Internal fields in
PT/PVDF–TrFE 0–3 Composites

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Abstract – Composites of ferroelectrics have a promising potential for applications, as it is possible to obtain new properties by combining two different ferroelectric materials. The spontaneous polarization of lead titanate (PT) is about an order of magnitude higher than that of vinylidenefluoride-trifluoroethylene copolymer (PVDF-TrFE). Therefore, in order to polarize the PT inclusions in a PT/PVDF-TrFE 0-3 composite, the depolarizing field must be compensated to a large extent by a counter field due to charge accumulated at the interface between the matrix and inclusions. An internal field will arise within the composite when the accumulated charge is insufficient to generate a fully compensating counter field. To demonstrate the existence of such an internal field we have studied the pyroelectric activity of composites with 27 volume % of PT in 56/44 mol % PVDF-TrFE. In the temperature range around the ferroelectric phase transition of the copolymer, induced pyroelectric activity is observed. The internal field can be estimated from an analysis of the pyroelectric activity of the composite.

INTRODUCTION

The interaction of charge and polarization plays an important part in inhomogeneous ferroelectrics. In semicrystalline polyvinylidene fluoride (PVDF) and its copolymers with trifluoroethylene (PVDF–TrFE) charges are essential to stabilize the polarization of the crystalline phase [1, 2]. The interfacial charges compensate the polarzation of the crystalline phase locally, but overcharging of the interfaces has also been reported [3]. To polarize the ceramic inclusions in 0–3 composites of e.g. lead titanate (PT) in PVDF–TrFE charges must be injected into the material and migrate through the copolymer to the interfaces with the PT particles [4], a fact which can also be used to polarize the matrix and inclusions separately [5].

When the compensation of polarization by charge is not precise, i.e. when the interfaces between polar and nonpolar regions or between regions with different remanent polarizations are undercharged or overcharged, electric fields will persist in the material. A better understanding of the polar state of composite ferroelectrics is important for the further optimization of these materials and their processing. Here, we report a study of internal fields in 0-3 composites by pyroelectric investigations.

THEORY

A model for the pyroelectric coefficient of a composite of spherical pyroelectric inclusions embedded in a pyroelectric matrix with 0–3 connectivity is given in [6]. In the following we consider an unpoled, i.e., nonpyroelectric matrix.

We assume that the surfaces of the spherical inclusions with a homogeneous polarization in z-direction $\vec{P}_{ri} = (0, 0, P_{ri})$ are covered by charges with a surface charge density $\sigma(\Theta) = -\sigma_0 \cos \Theta$ (see Fig. 1). When the polarization is fully compensated by charge, i.e. $P_{ri} = \sigma_0$, the electric field in the matrix and inclusions is zero, and the pyroelectric coefficient of the composite is [6]:

$$p = \frac{\varepsilon - \varepsilon_m}{\varepsilon_i - \varepsilon_m} \, p_i \tag{1}$$

p_i is the pyroelectric coefficient of the inclusions, ε_m and ε_i are the dielectric permittivities of the matrix and inclusions, respectively, and ε is the effective dielectric permittivity of the composite.

If the polarization is not precisely compensated by charges an electric field persists in the material. When the permittivity of matrix or inclusions varies with temperature T an induced pyroelectric activity contributes also to p and Eq. (1) is extended to:

$$p = \frac{\varepsilon - \varepsilon_m}{\varepsilon_i - \varepsilon_m} \, p_i + f \, \Delta P_r \tag{2}$$

with

$$f = \frac{d}{dT} \left(\frac{\varepsilon - \varepsilon_m}{\varepsilon_i - \varepsilon_m} \right). \tag{3}$$

$\Delta P_r = P_{ri} - \sigma_0$ is the uncompensated part of the polarization, whereby $\Delta P_r > 0$ indicates undercharging and $\Delta P_r < 0$ overcharging. $\Delta P_r = P_{ri}$ would indicate the absence of any compensating charge.
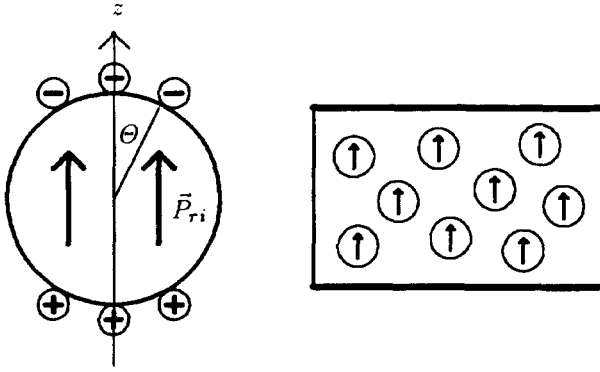
Fig. 1 : Homogeneously polarized sphere covered with compensating charge and illustration of the sample with poled particles dispersed in the polymer.

