Separate Poling of Inclusions and Matrix in PT/P(VDF–TrFE) 0–3 Composites

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Abstract – A procedure for separate poling of the ceramic particles and the copolymer matrix of 0–3 composites has been developed. 2.5 μm thick films of 56/44 mol–% vinylidene fluoride–trifluoroethylene (P(VDF–TrFE)) copolymer embedded with 8 volume–% lead titanate (PT) ceramic particles were investigated. First, the ceramic particles in the composite are polarized under a DC–field at temperatures above the Curie temperature of the copolymer. In the second step the P(VDF–TrFE) matrix is poled at room temperature in an AC–field at a frequency of 1 Hz. The degree of poling of the composite is then investigated by the measurement of the second order permittivity and the pyroelectric coefficient over a temperature range covering the ferroelectric and paraelectric phase of the copolymer matrix. The results show that the polarization of the ceramic is unchanged by the subsequent AC poling of the copolymer matrix.

INTRODUCTION

Composites of ferroelectric ceramics and ferroelectric copolymers combine the high pyroelectric and piezoelectric coefficients of the ceramic with the excellent mechanical properties of the copolymer. The copolymer with embedded ceramic particles can be easily deposited from solution onto the surface of a silicon chip, thereby facilating the application in integrated devices. The use of composites allows the design of materials with dielectric properties taylored to specific applications by appropriate choices of the matrix and inclusion materials and their volume fractions. The procedure for the independent poling of inclusions and matrix, which is described in the following sections, introduces an additional degree of freedom for the design of composite properties. The pyroelectric coefficients of PT and P(VDF–TrFE) have the same sign while the piezoelectric coefficients have opposite signs. This particular behavior, together with the possibility of polarizing matrix and inclusions separately, opens a way for the fabrication of piezoelectric materials in which pyroelectricicty is internally compensated, or vice versa.

CHARACTERIZATION TECHNIQUES

To analyze the degree of poling of the composite without changing its polarization, the second order permittivity and the pyroelectric coefficient were investigated.

Second Order Dielectric Permittivity

The second order permittivity is a sensitive parameter for investigating the degree of poling [1, 2, 3]. The coefficients ε_n in the expansion of the dielectric displacement D as a power series of the electric field E

$$D = P_r + \varepsilon_0 \varepsilon_1 E + \varepsilon_0 \varepsilon_2 E^2 + \dots \qquad (1)$$

are measured by the application of a sinusoidal electric field at a frequency of 1 kHz and with an amplitude small compared to the coercive field of the sample. The Fourier coefficients of the dielectric displacement were measured. An appropriately small exitation amplitude is selected such that the higher order even harmonics are small compared to the second order harmonic and the second order permittivity is evaluated (e.g. [2]). The second order permittivity vanishes for unpoled samples, i.e., the remanent polarization P_r is equal to zero, and it increases with increasing degree of poling. For P(VDF–TrFE) the quotient $\varepsilon_2/\varepsilon_1^3$ is proportional to the remanent polarization [3].

The linear and the nonlinear dielectric properties of the ceramic and the copolymer combine to give the composite dielectric properties. As the dielectric permittivity of PT is an order of magnitude higher than that of P(VDF–TrFE), the dependence of the second order permittivity ε_2 of the 0–3 composite on the second order permittivity of the ceramic inclusions ε_{c2} and of the copolymer matrix ε_{p2} is given by the following approximation:

$$\varepsilon_1 \approx (1 + f v)\, \varepsilon_{p1} \qquad (2)$$

$$\varepsilon_2 \approx (1 + g_p v)\, \varepsilon_{p2} + g_c v \,\frac{\varepsilon_{p1}^3}{\varepsilon_{c1}^3}\, \varepsilon_{c2} \qquad (3)$$

where ε_{c1} and ε_{p1} are the linear permittivities of the ceramic inclusions and the copolymer matrix, respectively, v is the ceramic volume fraction (assumed to be small) and the coefficients f, g_p, g_c depend on the shape of the inclusions. It is assumed that the divergence of the polarization at the boundary between matrix and inclusions is locally compensated by charge. For a capacitor model, the coefficients have already been given in [3]. ε_{p1} is strongly temperature dependent and has a maximum at the Curie temperature of the copolymer. The Curie temperature of the ceramic is far above the melting point of the copolymer, thus ε_{c1} can be regarded as temperature independent.

