

Poling of Ferroelectric Composites

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Abstract

In 0–3 nanocomposites of lead titanate (PT) in polyvinylidene fluoride trifluoroethylene (PVDF-TrFE) it is possible to polarize the inclusions and the matrix separately. The pyroelectric coefficients of both components have the same sign, but the piezoelectric coefficients have the opposite sign. If matrix and inclusions of a composite of PT in PVDF-TrFE are polarized in the same direction, then the pyroelectric response of both components overlays constructively, the piezoelectric response destructively. By poling in opposite directions a material with reduced pyroelectric but increased piezoelectric sensitivity is produced. Under special poling conditions and for a certain ceramic volume fraction the pyroelectric coefficient vanishes completely for the antiparallel poled case but is piezoelectric with a piezoelectric coefficient of 20 pC/N. Such a material with internally compensated pyroelectricity is of high interest for the application in piezoelectric sensors where the cross sensitivity of piezoelectric sensors to temperature changes is often a large obstacle for their practical use.

1. Introduction

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 custom tailored properties. If not only the inclusions but also the matrix is ferroelectric (e.g. a PVDF matrix [1]) the poling state of the matrix provides an additional degree of freedom. For our investigations we choose P(VDF-TrFE) 56/44 mol-% as a matrix material, as it can easily be depolarized by heating it from the ferroelectric to the paraelectric phase above the transition temperature at 65 °C. This allows to polarize the inclusions alone [2, 3], as well as to investigate their contribution to the combined pyroelectric coefficient after depolarizing the copolymer matrix. Investigations on 2.5 μm thick spin-coated PT / P(VDF-TrFE) composites with 8 vol-% PT [4] had shown that using a special poling procedure matrix and inclusions can be polarized independently from each other. In particular, it is possible to polarize matrix and inclusions in opposite direction. 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. In the following, results on 30 μm heat pressed samples with a volume fraction of up to 34 vol-% PT are presented.

2. Experimental

Composites of nanocrystalline lead titanate (PT) ceramic powder [5] embedded in a P(VDF-TrFE) 56/44 mol-% copolymer matrix with ceramic volume fractions of 15, 27 and 34 vol-% have been prepared. The copolymer was dissolved in Methyl ethyl ketone and the ceramic powder dispersed in

the copolymer solution by ultrasonic excitation. After evaporating the solvent, 30 μm thick films were prepared by compression molding.

The composites were poled under two different conditions: 1) At room temperature several cycles of a sinusoidal electric field with frequency $f = 10$ Hz and amplitude $E_{\sim} = 80$ V/ μm are applied to the sample. 2) At 100 °C, which is in the paraelectric phase of the copolymer matrix, a constant electric field of 55 V/ μm is applied for one hour. The poling state of matrix and inclusions has been characterized by the measurement of the pyroelectric coefficient as a function of temperature in the ferroelectric and in the paraelectric phase of the copolymer matrix. The PT inclusions are ferroelectric in the entire investigated temperature range. A comparison of the pyroelectric coefficient before and after the thermal depolarization of the matrix gives access to the poling state of both the ceramic inclusions and the copolymer matrix.

For the measurement of the pyroelectric coefficient at a certain temperature T_0 the sample temperature is sinusoidally modulated ($T = T_0 + T_{\sim} \sin 2\pi ft$) with frequency $f = 5$ mHz and amplitude $T_{\sim} = 1$ K using a Peltier element [6, 7]. The pyroelectric current signal is recorded with an electrometer and the amplitude measured with a Lock-In amplifier. After setting a new temperature T_0 the specimen was kept at T_0 for 15 min before the pyroelectric measurement was performed, such that the signal had become stable.

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

3. Results and Discussion

Fig. 1 a) shows the pyroelectric coefficient of PT / P(VDF-TrFE) 56/44 mol-% with 27 vol-% PT as a function of temperature during heating and cooling. The sample was poled at room temperature under condition 1). After heating the composite above the Curie temperature of the copolymer matrix the pyroelectric coefficient vanishes and stays zero during cooling. This shows that the application of an AC voltage to the composite at room temperature poles the copolymer matrix while the inclusions are not affected. Then the sample has been poled at 100 °C under condition 2). The pyroelectric coefficient is shown in Fig. 1 b). The measurements during the heating and the cooling cycle give the same result, i.e., thermal depolarisation of the copolymer matrix does not change the pyroelectric coefficient. Under this condition only the ceramic inclusions are polarized. The temperature dependence of the pyroelectric coefficient is mainly due to the dielectric permittivity of the copolymer matrix (at $f = 5$ mHz).

