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CORRELATION BETWEEN POLARIZATION AND SPACE CHARGE PHENOMENA IN CORONA POLED FERROELECTRIC POLYMERS

Polarization and space charge phenomena in ferroelectric polymers are interrelated due to existence of the depolarizing field. This field must be compensated anyhow in order to obtain stable residual polarization. It is shown that in corona poled PVDF this compensation is performed by injected and deeply trapped charges. Experimental evidence for the charge trapping has been obtained from the dynamics of apparent conductivity during poling. Irreversible decrease in the conductivity has been observed during the buildup of ferroelectric polarization independently on poling conditions. Appropriate calculations have shown that compensating charges are trapped not at the boundaries of crystallites, as usually believed, but in transition zones separating polarized parts of the volume from non-polarized ones.

1. Introduction

Polyvinylidene fluoride (PVDF) and some of its copolymers belong to the class of ferroelectric polymers, due to possession of spontaneous switchable polarization in one of the crystalline polymorphs called the β phase [1]. It has been proved experimentally that the piezoelectric and pyroelectric coefficients in PVDF were proportional to the magnitude of the remanent polarization [2]. At the same time, there is strong evidence that the injected space charge also affects the specific properties of the ferroelectric polymers [3—5]. The role of the space charge has been discussed for the past twenty years or so, but no agreement has been reached on this point so far. Some researchers believe that presence of space charge in ferroelectric polymers is important, but others think that its influence can be neglected [6]. It is implied in many cases that polarization and space charge do not depend on each other. However, as will be shown below, correlation between them must be certainly considered.

It is known that switching of polarization in ferroelectrics is accompanied by appearance of the depolarizing field that attempts to restore the original electric state with zero average polarization. If this field is not neutralized (or compensated) anyhow, the residual polarization is low and unstable. Compensation of the depolarizing field in conventional ferroelectrics is usually done either by charges adsorbed on the surfaces, or through a short-circuiting of samples between electrodes. In case of the ferroelectric polymers, phenomenon is more complicated, because crystallites are dispersed in disordered amorphous phase. It is not known so far where the compensating charge resides [7—8] and how the charge trapping can be recognized and identified experimentally.

It has been found earlier that the poled PVDF was less conductive than the unpoled one [9]. Measurement in the spatial distribution of polarization has proved that the injection of charges took place and the charges disturbed the uniformity of polarization [3, 5, 7]. We proposed a model for the buildup of polarization in PVDF and other ferroelectric polymers assuming that trapped charges and polarization formed the self-consistent well-balanced system [4, 10—12]. In this work we provide new experimental data on trapping of compensating charges in corona poled PVDF films. It is shown by appropriate calculations that the trapped charges reside at the boundaries of the macroscopic polarized zones.

2. Experimental

The study was performed on 25 μm -thick uniaxially stretched PVDF films containing amorphous and crystalline phases in almost equal proportion. The crystallites consisted of a ferroelectric β phase (56%) and non-polar α phase (44%). Samples were electroded from one side by evaporation of aluminum and placed in corona triode the non-metallized surface exposed to corona ions. A pointed tungsten electrode kept at constant potential of -20 kV initiated the corona discharge. The grid was made vibrating in order to measure effective surface (electret) potential by Kelvin's method directly during the poling and immediately after it was completed [4].

Three different kinds of poling conditions were applied. In the first series of experiments, the quasi-stationary I — V characteristics have been obtained at room temperature by increasing negative d. c. voltage at the control grid in steps of 100 V from 0,6 kV to 3 kV and recording the poling current. The samples were kept at each voltage for 15 min before application of the next voltage step. The ex-

periment was repeated again with already poled samples.

In the second series, the constant current of $80 \mu A/m^2$ was applied periodically for 5 min at room temperature followed by intervals of the same duration when the poling was discontinued [13]. The grid was kept at constant potential of $-3 kV$ while the voltage at the corona electrode was controlled automatically by a feedback circuit, so that a complete poling was performed in 11 charging-discharging cycles. The buildup and the decay of the electret potential were recorded during the corresponding fractions of each cycle.

In the third series of experiments, temperature increased linearly from $20^\circ C$ to $100^\circ C$ at the rate of $3 K/min$, while the grid voltage, and consequently the electret potential, was kept constant. Samples were cooled to room temperature under the applied field and the experiment was repeated again under the same conditions. In presentation of experimental results we use a concept of the apparent conductivity g defining it as

$$g = I_{x_0}/VA,$$

where I is measured current, V is applied voltage, x_0 is thickness of the sample, A is surface area.