Fig. 2 : Dielectric permittivity of PVDF–TrFE 56/44 mol-% as a function of temperature measured at 5 mHz.

The effective dielectric permittivity ε of a 0–3 composite with a volume fraction v of spherical inclusions may be described by the Bruggeman formula [7]:

$$\frac{\varepsilon_i - \varepsilon}{\varepsilon^{1/3}} = (1 - v)\frac{\varepsilon_i - \varepsilon_m}{\varepsilon_m^{1/3}} \tag{4}$$

The temperature range considered in this paper is in the vicinity of the ferroelectric to paraelectric phase transition of the matrix, thus ε_m is strongly temperature dependent. In comparison, the dielectric permittivity of the ceramic inclusions ε_i can be considered as temperature independent in this temperature interval. Using Eq. (4) and $d\varepsilon_i/dT = 0$, Eq. (3) becomes:

$$f = \frac{\varepsilon - \varepsilon_i}{(\varepsilon_i - \varepsilon_m)^2}\left(1 - \frac{\varepsilon}{\varepsilon_m}\frac{\varepsilon_i + 2\varepsilon_m}{\varepsilon_i + 2\varepsilon}\right)\frac{d\varepsilon_m}{dT} \tag{5}$$

f is proportional to the derivative of the permittivity of the copolymer matrix with respect to temperature, which is highest near the Curie transition. When the voltage over the composite material is zero, the mean electric fields E_i and E_m in the inclusions and the matrix are given by

$$E_i = -\frac{\Delta P_r/\varepsilon_0}{\varepsilon_i + 2\varepsilon_m + 3\varepsilon_m v/(1 - v)} \tag{6}$$

$$E_m = -\frac{v}{1 - v}E_i \tag{7}$$

EXPERIMENTAL

PT ceramic powder of about 100 nm particle size has been embedded in 56/44 mol-% PVDF–TrFE copolymer to form a 0–3 composite with a ceramic volume fraction of 0.27. 30 μm thick composite films were prepared by compression molding. The ceramic inclusions were polarized at 100 °C, i.e. in the paraelectric
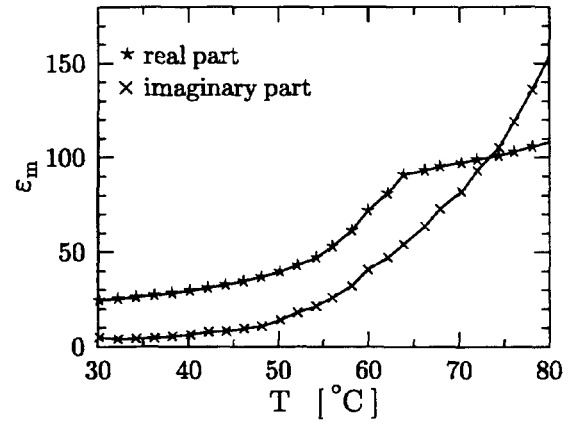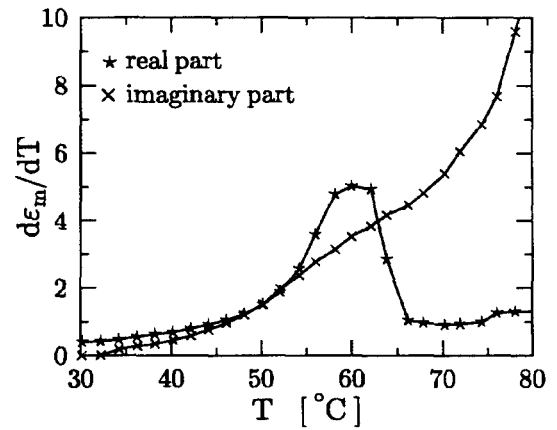

Fig. 3 : Derivative of the dielectric permittivity of PVDF–TrFE 56/44 mol-% (Fig. 2) with respect to temperature.

phase of the copolymer matrix, using a dc electric field of 55 V/μm applied for one hour [5, 6].

An ac method was used to measure the pyroelectric coefficient. The sample temperature was sinusoidally modulated with frequency 5 mHz and amplitude 1 K around the temperature T using a Peltier element. The pyroelectric current signal was amplified with an electrometer and analysed with a lock–in amplifier. The dielectric permittivity was measured at the same frequency 5 mHz with a sinusoidal electric field of amplitude 1 V/μm. The electric current through the sample was amplified with an electrometer and the real and imaginary parts of the signal were measured with a lock–in amplifier.