Pyroelectric Coefficient

The pyroelectric coefficient is measured by sinusoidally modulating the sample temperature using a Peltier element and recording the pyroelectric current with a lock-in amplifier. To the same approximation as mentioned above the pyroelectric coefficient p of the composite can be expressed as a function of the pyroelectric coefficients of the ceramic particles p_c and the copolymer matrix p_p:

$$p \approx p_p + f v \frac{\varepsilon_{p1}}{\varepsilon_{c1}} p_c. \tag{4}$$

Table 1 : Results of five consecutive poling experiments. An electric field E was applied for a duration t to the sample at temperature T. In step 3 one cycle of a sinusoidal field with amplitude E had been used. After each poling experiment the second order permittivity ε_2 was determined at 80 °C as a measure of the degree of poling of the ceramic. The arrows indicate the directions of E (in step 3, of the second half cycle of E) and of P_r as determined from ε_2 .

	poling procedure			result
	T [°C]	t [min]	E [V/μm]	ε_2 (80 °C) [10^{-8} m/V]
1	30	5	80 ↓	< 0.2
2	100	5	80 ↓	1.0 ↓
3	30	(1 Hz)	96 ↑	0.9 ↓
4	30	5	80 ↑	< 0.2
5	30	30	80 ↑	< 0.2

POLING EXPERIMENTS AND RESULTS

0-3 composites of 56/44 mol-% P(VDF-TrFE) copolymer with 8 volume-% PT ceramic particles embedded have been produced. The copolymer pellets were dissolved in dimethylformamide and the PT particles were dispersed in the solution by ultrasonic agitation. 2.5 μm thick films were produced by spin-coating and the films were annealed at 120 °C for 4 h.

To demonstrate the poling behaviour of the ceramic inclusions in the composite, the results of 5 consecutive poling experiments are summarized in Table 1. The resulting poling status of the ceramic particles has been determined after each poling experiment by a measurement of the second order permittivity of the composite at 80 °C, i.e. in the paraelectric phase of the copolymer matrix. Above the Curie temperature of the copolymer at about 65 °C its polarization vanishes and ε_2(80 °C) of the composite is a measure of the degree of poling of the ceramic inclusions. While the application of a DC field of 80 V/μm for 5 min at room temperature does not polarize the ceramic fraction (step 1), the ceramic particles can be polarized at 100 °C (step 2) [4]. This is due to the increase in the dc conductivity of the copolymer at high temperature. The ceramic inclusions can only be polarized when a substantial transport of charge through the copolymer matrix to the boundaries of the inclusions takes place because the large spontaneous polarization of PT is much higher than the maximum polarization of the copolymer.

In step 3 one cycle of a sinusoidal electric field with amplitude 96 V/μm and frequency 1 Hz is applied to the sample, again at room temperature, with the direction of the field in the second half cycle being opposite to those in steps 1 and 2. The polarization of the ceramic remains nearly unchanged. The application of an electric field in the opposite direction for a longer duration (5 min), however, leads to a complete depolarization of the inclusions (step 4). The application of the same electric field for a duration of 30 min does not result in a switching of the polarization to the opposite direction, i.e., the ceramic particles remain in the unpoled state (step 5). This behaviour can be explained if the dc conductivity of the ceramic inclusions increases with decreasing poling degree. After step 5 has been completed, the sample is in the same state as at the beginning, and the procedure can be repeated in the same way or with the applied electric fields and the resulting ε_2 reversed. As the copolymer matrix can be poled at room temperature in either direction without changing the polarization of the inclusions, the composite can be prepared in five different states: both phases unpoled, only the matrix polarized, only the inclusions polarized, both phases polarized in parallel, or the two phases polarized antiparallel.

The dielectric properties of two samples have been investigated as a function of temperature in more detail. Samples A and B are composites with unpoled and poled ceramic inclusions, respectively. The copolymer matrix of both samples has been poled at 30 °C with a full cycle of a sinusoidal electric field of frequency 1 Hz. In the first experiments the second half cycle was pointing in the same direction as the dc electric field with which the ceramic phase of sample B had been poled. Starting from room temperature, the linear and the second order permittivity have been measured

