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]:

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

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]:

$$p_I = \frac{\varepsilon - \varepsilon_m}{\varepsilon_i - \varepsilon_m} p_i + \frac{\varepsilon_i - \varepsilon}{\varepsilon_i - \varepsilon_m} p_m \qquad (2)$$

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_I.

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