Fig. 2 shows the pyroelectric coefficients for samples with 15, 27 and 34 vol-% PT in which first the ceramic inclusions are polarized using procedure 2) and afterwards poling procedure 1) is applied with the field either in parallel or antiparallel to the direction of the electric field in procedure 2). The results show that the polarization of the inclusions is not changed by poling procedure 1). For the composite with 27 vol-% PT Fig. 2 b) the contributions of matrix and inclusions to the pyroelectric coefficient cancel for the antiparallel poled case at room temperature. However, due to the opposite sign of their piezoelectric coefficients, the piezoelectric activities of inclusions and matrix overlay constructively. As shown in Table 1 it is $d_{33} = 20$ pC/N. Thus a piezoelectric composite has been prepared which is not pyroelectric. On the other hand, poling matrix and inclusions of the composite with 27 vol-% PT in parallel produces a pyroelectric material which is not piezoelectric (Table 1).

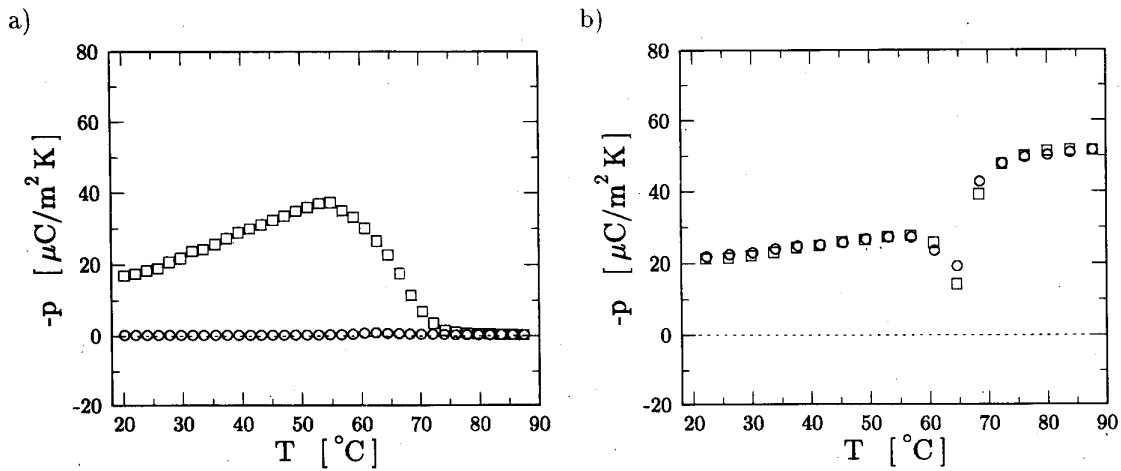


Figure 1 Pyroelectric coefficient of PT / P(VDF-TrFE) with 27 vol-% PT as a function of temperature a) with only the copolymer matrix poled b) with only the ceramic inclusions poled (\square : heating, \circ : cooling).