3. Results and discussion

There are three elements at $I-V$ characteristics corresponded to three stages of initial poling (fig. 1).

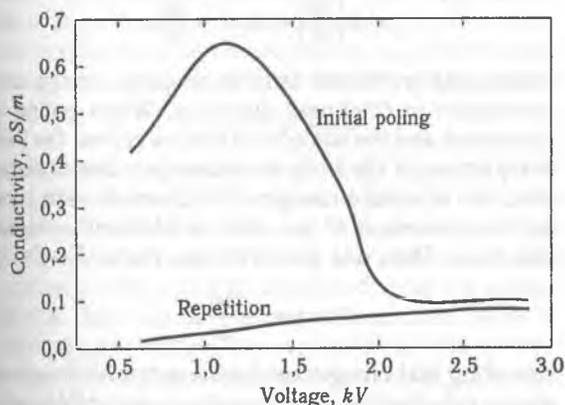


Fig. 1. Dependence of the apparent conductivity on applied voltage. The experiment has been repeated on the poled samples after completion of the initial poling

At first, the current grows faster than the applied voltage until the apparent conductivity reaches its maximum at poling field of $55 MV/m$, being very close to coercive field for PVDF [14]. At the second stage, the conductivity drops abruptly to the minimum at field of $110 MV/m$, followed by slight increase at the higher voltages. Repeated measurements on the same sample show that low values of apparent conductivity are retained in the poled samples, indicating that the changes occurred during the poling are irreversible. The field at the second stage was higher than the coercive value; therefore the

main part of the ferroelectric polarization has been formed at this stage. Since the decrease of conductivity and the buildup of polarization are observed in the same range of the poling field, it is very probable that these two phenomena are interrelated.

Poling conditions have been changed in the second series of experiments, so that the constant current was applied periodically. It is seen in fig. 2 that the electret potential decays almost to zero in 300 s with the time constant of about 200 s after

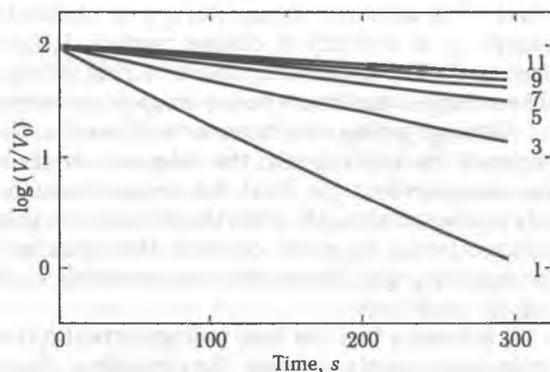


Fig. 2. Decay of the electret potential at intervals between periodic applications of constant poling current. Numbers of the applied poling cycles are indicated beside each curve

completion of the first cycle of poling. This value of time constant corresponds to Maxwell's relaxation time for PVDF at room temperature [15]. The electret potential becomes more stable with increasing number of the poling cycles. For example, the relaxation time of 1300 s was observed after application of 11 poling cycles showing that the apparent conductivity was decreased during the poling in 6,5 times.

At the third series, we observed anomalous behavior of the poling current during the linear increase of temperature at constant applied voltage. as one can see in fig. 3, the apparent conductivity

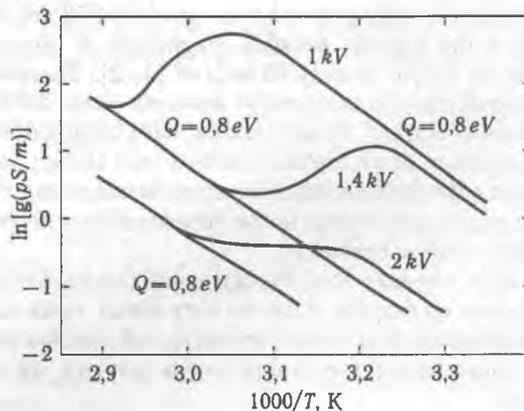


Fig. 3. Dynamics of the apparent conductivity during the initial thermally stimulated poling (solid symbols) and during repeated experiments on the poled samples (hollow symbols). Poling voltage and activation energy are also shown

became lower or remained constant during the poling depending on the value of applied voltage, but the activation energy of the apparent conductivity did not change, being about 0,8 eV in unpoled and poled samples, as it followed from the slope of graphs in fig. 3. It is assumed here that temperature dependence of conductivity obeys the Arrhenius law

$$g = e\mu n_0 \exp\left[-\frac{Q}{kT}\right], \quad (1)$$

where Q is activation energy, k is Boltzmann's constant, T is absolute temperature, e is elementary charge, μ is mobility of charge carriers. It seems that coefficient n_0 becomes smaller during poling, as if free charge carriers are deeply trapped somewhere.