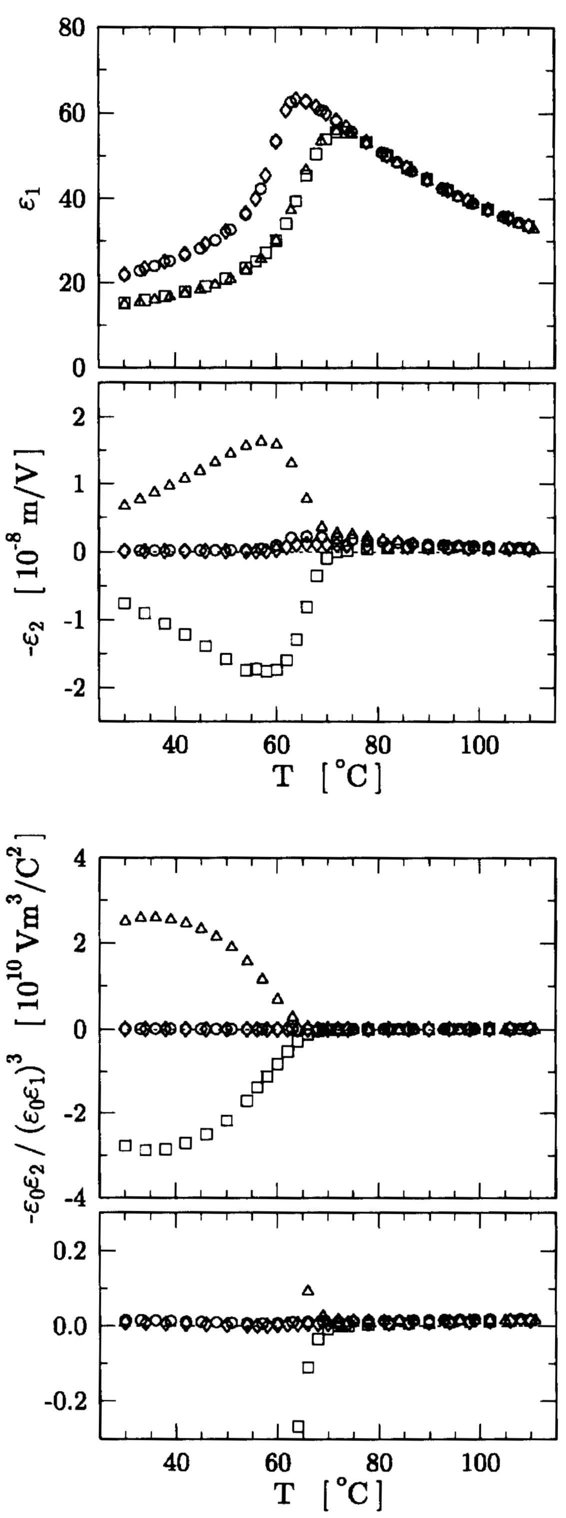

Fig. 1 : Linear and second order permittivity and quotient $(\varepsilon_0\varepsilon_2)/(\varepsilon_0\varepsilon_1)^3$ for sample A (ceramic phase unpoled) as a function of temperature. The composite was poled at 30 °C in the positive direction in a sinusoidal electric field of frequency 1 Hz and amplitude 96 V/μm, then a temperature scan was performed (△ heating, ◇ cooling). Afterwards the sample was poled at 30 °C in the negative direction and a second temperature scan was performed (□ heating, ○ cooling).

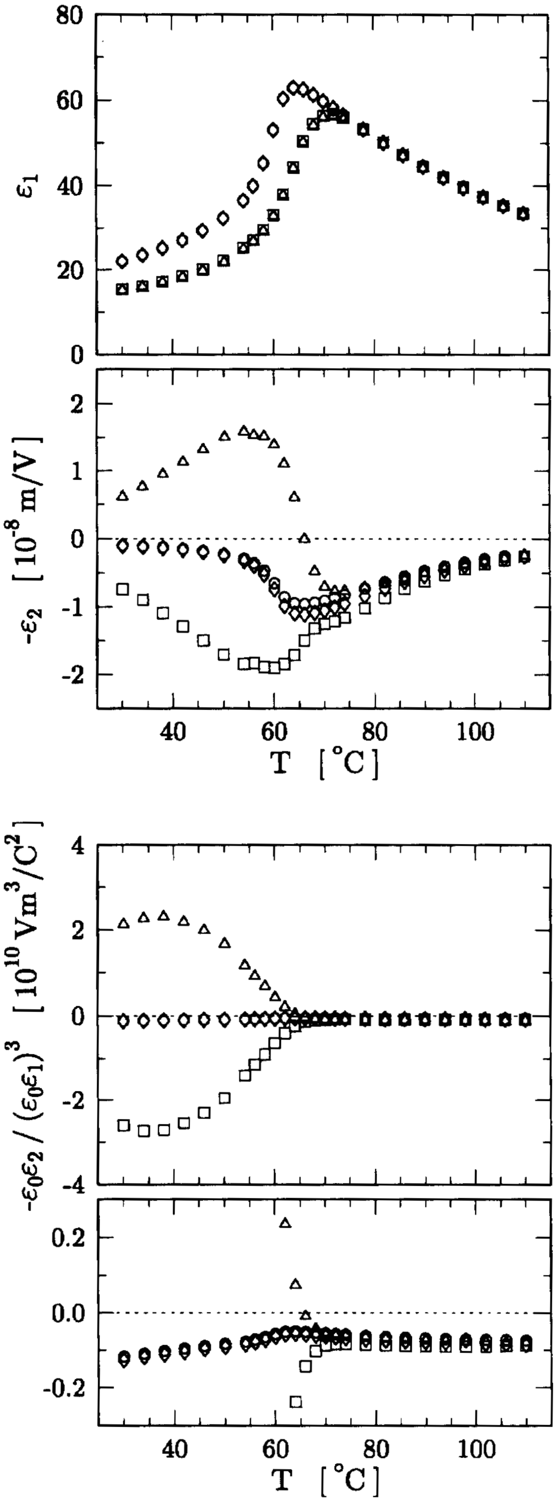

Fig. 2 : Linear and second order permittivity and quotient $(\varepsilon_0\varepsilon_2)/(\varepsilon_0\varepsilon_1)^3$ for sample B (ceramic phase poled) as a function of temperature. Before the measurement the ceramic inclusions were poled in the negative direction by the application of a DC field of 52 V/μm to the composite for 45 min during cooling from 120 °C to 80 °C. Subsequently, the matrix was AC–poled at 30 °C. Measurement and symbols as explained in Fig. 1.