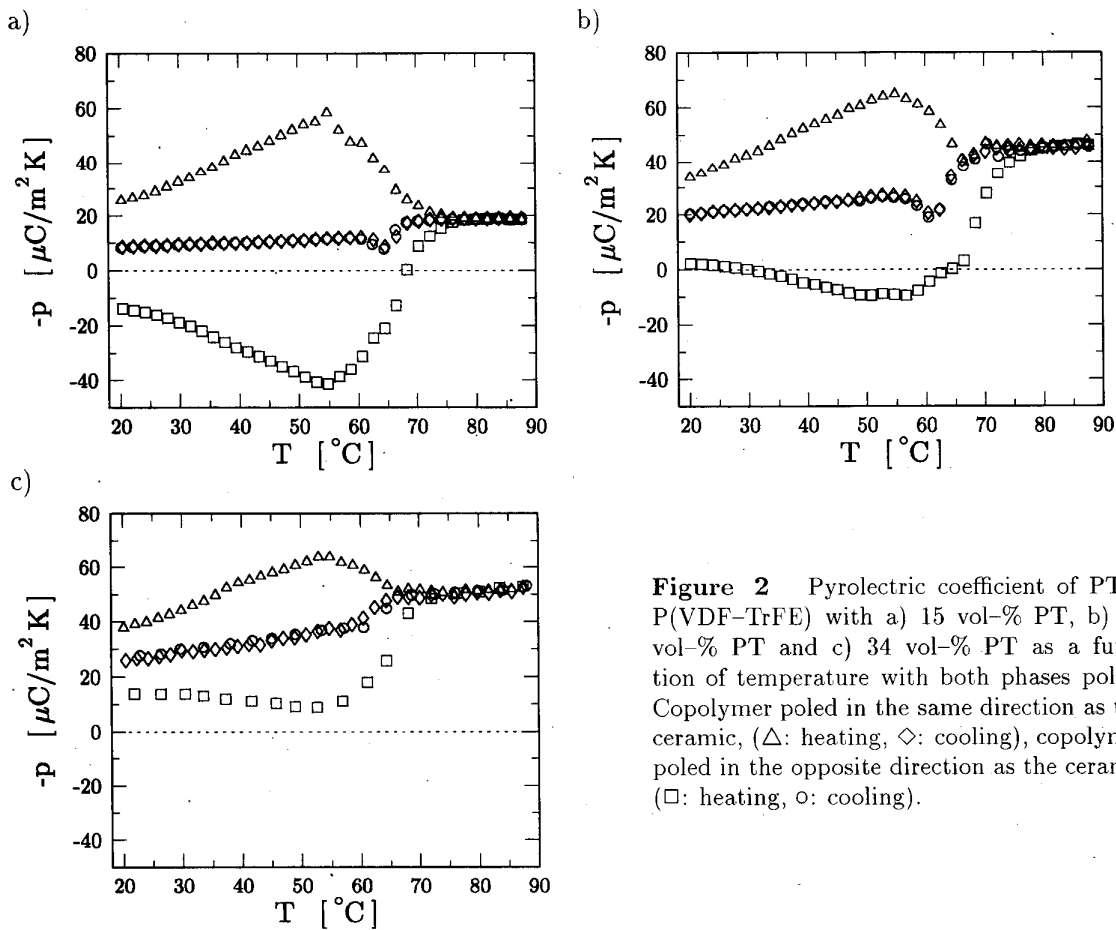


Figure 2 Pyroelectric coefficient of PT / P(VDF-TrFE) with a) 15 vol-% PT, b) 27 vol-% PT and c) 34 vol-% PT as a function of temperature with both phases poled: Copolymer poled in the same direction as the ceramic, (Δ : heating, \diamond : cooling), copolymer poled in the opposite direction as the ceramic (\square : heating, \circ : cooling).

Table 1 Pyroelectric and piezoelectric coefficient at room temperature of PT / P(VDF-TrFE) with different PT volume fraction for different poling states.

	15 vol-% PT		27 vol-% PT		34 vol-% PT	
	$-p[\frac{\mu C}{m^2 K}]$	$d_{33}[\frac{pC}{N}]$	$-p[\frac{\mu C}{m^2 K}]$	$d_{33}[\frac{pC}{N}]$	$-p[\frac{\mu C}{m^2 K}]$	$d_{33}[\frac{pC}{N}]$
only copolymer poled	24	-13	19	-9	15	-9
copolymer and ceramic poled in parallel	30	-6	39	1	42	11
only ceramic poled	9	4	22	12	28	18
copolymer and ceramic poled antiparallel	-16	17	1	20	14	21

4. Conclusion

The application of two different poling procedures allows a separate poling of inclusions and matrix in PT / P(VDF-TrFE) composites. The poling state of the single constituents can be determined separately by the comparison of the pyroelectric coefficient before and after the thermal depolarization of the copolymer matrix. For a PT volume fraction of 27 vol-% a pyroelectrically compensated piezoelectric was obtained by an antiparallel poling of inclusions and matrix. Such a material is of high interest for applications in piezoelectric sensors. The cross sensitivity to temperature changes which is an inherent problem of the usual piezoelectric materials and which often requires a complex compensation circuit is completely avoided by the use of these internally compensated composites.

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