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S.N. Fedosov, A.E. Sergeeva, J.A. Giacometti*, S.G. Polischuk
**Switching of polarization and relaxation phenomena in corona
poled ferroelectric polymers**

*Department of Physics, Odessa State Academy of Food Technologies,
str. Kanatnaya 112, Odessa, Ukraine, 65039
E-mail: aeserg@eurocom.od.ua*

**Instituto de Física de São Carlos,
Universidade de São Paulo, CP 369, 13560-970,
São Carlos, SP, Brazil,
E-mail: giacomet@ifsc.usp.br*

Polarization build-up and switching phenomena in uniaxially and biaxially stretched PVDF have been studied by a constant current corona poling method. The values of the residual polarization and the coercive field have been found, as well as some other parameters. It has been proved that the residual polarization consists of two components, the stable one and the slowly relaxing one. The stabilizing effect of the space charge has been confirmed.

Key words: PVDF, ferroelectric polymers, corona poling, polarization switching.

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I. Introduction

Ferroelectric polymers form a class of dielectrics where highly ordered and disordered phases coexist in one material. Due to high piezo- and pyroelectricity, ferroelectric polymers may replace conventional inorganic materials in sensors and transducers. Specific properties of ferroelectric polymers depend on residual polarization, but processes of its formation and relaxation were not consistently studied so far.

Several techniques have been used for poling of ferroelectric polymers. In samples with metal electrodes, a dc constant voltage can be applied. In the case of "hysteresis poling", a periodically varying bipolar voltage exceeding the positive and negative coercive fields is applied [1]. In corona poling, ions generated by a corona discharge bombard the bare sample surface and no electrode is required on this side. In a corona triode, a grid is inserted between the sample and the pointed electrode in order to control the poling process [2]. Recently, the corona triode was improved to allow poling under constant current by controlling the grid voltage [3]. The sample potential as a function of time can be readily measured from the grid voltage [4] and the polarization buildup and switching phenomena can be studied [5].

In this paper we applied the constant-current corona poling to study polarization processes in PVDF films. The relationship between the potential buildup curves and polarization switching has been found and values of

the residual polarization and the coercive field obtained. The relaxation processes in poled samples have been studied by the thermally stimulated depolarization (TSD) current method.

II. Constant current poling and switching of polarization

The study was performed on biaxially and uniaxially stretched PVDF films of 10-30 μm thickness produced by Kureha Chemical Co., Japan and Plastpolymer, Russia. A specially designed corona triode (Fig. 1) was used to pole samples at constant current conditions [6]. The value of the electret potential was measured continuously during poling. It has been found that the initial poling and switching process in dry air in all studied samples consisted of three stages, each one corresponding to a definite part of the potential-time curve (Fig. 2). The fast increase of the surface potential was observed at the first stage indicating that the capacitive component prevailed in the poling current. At the second stage, there was a plateau at the voltage-time curve related, most probably, to the switching of the ferroelectric component of polarization [7]. The surface potential again increased sharply at the third stage where the switching has been completed. If poling was repeated with the same polarity

of corona, the plateau was not seen. It is known that polarization is distributed uniformly in samples poled in dry air [8]. In case of humid air, saturation of voltage has

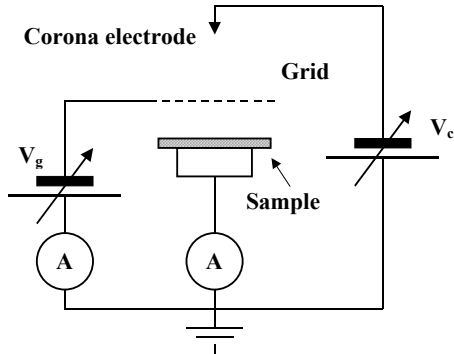


Fig. 1. Schematic diagram showing the experimental set-up for a constant current corona poling.

been observed indicating that the conductivity component of the current existed. The distribution of polarization in this case was non-uniform due to effect of the injected charge carriers [9]. Polarization (P) in ferroelectric polymers depends nonlinearly on the field (E), so the P(E) function is presented by a hysteresis loop. From this curve, such important parameters as

uniformly distributed in the thickness direction of the film. If conductivity is neglected, there will be three components of polarization, electronic (P_e), dipole (P_d) and ferroelectric (P_f) ones. It is reasonable to assume also that all the components follow the electric field, since poling process is relatively slow (quasi-stationary case). The field dependencies of P_e and P_d are linear in the whole range of poling fields, while $P_f(E)$ is given by the hysteresis loop. The following is the general expression for the poling current

