current signal was recorded.

Figure 1 shows the pyroelectric coefficient of PT/P(VDF-TrFE) 56/44 mol % with 27 vol % PT as a function of temperature first measured in a heating cycle and then in a cooling cycle. The sample has been poled at room temperature under condition (i). Starting at 20 °C,  $-p$  increases with temperature by a factor of 2 to a maximum at 55 °C. The drop in  $-p$  between 55 and 72 °C is due to the phase transition. After heating above the Curie temperature of the copolymer matrix the pyroelectric coefficient vanishes and remains zero during cooling. This shows that the application of the ac voltage to the composite at room temperature polarizes only the copolymer matrix while the inclusions are not affected.

Next, we study a sample poled at 100 °C under condition (ii). After the electric field had been removed and the sample cooled down to room temperature, the pyroelectric coefficient was measured in a heating and a cooling cycle. As shown in Fig. 2 the results during the heating and the cooling cycles are the same, i.e., the copolymer matrix has remained unpoled. Under condition (ii) only the ceramic inclusions are polarized. The observed dip of  $-p$  of the composite at 65 °C reflects essentially the influence from the temperature dependence of the dielectric permittivity of the copolymer matrix. This phenomenon will be discussed in detail in another article.

Finally we consider applying the two poling procedures

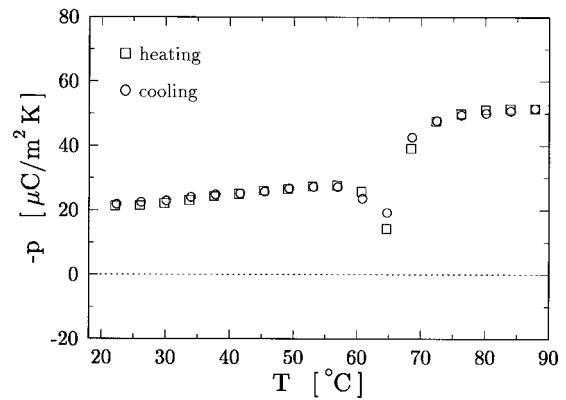


FIG. 2. Pyroelectric coefficient of PT/P(VDF-TrFE) with 27 vol % PT as a function of temperature with only the ceramic inclusions polarized.

in succession. First the ceramic inclusions are polarized using procedure (ii) and then the copolymer matrix is polarized by procedure (i). In applying the latter procedure, there is the option of polarizing the matrix parallel or antiparallel to the polarization direction of the ceramic established by the former procedure. This can be controlled by noting that the final polarization direction of the matrix is determined only by the electric field direction in the last half cycle of the ac voltage used in procedure (i). We have thus prepared samples with aligned ceramic and matrix polarization directions as well as samples in which these directions are antiparallel. The results in Fig. 3 show that the polarization of the inclusions is not changed by poling procedure (i), as evidenced by the overlapping cooling curves.

For the composite with 27 vol % PT the contributions of the matrix and inclusions to the effective pyroelectric coefficient cancel out for the antiparallely poled case at room temperature, while due to the opposite signs of their piezoelectric coefficients, the piezoelectric activities of the matrix and inclusions reinforce each other to give a piezoelectric coefficient of  $d_{33} = 20$  pC/N. Thus a piezoelectric composite has been prepared which is not pyroelectric. On the other hand, poling the matrix and inclusions in parallel directions produces a material with a pyroelectric coefficient  $-p$  of

