Binding Energies of Trapped Charges in PVDF and P(VDF/TrFE)

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Abstract. The remanent polarization in PVDF and P(VDF/TrFE) is stabilized by trapped charges. We measured the remanent polarization P as function of temperature during heating from room temperature to 180 °C. The discharge current is then computed as the first derivative -dP/dT. Assuming a Debye relaxation and a continous distribution of binding energies g(E) of the trapped charges we can show that the discharge current I(T) is proportional to g(E=mT), with $m = const.$ The constant m can either be calculated numerically or by analytical approximation. With this method the distribution g(E) can be determined. These data are consistent with the extraordinary long life time of the remanent polarisation in PVDF and P(VDF/TrFE) at room temperature.

1 Introduction

PVDF and P(VDF/TrFE) are semicrystalline polymers with small crystalline regions (typical dimension some 100 nm) embedded in an amorphous matrix [2]. The polymer chains have a strong dipole moment normal to the chain direction. Exposed to high electric fields (E>50 MV/m) the crystallite dipoles are oriented [5]. Simultaneously charges are injected into the material [1]. These charges are trapped at the surfaces of poled crystallites [4]. Thus, the polarization is stabilized by the trapped charges. To reduce the polarization charges have to be removed from their traps. Therefore, the trap energy is the activation energy of the depolarization. For a constant temperature an exponential decay of the polarization is expected and the activation energy can be calculated from the decay constant [6]. It is known that the polarisation at room temperature in PVDF and P(VDF/TrFE) is unchanged for years. Therefore we measured the decay of the polarization as function of temperature by increasing the temperature with a constant heating rate of 2K/min from room temperature up to 180 °C.

2 Experimental

The polarization was measured spatially resolved with the PPS method (piezoelectrically induced pressure step wave) [3] with a repetition rate up to 100 Hz. A high voltage step is transformed to a pressure step by a quarz disk and then coupled into the sample. The pressure step probagating in the sample with sound velocity creates a charge displacement short circuit current $i_D(t)$ in proportion to the local polarization $P(x= c \cdot t)$. The displacement current is measured with a braod band amplifier in the outer circuit and detected with a 1GHz real time oscilloscope. In the evaluation we referred to the maximum of the spatial distribution of the polarization.

3 Measurements

a) P(VDF/TrFE):

We determined the thermal depolarization for a 25μm thick P(VDF/TrFE) 65/35 -film which was poled at room temperature for 2 minutes with a field strenght of E=60 MV/m (see fig.1 left). The depolarization decays in a narrow temperature range of about 25 K. From these data we expect a dominant binding energy E_b for the trapped charges or a narrow distribution function. The energy was obtained from the initial slope of the thermal depolarization [6] and we found $E_b = 2.2 \pm 0.5$ eV

b) PVDF:

Unlike P(VDF/TrFE) we find in PVDF a decrease of the polarization within a wide temperature range from poling temperature (20 °C) to 180 °C. (see fig.1 right). The PVDF-sample (38μm thick) was poled at room temperature for 1 minute with a field strength of E=160 MV/m. As evident from the data we obtain a wide distribution function for the binding energies of the trapped charges.

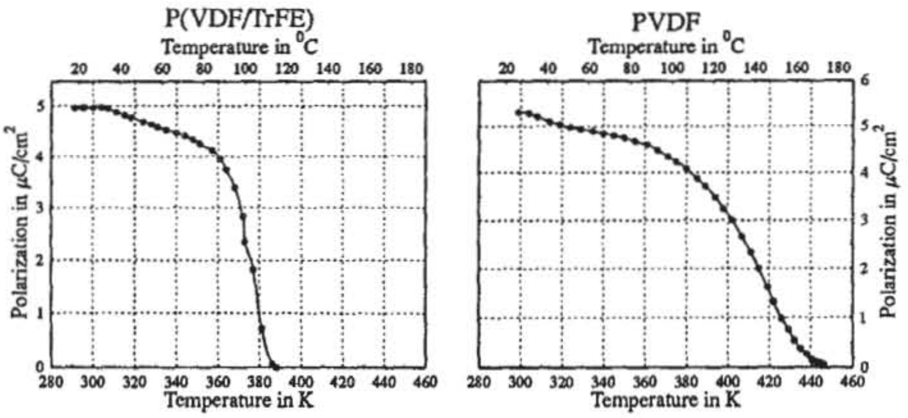

Figure 1: *Thermal depolarization of P(VDF/TrFE) 65/35 (left) and pure PVDF (right)*