$$I_0 = i_0 A = (\epsilon_0 A/x_0)(\epsilon_e + \epsilon_d + \epsilon_f + \epsilon_f')(dV/dt), \quad (1)$$

where i_0 is the current density, A the sample area, x_0 the sample thickness, ϵ_0 the permittivity of a vacuum, ϵ_e , ϵ_d , ϵ_f the electronic, dipole and ferroelectric dielectric constants, ϵ_f' corresponds to unstable part of the ferroelectric polarization, V the time dependent electret potential. If E_c and E_s are the coercive field and the field corresponded to the onset of the saturated polarization, then $\epsilon_e \neq 0$ and $\epsilon_d \neq 0$ in all experiments and at all fields; $\epsilon_f \neq 0$ and $\epsilon_f' = 0$ during the initial poling and switching experiments in the range of $E_c \leq E \leq E_s$; $\epsilon_f = 0$ and $\epsilon_f' \neq 0$ during the repeated poling at $E \leq E_s$.

Calculations performed using Eq.(1) and inclinations at the initial parts of curves I and IV give $\epsilon_e + \epsilon_d = 9$. The

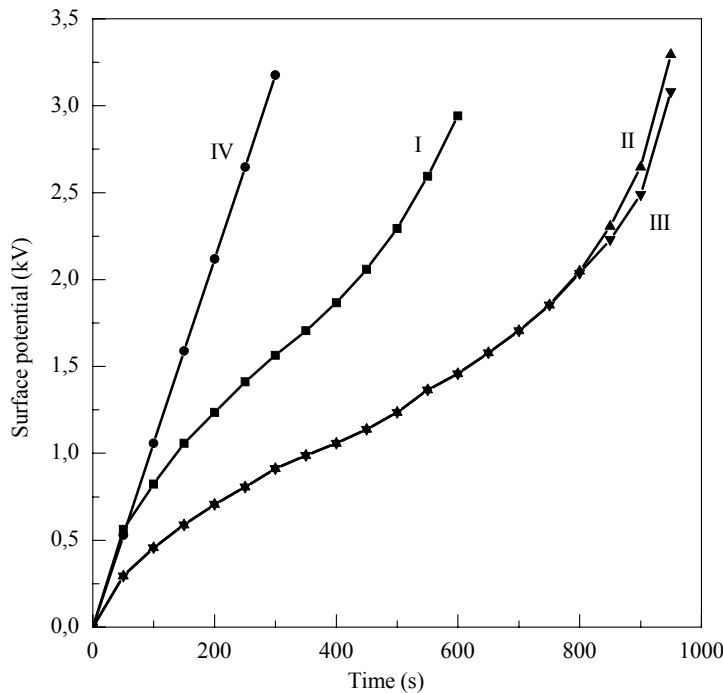


Fig. 2. Potential buildup curves for a 12 μm PVDF sample poled at ± 30 nA in dry air. Curve I corresponds to the first positive charging. Curves II and III correspond to subsequent charging with negative and positive corona polarity, respectively. Curve IV corresponds to the repeated poling in a positive corona.

remnant polarization and coercive field can be found. The P(E) dependence can be obtained from the curves shown in Fig. 2. The following is a simplified description of the method and an example of its application.

Let us assume that polarization and field are

plateau at curves II and III corresponds to the switching of the ferroelectric polarization. We got there $\epsilon_e + \epsilon_d + \epsilon_f = 104$. In the middle of the curve II calculations give $\epsilon_e + \epsilon_d + \epsilon_f' = 13,4$. Assuming $\epsilon_e = 2$ one gets finally, $\epsilon_d = 7$, $\epsilon_f = 95$, $\epsilon_f' = 4$. From the plateau on curves II and

III we obtained $E_c = 100$ MV/m $E_s = 230$ MV/m. It follows from our results that one part of the ferroelectric polarization is unstable, because the curve IV is not a straight line and a part $\Delta P = P_s - P_r$ is lost after poling is completed. ΔP can be calculated as $\Delta P = i_0 \Delta t_1 = 4$ mC/m² where Δt_1 is the time difference between the real curve

III. Thermally stimulated depolarization of poled PVDF

The thermally stimulated depolarization (TSD) is known as a powerful method of studying relaxation processes in polymer electrets. Although a theory of the