RESULTS

The complex dielectric permittivity ε_m of unpoled PVDF–TrFE measured at a frequency of 5 mHz is
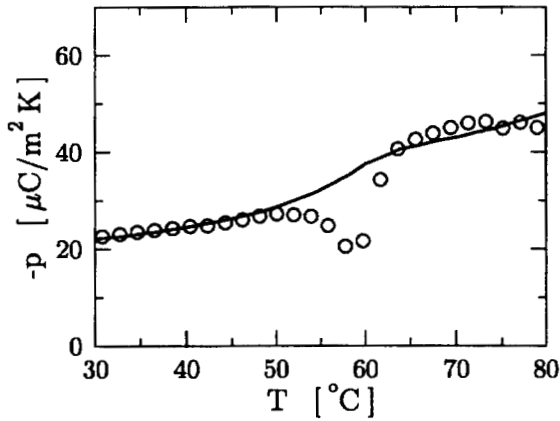
Fig. 4 : Pyroelectric coefficient of PT/PVDF–TrFE with polarized PT inclusions and unpoled matrix as a function of temperature. The experimental data (symbols) are compared with prediction according to Eq. (1) (line) with $p_i = -160 \frac{\mu C}{m^2 K}$.

Fig. 5 : Pyroelectric coefficient of PT/PVDF–TrFE with polarized PT inclusions and unpoled matrix as a function of temperature. The experimental data (symbols) are compared with prediction according to Eq. (2) (line) with $p_i = -200 \frac{\mu C}{m^2 K}$ and $\Delta P_r = 0.3 \frac{\mu C}{cm^2}$.

shown in Fig. 2. At such a low frequency the real part ε'_m does not show a maximum around the Curie temperature $T_C \approx 65$ °C (a feature normally observed above 10 Hz). The ferroelectric phase transition is only seen as a step in the real part of ε_m at T_C. The strong rise in the imaginary part ε''_m above $T \approx 60$ °C is assumed to be related to the slow relaxation processes in the amorphous phase and also to dc conduction. The derivative of ε_m with respect to temperature is depicted in Fig. 3. The real part exhibits a peak at the phase transition.

Fig. 4 shows the pyroelectric coefficient p of the PT/PVDF–TrFE composite with polarized ceramic inclusions and unpoled copolymer matrix as a function of temperature. Except for a temperature range around the Curie transition of the matrix, the pyroelectric coefficient of the composite increases with temperature, reflecting the increase in the dielectric permittivity of the matrix (Fig. 2). At the phase transition of the matrix a dip in the curve is observed. This dip remains unchanged when the temperature cycle is repeated, and shows no significant change after storing the sample for a month.

A similar feature is observed in the pyroelectric activity of unpoled PVDF–TrFE under the influence of an external electric field. Fig. 6 shows the induced pyroelectric coefficient of PVDF–TrFE as a function of temperature under a small external dc electric field of 0.3 V/μm. This field is far below the coercive field of the material, so that no permanent polarization is induced.

The similarity in the induced pyroelectric coefficient in PVDF–TrFE and the dip in the pyroelectric coefficient of the composite suggests an electric field in the copolymer matrix of the composite. Such a field
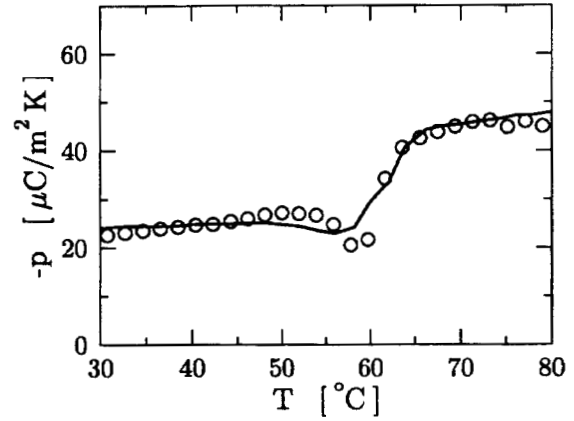
occurs, if the polarization of the ceramic inclusions is not fully compensated by charge on their surfaces. This phenomenon is discussed quantitatively in the following section.