as functions of temperature up to 120 °C first with increasing and then with decreasing temperature. After poling the copolymer matrix in the opposite direction, the same experiment has been repeated. Figs. 1 and 2 show the linear and the second order permittivity and the quotient $(\varepsilon_0\varepsilon_2)/(\varepsilon_0\varepsilon_1)^3$ for samples A and B, respectively.

In the paraelectric phase of the copolymer and for the cooling measurements the second order dielectric nonlinearity of the composite is caused by the inclusions alone. In the cooling curves the second order permittivity of sample B (i.e., its absolute value) shows a maximum at the Curie temperature of the copolymer matrix. For temperature independent linear and nonlinear dielectric properties of the inclusions, ε_2 of the composite is proportional to ε_{p1}^3 (Eq. (3)). In the quotient $\varepsilon_2/\varepsilon_1^3$ the strong temperature dependence of ε_2 and ε_1 cancels out (Eqs. (2,3)). Fig. 2 shows that the ceramic poling degree is not influenced by the AC poling of the composite at room temperature.

For the material with a volume fraction of 8 % PT in P(VDF-TrFE) the contributions of the copolymer matrix and of the inclusions to the polarization of the composite are comparable. (The polarization of PT is about an order of magnitude higher than that of the copolymer.) Nevertheless, if the copolymer phase is poled, the second order permittivity of the composite at room temperature is dominated by the copolymer matrix and the contribution from the ceramic inclusions is small (Fig. 2). The reason is the large permittivity of PT compared to the copolymer. It causes the electric field in the ceramic to be much smaller than in the matrix and further prevents an efficient coupling of the nonlinear dielectric response of the inclusions to the composite (Eq. (3)).

The pyroelectric coefficient of sample B measured under the same conditions as the dielectric properties is shown in Fig. 3. At room temperature the pyroelectric coefficient is dominated by the matrix and the contribution from the inclusions is only around 10 %. Like in the case of the second order permittivity the reason is the large difference in the permittivities between matrix and inclusions which prevents an efficient coupling of the pyroelectric response of the inclusions to the composite. In the paraelectric phase of the copolymer the pyroelectric signal from the inclusions is clearly seen. It is maximum near the temperature of maximum permittivity of the copolymer, i.e. near its Curie temperature.

CONCLUSION

A procedure has been developed which allows the separate poling of matrix and inclusions in PT/P(VDF-TrFE) 0-3 composites. The phases can be polarized in parallel or antiparallel. This allows the fabrication of materials in which the piezoelectric responses of the matrix and inclusions add in a constructive, the pyroelectric responses however in a destructive way, or vice versa. By a precise internal compensation it might become possible to design an artificial smart material which is piezoelectric but not pyroelectric or which is pyroelectric but not piezoelectric. Both would be of high impact to the application in sensors as the cross sensitivity would be significantly reduced without the need for external compensation circuitry. For this purpose the pyroelectric and piezoelectric contributions from the inclusions to the effective material must be enhanced. The path which must be followed for this to materialize is an increase of the volume fraction of the inclusions and a selection of materials for matrix and inclusions with a reduced dielectric mismatch between them.

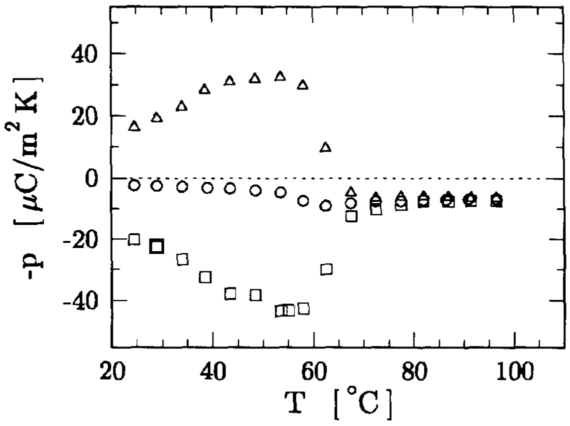

Fig. 3 : Pyroelectric coefficient of sample B as a function of temperature (○ only ceramic phase poled, □ both phases poled in parallel, △ both phases poled antiparallel).

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