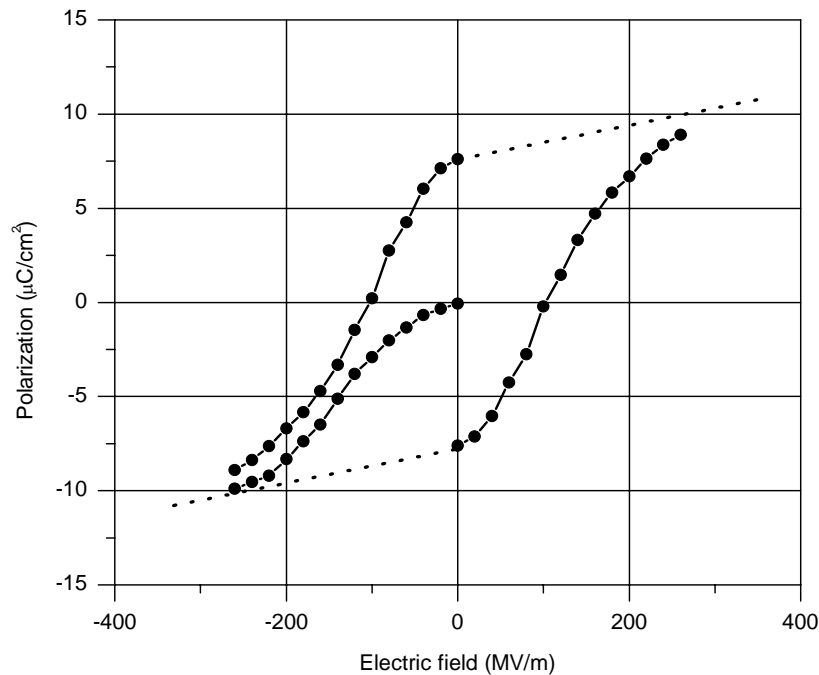


Fig. 3. The P(E) hysteresis loop calculated using the results shown in Fig. 2.

IV and the straight line extrapolating the initial part of this curve. Calculations show that the polarization changes during the switching by $\Delta P_f = 132$ mC/m². From another side, $\Delta P_f = 2P_r + \Delta P$. Considering $\Delta P = 4$ mC/m², we got $P_r = 64$ mC/m² and $P_s = P_r + \Delta P = 68$ mC/m². With each subsequent switching P_r increased by $\Delta P' = 3$ mC/m² (not shown in Fig. 2) This is consistent with hysteresis measurements that show small increase of the remanent polarization after every cycle [1]. The hysteresis loop calculated from the data of Fig. 2 is shown in Fig. 3.

We also poled extruded and uniaxially stretched PVDF films of $x_0 = 25$ μ m thickness in normal humid conditions at current density of $i_0 = 100$ μ A/m². The steady-state current at 2,7 kV was found to be $i_s = 9$ μ A/m² corresponded to the conductivity $g = 8 \cdot 10^{-14}$ Ohm⁻¹m⁻¹. The dielectric constant $\epsilon_f = 40$, the saturated polarization $P_s = 42$ mC/m² and the coercive field $E_c = 48$ MV/m have been obtained, all values being lower than those found for the biaxially stretched PVDF. Obtained values of conductivity, remanent polarization and coercive field for PVDF are in agreement with the data reported in other studies [10,11].

method has been developed mostly for thermally frozen Debye processes [12], it has been often used to study relaxation in ferroelectric polymers [13,14]. We have shown recently that trapped charges play an important role in the buildup of polarization [15,16]. In this paper we study TSD currents in corona poled PVDF in order to distinguish between relaxation of the polarization and that of the space charge. TSD currents were measured at the heating rate of 4 K·min⁻¹ in the open circuit (OC) mode with a 25 μ m-thick FEP-Teflon spacer used as a dielectric gap. It is known that in the OC mode both the relaxation of dipoles and that of the space charge produce TSD current peaks, seen on the opposite sides from the zero line. A group of corona poled samples was studied 1 h after poling, but another group was stored after poling for 14 months before the TSD measurements have been performed.

There were two oppositely directed TSD peaks at the samples studied immediately after poling (Fig. 4). Comparing TSD currents on freshly poled samples with those stored for 14 months, we have found that two additional peaks appear in the range from 60 °C to 80 °C at the samples stored for a long time. The obtained results indicate that probably four relaxation processes are involved, two of them are associated with the dipole relaxation and another two related to the space charge.

To explain existence of four relaxations, one should consider that ferroelectric polymers differ notably from polar electrets. The former have not only ferroelectric β phase crystallites, but also a polar amorphous phase typical for electrets. Therefore, both the ferroelectric polarization and the dipole electret polarization must be present. Moreover, it seems that both of them are accompanied by two kinds of the space charge. It is known that polarization in electrets is usually thermally frozen and thermodynamically unstable, while the ferroelectric polarization is stable, provided the depolarizing field is neutralized anyhow [17]. The most easily this can be done by the surface or space charge. As one can see from Fig. 4, the space charge (positive)

the dipole polarization in amorphous phase, but at this stage it is difficult to distinguish between slowly relaxing dipole polarization in amorphous phase and the unstable (not completely compensated) part of the ferroelectric polarization. In any case, to obtain the high and stable polarization in ferroelectric polymers, it is necessary to remove the unstable component.