COMPARISON WITH THEORY

Fig. 4 shows a comparison of the measured pyroelectric coefficient of the composite with a calculation according to Eq. (1). The dielectric permittivity of the copolymer ε_m measured on pure copolymer material is shown in Fig. 2. The dielectric permittivity of the ceramic inclusions ε_i cannot be measured directly, as it is likely to differ from that of the bulk material. ε_i is obtained by a fit of the dielectric permittivity of the composite with the Bruggeman model using the measured data for $\varepsilon_m(T)$ and assuming ε_i is temperature independent between 30 °C and 80 °C. As shown in [6] the theoretical prediction is in good agreement with the experimental data, and the dielectric permittivity of the inclusions is determined as $\varepsilon_i = 140$ with negligible imaginary part. After ε_m, ε_i and $\varepsilon(\varepsilon_m, \varepsilon_i)$ are determined from the dielectric measurements and by Eq. (4), the only unknown parameter in Eq. (1) is the pyroelectric coefficient p_i of the inclusions. It is assumed to be temperature independent in the investigated temperature range and determined as $p_i = -160$ μC/cm² by a fit of Eq. (1) to the measured pyroelectric coefficient of the composite beween 30 °C and 50 °C. Fig. 4 shows that the experimental data are well described by the theory at low and at high temperatures. However, the observed dip at the phase transition temperature of the copolymer matrix cannot be described by Eq. (1).

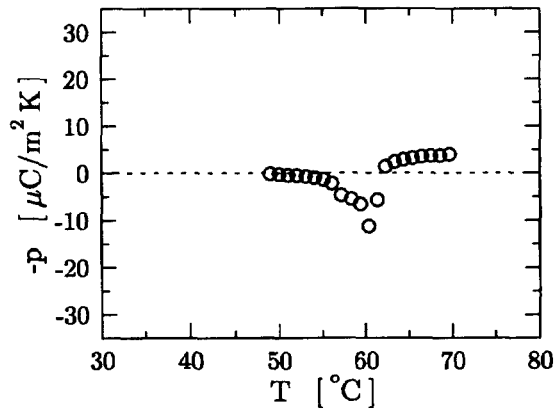In Fig. 5 the measured pyroelectric coefficient of

Fig. 6 : Induced pyroelectric coefficient of unpoled PVDF–TrFE 56/44 mol-% using a small electric field of 0.3 V/μm as a function of temperature.

the composite is compared with data evaluated according to Eq. (2) which takes into account that the polarization of the inclusions may not be perfectly compensated by charge. There are now two fit parameters, p_i and the uncompensated polarization ΔP_r. The derivative $d\varepsilon_m/dT$ is calculated from the measured ε_m (Fig. 3). As shown in Fig. 5 this model can describe the dip at the Curie transition of the matrix with $\Delta P_r = 0.3 \frac{\mu C}{cm^2}$. At high and low temperatures the experimental data are in good agreement with the theoretical prediction using $p_i = -200 \frac{\mu C}{m^2 K}$. I.e., when an uncompensated polarization is assumed to describe the dip at the phase transition, a higher pyroelectric coefficient of the inclusions than determined by the fit with Eq. (1) is obtained. Compared to literature data of the remanent polarization $P_r \approx 50 \frac{\mu C}{cm^2}$ of PT the detected uncompensated part of the polarization is only 0.6 %, i.e., the remanent polarization of the ceramic particles is nearly completely compensated by charges.

The mean electric fields in the inclusions and the matrix after Eqs. (6) and (7) are $E_i = 0.9$ V/μm and $E_m = 0.3$ V/μm. E_i is clearly below the coercive field of PT. The induced pyroelectric coefficient of unpoled PVDF-TrFE and its temperature dependence measured under an external field of 0.3 V/μm shown in Fig. 6 agrees very well with the structure observed in the pyroelectric coefficient of the composite.

CONCLUSION

At temperatures around the Curie transition the dielectric permittivity of PVDF-TrFE shows a strong variation with temperature, and a relatively small electric field can already induce a clearly detectable pyroelectric activity. By including this induced pyroelectric activity into the theoretical prediction of the pyroelectric coefficient of a composite, the dip observed in

the pyroelectric coefficient of PT/PVDF-TrFE composite at the Curie transition temperature of PVDF-TrFE is well described. The analysis of the pyroelectric activity shows that the remanent polarization P_{ri} of the PT particles is nearly fully compensated by interfacial charges. Only about 0.6 % of P_{ri} or 0.3 $\frac{\mu C}{cm^2}$ are uncompensated, causing a small electric field in the copolymer matrix with a mean value $E_m = 0.3$ V/μm. This field shows long term stability; no decrease was detectable after a month.

ACKNOWLEDGEMENT

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