

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) matrix¹] 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,^{2,3} 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.⁴ 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 powder⁵ 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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