IV. Conclusion

The developed method of studying hysteresis phenomenon and obtaining the P(E) dependence gives accurate and reliable values of the four important parameters of any ferroelectric material, i.e. dielectric

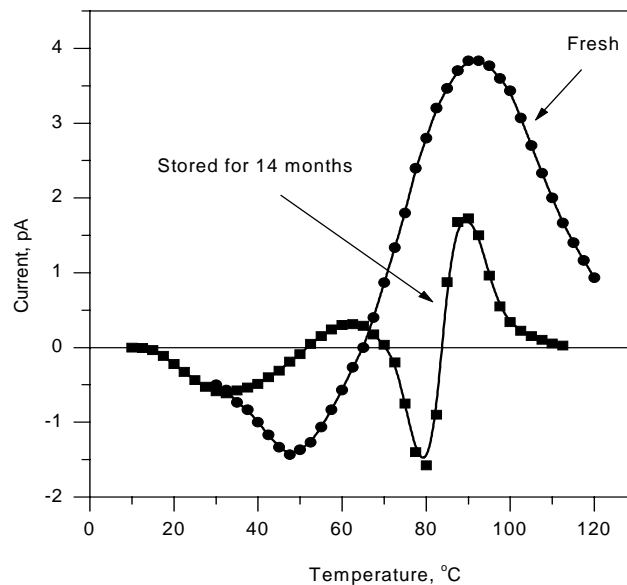


Fig. 4. The TSD current of PVDF poled in a negative corona at 100 °C with 2 kV of grid voltage.

peaks appear at higher temperature than the dipole ones pointing out that the space charge is generally more stable than the dipole polarization.

Since the crystalline phase is ferroelectric, the electret part of polarization is concentrated, most probably, in the amorphous phase. Considering the above mentioned, the TSD peaks of the aged samples (Fig. 4) can be attributed to the following processes. The negative peak at 53 °C corresponds to the dipole relaxation in amorphous phase, the positive peak at 70 °C reflects relaxation of the space charge associated with the dipole polarization in amorphous phase, the negative narrow peak at 78 °C is related to the ferroelectric polarization and the positive peak at 85 °C corresponds to relaxation of the space charge by which the depolarizing field is neutralized. In fresh samples only two peaks are seen, because at low temperatures the dipole polarization dominates over the space charge and at high temperatures the space charge peak suppresses the ferroelectric polarization peak. Our calculations have shown that the surface or space charge can stabilize not only the ferroelectric polarization in crystallites, but also

constant, apparent conductivity, remnant polarization and coercive field. All data necessary for calculations are obtained by direct measurements in one sequence of experiments. The method can be recommended for materials having hysteresis-like dependence of polarization from applied field.

It follows from our results that very slow redistribution of charges and polarization takes place in ferroelectric polymers after poling is completed, until the electret and ferroelectric components of polarization are finally separated, both accompanied by the trapped charges.

S.N. Fedosov – Dr. Phys.-Math. Sci., Prof. of Physics Depart.;

O.E. Sergeeva – Dr. Phys.-Math. Sci., Prof., Head of Physics Depart.;

J.A. Giacometti – Professor of the Physics Department, University Sao Paulo;

S.G. Polischuk – Cand. Techn. Sci., Docent of Physics Depart.

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С.Н. Федосов, О.Є. Сергєєва, Ж.А. ДжиакOMETTІ, С.Г. Поліщук

Переключення поляризації та релаксаційні явища в сегнетоелектричних полімерах, електризованих в коронному розряді

*Department of Physics, Odessa State Academy of Food Technologies,
str. Kanatnaya 112, Odessa, Ukraine, 65039, E-mail: aeserg@eurocom.od.ua*

**Instituto de Física de São Carlos,
Universidade de São Paulo, CP 369, 13560-970,
São Carlos, SP, Brazil, E-mail: giacometi@ifsc.usp.br*

Явища розбудови та переключення поляризації в одноісно орієнтованих плівках полівініліденфториду вивчались методом коронного зарядження постійним струмом. Було знайдено величини залишкової поляризації та коерцитивного поля, а також встановлені деякі інші параметри. Було доведено, що залишкова поляризація складається з двох частин, а саме з стабільної та повільно релаксуючої компонент. Була підтверджена стабілізуюча дія просторового заряду.