4 Theoretical Consideration

Asuming a Debye relaxation $dP/dT=-\alpha(T)\cdot P$ for the polarization P and an Arrhenius law for the decay constant $\alpha(T)$ the temperature dependence of the polarization follows as (see ref. [6])

$$P_a(T) = P_0 \cdot exp\left[-h \cdot \alpha_0 \int_{T_0}^{T} e^{-\frac{a}{T'}}\, dT'\right] \qquad \text{with} \qquad a = \frac{A}{k} \tag{1}$$

with a constant heating rate h^{-1}=dT/dt. α_0 is the natural relaxation frequency, A means the activation energy and k is the Boltzmann constant. The index a indicates that the process corresponds to a single activation energy. For the thermal depolarization current i(T)=-dP/dT we obtain:

$$i_a(T) = \left(h \cdot \alpha_0 \cdot e^{-\frac{a}{T}}\right) \cdot P_0 \cdot exp\left[-h \cdot \alpha_0 \int_{T_0}^{T} e^{-\frac{a}{T'}}\, dT'\right] \tag{2}$$

i_a(T) is a peak with its maximum at

$$T_{max} \approx \frac{a}{m(h \cdot \alpha_0)} \tag{3}$$

and a constant relative width $\Delta T/T_{max}$ for a fixed set of parameters α_0 and h. We found for the dependence $m(h \cdot \alpha_0) = 0.95 \cdot ln(h \cdot \alpha_0) + 4.6$. For a distribution of activation energies the thermal depolarization current results as a superposition of all relaxation contributions with different activation energies.

$$i(T) = \int_0^{\infty} g(a) \cdot i_a(T)\, da \tag{4}$$

where g(a) is the distribution function of the activation energies. If i_a(T) is narrow in comparison with i(T) we can approximate

$$i_a(T) \approx \delta(T - T_{max}) \tag{5}$$

Combining eqn. 5, 3 and 4 we find for the depolarization current

$$i(T) = \int_0^{\infty} g(a) \cdot \delta\left(T - \frac{a}{m}\right) da \tag{6}$$

$$= \int_0^{\infty} g(a) \cdot m \cdot \delta(m \cdot T - a)\, da \tag{7}$$

Thus, the depolarization current is an image of the distribution function:

$$i(T) \propto g(m \cdot T) \tag{8}$$

Taking i(m·T) as the energy distribution function g(a) and using m as a fitting parameter the thermal depolarization can be calculated numerically from eqn 4.

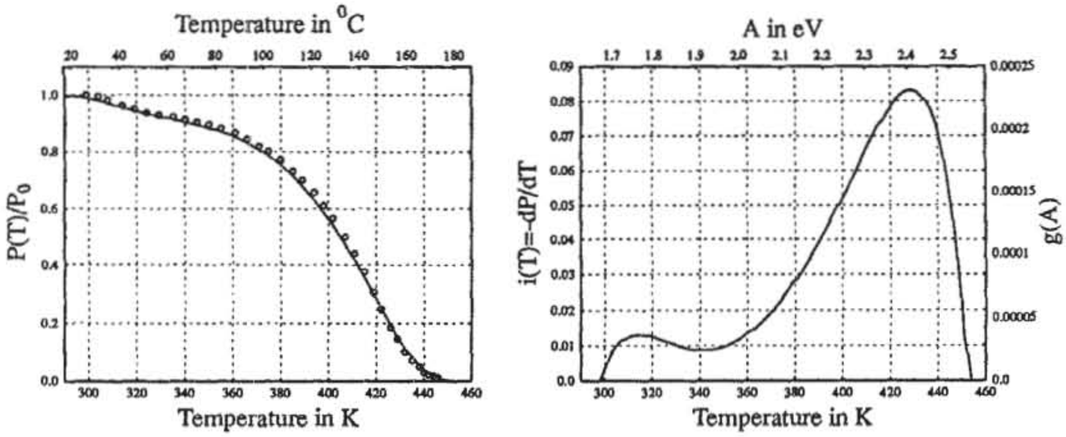

Figure 2: *left: Measured thermal depolarization (o) and result of model calculation (——)*
right: Computed depolarization current and distribution function, respectively

Fig.2 represents the result of this evaluation for the thermal depolarization of the PVDF sample above. The left side of the figure shows the measured data points of the polarization (o) and the result of the approximation (solid line). The right side shows the computed depolarization current and the distribution function for the fit, respectively. Furthermore, by determing m we can calculate α_0. We found for the the fitting parameter m:

$$m=65$$

and for the natural relaxation frequency follows:

$$\alpha_0 = 1.36 \cdot 10^{26}\ s^{-1}$$

For the range of the activation energies we found

$$1.63\ eV < A < 2.52\ eV.$$

For P(VDF/TrFE) this method gives fair agreement between experiment and approximation as shown in fig. 3. The widening of the calculated depolarization is caused by the approximate nature of the model calculation. Nevertheless, it is obvious that the principles are correct, the distribution function is mainly a narrow peak around A=2.2 eV. The fit can be improved by an iteration process resulting in a narrower peak. For the fitting parameter m we found for P(VDF/TrFE)