Although poling conditions were different in three series of the experiments, the obtained results had two common features. First, the apparent conductivity decreased abruptly when the ferroelectric polarization started to grow. Second, the decrease in conductivity was irreversible independently on the poling conditions.

It is known that the total poling current $i(t)$ has three components, namely, the capacitive, the polarization and the conductive ones according to the following equation

$$i(t) = \varepsilon_0 \varepsilon \left(\frac{dE}{dt} \right) + \frac{dP}{dt} + gE, \quad (2)$$

where $i(t)$ is current density, ε_0 is permittivity of vacuum, ε is dielectric constant, E is field, P is ferroelectric polarization. The capacitive component represented by the first term at the right side of eq. (2) can be neglected, because we applied constant field at the first and the third series of experiments, while the voltage (electret potential) changed very slowly in the second series. It is not possible to calculate precisely the contribution of the polarization component to the total current, but this can be estimated by comparing the integral of total current with the highest theoretically obtainable value of the residual polarization in PVDF. Our calculations show that the integral under the current peak during the thermally stimulated poling at 1 kV is equal to 260 mC/m², while the highest possible magnitude of polarization in PVDF is only 65 mC/m² [1, 2]. Therefore, the polarization component amounts about 25% of the total current. Similar results were obtained from integration of absorption currents (not shown here) during the first series of experiments showing that the main contribution to the measured current gives conductive component.

It is obvious that the apparent conductivity g depends on density of free carriers which, in its turn, is composed of intrinsic carriers n_0 and injected ones n_i . Considering one kind of mobile carriers, we can write

$$g = e\mu(n_0 + n_i). \quad (3)$$

While n_0 depends mostly on temperature, n_i is effected by poling conditions. It seems that charges in our experiments were injected in the bulk dur-

ing the first stage of poling and then trapped when ferroelectric polarization started to grow. We have shown recently that favorable conditions for trapping of charge carriers exist at the boundaries of polarized crystallites [8, 12]. Let us calculate what would be the density of compensating charges, if they were trapped at the boundaries crystallites. Assuming that PVDF has a brick-like structure [16], shown schematically in fig. 4, we get

$$\bar{n}_c = \frac{abP_s}{eV_c}, \quad (4)$$

where $a = 7,5$ nm and $b = 3,5$ nm are the average length and width of crystallite [16], $V_c = 1,2 \times 10^{-25}$ cm³ is volume occupied by one crystallite together with amorphous phase attached to it, $P_s = 0,14$ C/m² [1] is the spontaneous polarization in crystallites. Calculations give the following value for $\bar{n}_c = 2 \times 10^{20}$ cm⁻³, while the real density of free charge carriers available for trapping is only $n_c = 10^{12} \dots 10^{14}$ cm⁻³, if typical for PVDF values of the apparent conductivity ($10^{-10} \dots 10^{-12}$ S/m) and mobility of charge carriers (2×10^{-8} cm²/Vs) are considered. The difference in value of n_c and \bar{n}_c is so huge that even a massive injection of charges will not provide sufficient number of carriers for trapping at the boundaries of all crystallites. Therefore, compensating charges are not trapped there, although energetic conditions are favorable for this. How then the depolarizing field is compensated? To answer the question, one should consider Poisson's equation

$$\varepsilon_0 \varepsilon \left(\frac{dE}{dx} \right) = \rho(x) + \frac{dP}{dx}, \quad (5)$$

where $\rho(x)$ is volume density of space charge, x is coordinate in thickness direction. When poling is completed and the sample is short-circuited, the field everywhere in the bulk becomes zero due to redistribution of mobile charges. The characteristic time for this process is of the order of Maxwell's relaxation time. Then one gets from eq. (5) at $E = 0$

$$\rho(x) = -\frac{dP}{dx}, \quad (6)$$

indicating that charges can reside in transition zones where polarization is non-uniform and $dP/dx \neq 0$. Thus, conditions for charge trapping are favorable not only at the boundaries of crystallites, but also in macroscopic transition zones separating polarized part of the volume from non-polarized ones, as it is shown schematically in fig. 5.