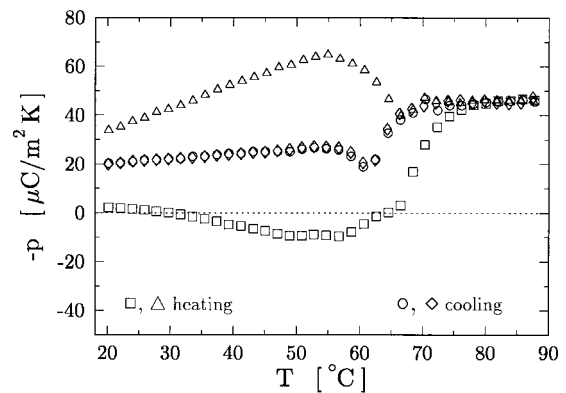


FIG. 3. Pyroelectric coefficient of PT/P(VDF-TrFE) with 27 vol % PT as a function of temperature with both phases polarized: (a) ceramic and copolymer polarized in the same direction [( $\Delta$ ) heating, ( $\diamond$ ) cooling], (b) ceramic and copolymer polarized in opposite directions [( $\square$ ) heating, ( $\circ$ ) cooling]. The sign of  $p$  refers to the polarization direction of the ceramic inclusions. The piezoelectric coefficient at room temperature is  $d_{33} = 1$  pC/N for case (a) and  $d_{33} = 20$  pC/N for case (b).

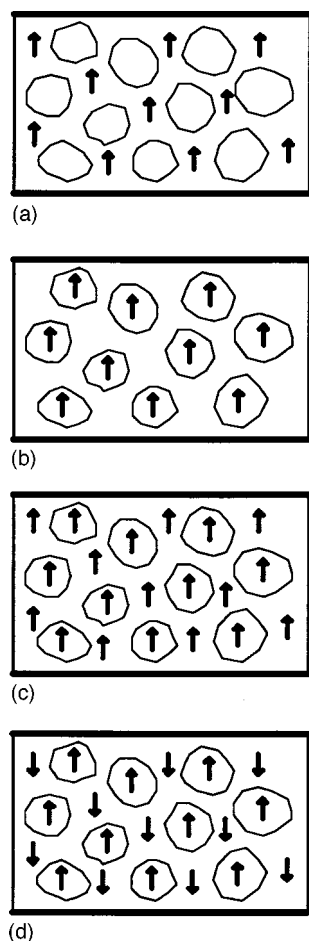


FIG. 4. A schematic view of the composites indicating the directions of the polarization vectors in the copolymer matrix and the ceramic inclusions: (a) only the copolymer matrix polarized; (b) only the ceramic inclusions polarized; (c) both phases polarized in parallel; and (d) in antiparallel directions.

$39 \mu\text{C}/\text{m}^2\text{K}$  but with zero piezoelectric activity around room temperature.

To illustrate the outcome of the poling procedures Fig. 4 shows a schematic view of the composites indicating the directions of the polarization vectors in the copolymer matrix and the ceramic inclusions. The achieved pyroelectric and piezoelectric coefficients at room temperature are summarized in Table I.

To conclude, the application of two different poling procedures allows a separate poling of the matrix and inclusions

TABLE I. Pyroelectric and piezoelectric coefficients of PT/P(VDF-TrFE) composites with 27 vol % PT in four different polarization states measured at room temperature.

Polarization direction			
Ceramic inclusions	Copolymer matrix	$-p \left( \frac{\mu\text{C}}{\text{m}^2\text{K}} \right)$	$d_{33} \left( \frac{\text{pC}}{\text{N}} \right)$
...	↑	19	-9
↑	...	22	12
↑	↑	39	1
↑	↓	1	20

in PT/P(VDF-TrFE) composites. The polarization state of the individual constituents can be determined separately by comparing the effective pyroelectric coefficient before and after the thermal depolarization of the copolymer matrix. For the composite with a PT volume fraction of 27 vol % a pyroelectrically compensated piezoelectric material or a piezoelectrically compensated pyroelectric material may be fabricated by antiparallel or parallel poling of the matrix and inclusions, respectively. Pyroelectricity without piezoelectricity does not exist in homogeneous materials. Homogeneous piezoelectrics which are not pyroelectric like quartz, have only comparatively weak piezoelectric activity. Therefore, the proposed inhomogeneous compensated materials are of much interest for sensor applications. The usual sensitivity of a piezoelectric sensor to temperature changes or of a pyroelectric sensor to mechanical vibrations and microphony, which often limits their use or makes complex external compensatory circuits necessary, can be completely avoided.

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