$$m=66$$

and for the natural relaxation frequency

$$\alpha_0 = 3.9 \cdot 10^{26}\ s^{-1}$$

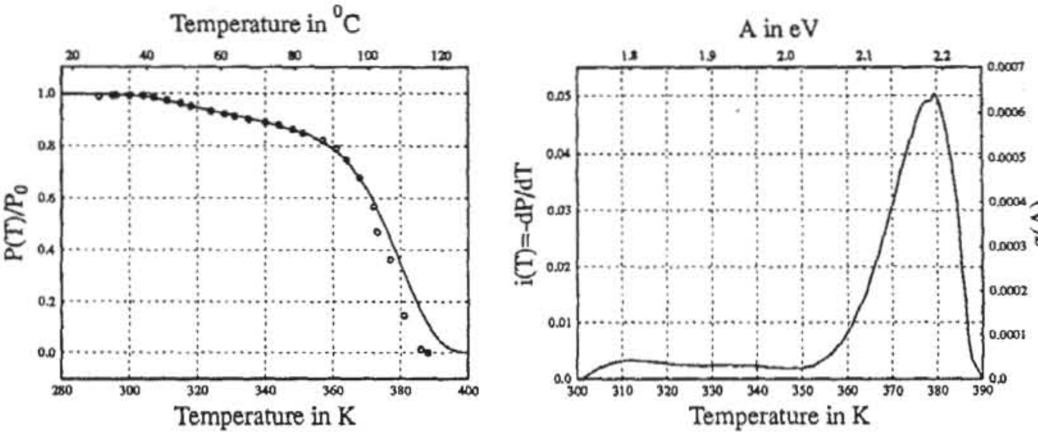

Figure 3: *left: Measured thermal depolarization (∘) and result of model calculation (——)*
right: Computed depolarization current and distribution function, respectively

5 Additional Measurements

In addition to the method discribed above we determined the range of the energy distribution alternatively. On the one hand we performed thermal depolarization measurements using various poling temperatures. The corresponding energy can be determined from the initial slope of the depolarization [6]. On the other hand we did some thermal sampling measurements, where the sample is poled at room temperature and then heated in cycles to higher temperatures. The activation energy results in the same way from the initial slope as if the sample was poled at the preheating temperature. Fig 4 shows the results of the two different measuremants. On the left we plotted the activation energy over the poling temperature, on the right the dependence of the activation energy on the prehaeting temperature is shown. All measurements were made with pure PVDF, 38μm thick.

6 Conclusions

With the determined values of the binding energy and the natural relaxation frequency we are able to explain the enormous stability of the polarisation at room temperature. For P(VDF/TrFE) about 90% of the charges are trapped with an energy around 2.2 eV. This leads to a decay constant at room temperature of $2 \cdot 10^5$ years. For a distribution of binding energies as it is the case for PVDF we of course have a distribution of decay constants. For a decrease of the polarization of 10% we find a decay time of 295 days, for a decrease of 50% the decay time will be $4 \cdot 10^5$ years.

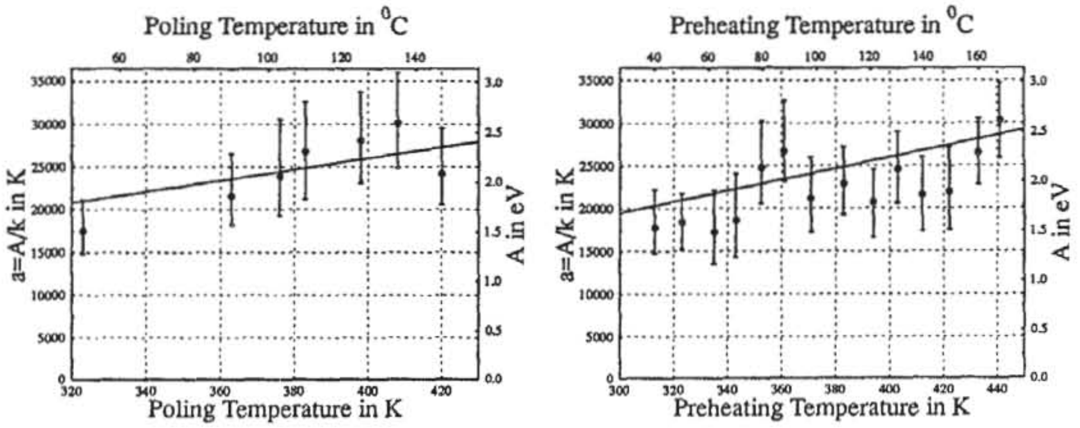

Figure 4: *Minimal activation energy for different poling temperatures (left) and for different preheating temperatures during a thermal sampling measuremant (right). The solid line shows dependence of the activation energy given in eqn. 3*

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