Trapping of charges in transition zones is very important, because these charges indeed compensate the depolarizing field in the crystallites. To prove this, we consider the definite case, for example, the uniform distribution of polarization in the bulk with narrow transition zones near surfaces [5], as it is shown in fig. 4. At equilibrium conditions the density σ_r of real charge at the surfaces is equal to the density of the polarization charge σ_p , and to the magnitude of the average polarization P' , i. e. $\sigma_r = \sigma_p = P'$. In its turn, $P' = x_c P_s$, where x_c is the crystallinity.

Let us find the field applied to a dipole inside a crystallite positioned, for example, at the point A. If the

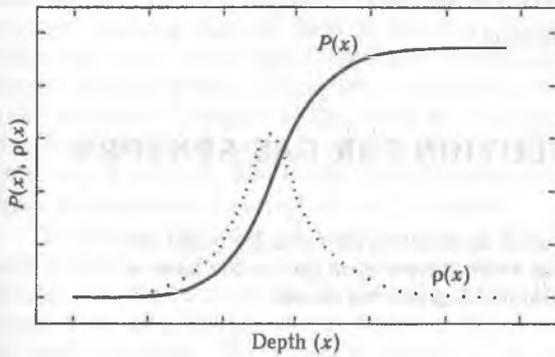


Fig. 4. A typical distribution of polarization and space charge in the thickness direction, according to Poisson's equation. Space charge is localized in a transition zone by which the polarized part of the volume is separated from the non-polarized one

one-dimension approximation is valid, the resulting field is zero, because the number of positively charged layers is equal to that of the negatively charged ones both above this point and below it. Therefore, the depolarizing field inside the crystallites is completely compensated by field of charges trapped either at the surface, or in transition zones. It is easy to show that in both cases the charge density related to the unit area does not depend on thickness of the transition zone and equal to the maximum value of polarization. For example, in order to compensate the depolarizing field in polarized crystallites, the volume density n_v of the trapped charge should correspond to the following equation

$$\sigma_t = x_c P_s = e n_v x_0. \quad (7)$$

Assuming $x_0 = 20 \mu\text{m}$, $x_c = 0,5$, $P_s = 0,14 \text{ C/m}^2$ we get $n_v = 5 \times 10^{16} \text{ cm}^{-3}$ which is lower than the density of intrinsic carriers n_c . This result is rather important, because it shows that there must be sufficient source of free charges during the poling, so that they can be trapped in transition zones in order to compensate the depolarizing field in crystallites. The charges can be either injected, as in case of corona poling, or emitted thermally inside the sample. For example, the required charge can be injected in 15 min, if the poling is performed at room temperature by a constant current of $160 \mu\text{A/m}^2$.

It is known that PVDF poled at elevated temperatures has higher value of residual polarization than that poled at room temperature. The thermal activation, most probably, not only improves alignment of dipoles, as in case of conventional polar electrets, but also provides the high density of free charge carriers necessary for further compensation of the depolarizing field. The electret component of polarization in PVDF is thermodynamically unstable and decays with time, negatively effecting stability of piezoelectric and pyroelectric coefficients. It is clear from fig. 4 that charged layers with density $+\sigma$, and $-\sigma$, remained uncompensated above and

below the point B positioned in amorphous phase. It means that the field created by those layers supports the electret polarization in amorphous phase. Moreover, this field tries to separate positive and negative charges, pressing them to boundaries of crystallites, but this did not affect the field inside crystallites that remained zero, as it has been already shown. Free movement of the separated charges is somewhat constrained and this can be one of the reason why the apparent conductivity decreases during the poling.

4. Conclusion

We have provided some additional experimental evidence on close correlation existing between polarization and space charge in PVDF and shown that the depolarizing field was compensated by charges trapped in macroscopic transition zones by which polarized parts of the volume were separated from non-polarized ones. The compensating charges are first injected in the bulk or created internally by a thermal emission and then trapped when the ferroelectric polarization is being formed. The clarification was necessary, because it was still commonly believed that charges were trapped at the boundaries of crystallites. Moreover, it is often assumed that the poling field itself is created by the trapped charges [6]. It follows from our results, however, that the charge trapping in PVDF and probably in other ferroelectric polymers is not the cause, but rather the result of the polarization buildup.

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