Distribution of the Ferroelectric Polarization in Polyvinylidene Fluoride During Initial Poling and Polarization Reversal

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The polarization profiles dynamics in polyvinylidene fluoride (PVDF) films was studied in situ by the piezoelectrically induced pressure step method. It was shown that a substantially inhomogeneous polarization profile was formed during poling and reversal switching in medium fields with the maximum of polarization near the positive electrode. However, poling of virgin samples in strong fields resulted in formation of a homogeneous polarization profile that remained uniform and easily switchable at any subsequently applied field. It appeared that it was impossible to improve the polarization homogeneity in PVDF by application of strong fields, if original poling was performed in weak or medium fields. The observed features were explained by a model assuming injection of negative charges and formation of a permanent blocking layer at the boundary between polarized and non-polarized zones. The obtained results should be considered while selecting poling conditions in design and production of sensors and actuators based on PVDF. The results have a practical importance in design of piezo- and pyro- sensors and activators using the ferroelectric PVDF films, because they should be considered while selecting poling conditions.

Keywords: Ferroelectric polymers, Polarization distribution, PVDF.

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1. INTRODUCTION

Ferroelectric polymers, of which polyvinylidene fluoride (PVDF) is a typical representative, have attracted scientists and technologists as candidates for a partial replacement of inorganic ferroelectrics in the field of sensors and actuators due to excellent mechanical properties of the polymers [1]. One of the important characteristics of charged PVDF films is the spatial distribution of polarization in the thickness direction, because the inhomogeneous distribution distorts piezo- and pyroelectric activity [2]. Therefore, a few experimental methods were applied for studying the distribution of polarization, such as the laser-intensity-modulation (LIMM) [3, 4], the laser-induced pressure pulse (LIPP) [5] and the piezoelectrically-generated pressure step (PPS) methods [2, 6].

Most methods for studying polarization profiles in dielectrics were applicable to already poled samples providing information about the final state, while the process of polarization formation remained inaccessible to direct experimental study. In this sense, a unique opportunity was provided by the PPS method [2], by which it was possible to perform in-situ measurements of the polarization profile directly during application of the polarizing voltage, short circuiting of the sample, changing direction and magnitude of the externally applied electric field. Such measurements of the polarization profile dynamics were extremely important for understanding physical processes occurring in ferroelectric polymers during their poling and the polarization reversal and for selection of poling regimes.

Considering the above mentioned, the aim of our study was to clarify physics of the polarization distribution formation during initial poling of PVDF, the short circuiting and the polarization reversal by applying middle fields close to the coercive value $E_c$ and strong fields much higher than $E_c$.

It has been found that the distribution of polarization was considerably inhomogeneous in the case of middle fields, while it was homogeneous and uniformly switchable in the strong fields. It has appeared that polarization uniformity cannot be improved by application of even very strong field, if initial poling was performed in weak or middle fields. This effect was of significant practical importance and showed how strong the relationship between polarization and space charge was. A corresponding physical model has been suggested and described assuming important role of injected charges and their coupling with the already formed ferroelectric polarization [6-9].

2. MATERIALS AND METHODS

2.1 Samples

We investigated extruded 20-30 μm thick ferroelectric polymer films of PVDF from pilot batches produced by the Plastpolimer Co., Saint Petersburg. The films were uniaxially stretched in a ratio of 1:4 at 100 °C and annealed at 120 °C for 1 hour. The degree of crystallinity was (47±3) % according to manufacturer's data. The average sizes of crystallites according to the results of X-ray analysis had the following values: $L_α = 96±6$ Å, $L_β = 70±8$ Å. The ratio between non polar $α$-phase and ferroelectric $β$-phase was 43:57 according to the magnitudes of peaks at 535 and 510 cm⁻¹ measured by the FT-IR Perkin-Elmer 1750 IR spectrometer.

2.2 PPS method

We applied PPS method based on propagation of a pressure step with a very steep front through a sample.
The pressure wave propagated in the thickness direction creating a current pulse, the shape of which repeated the profile of the polarization distribution over the film thickness [2]. The method and the setup schematic were described elsewhere [2, 6].

All used instruments (amplifier, spectrum analyzer, and oscilloscope) had a bandwidth of more than 1 GHz. The used experimental method provided a sufficient resolution of about 2 μm for films of 20-30 μm thickness used for constructing piezo- and pyro-sensors. It is known that the LIMM method assures better spatial resolution but only in the very narrow near-to-electrode region [3, 4].

Several series of experiments on PVDF films were carried out for studying the polarization profiles. Al electrodes of 4.5 mm diameter were preliminarily deposited on both sides of the samples by evaporation in vacuum. Initial poling, short-circuiting and polarization switching were carried out at room temperature by applying a DC voltage of a certain magnitude and polarity. The polarizing and switching field in a number of experiments was 60 MV·m⁻¹, i.e. slightly higher than the coercive field of PVDF (50 MV·m⁻¹) [7]. Such a regime was referred to as "medium fields". In other experiments, the field was 160 MV·m⁻¹, i.e. significantly higher than the coercive value. Such regimes were referred to as "strong fields". In both medium and strong fields, full cycles of poling and polarization reversal were studied on each sample. After each stage of poling or switching, the samples were short-circuited for the time sufficient to establish a quasi-stationary state (2000 s).

All results were presented in a form of graphs showing polarization versus the inward distance measured from the sample surface.

3. RESULTS

3.1 Poling and Switching in Medium Fields

As shown in Fig. 1 obtained under middle field of 60 MV·m⁻¹, the following features characterize the dynamics of the polarization profile:

1. The polarization distribution was uniform at the initial stage of poling (8 seconds after the start), but its magnitude was very low (0.5 μC·cm⁻²).

2. The polarization distribution over the film thickness became gradually non-uniform with a maximum near the positive electrode.

3. After completion of poling, a strongly asymmetrical distribution of the residual polarization was formed with a 5-7 μm thick region with zero polarization near the negative electrode.

4. When the sample was short-circuited after switching on the applied voltage, the distribution pattern of the polarization did not change and remained non-uniform, but the polarization in the region of the maximum decreased from 3.31 to 1.71 μC·cm⁻².

After changing the voltage polarity (Fig. 2), a minimum was formed at the spot of the former maximum at a depth of about 16 μm. The polarization at this point was not switched to the opposite direction, but was not even reached a neutral zero state.

Fig. 1 – Evolution of the polarization profile in PVDF films poling in the field of 60 MV·m⁻¹. The stage number corresponded to different times after starting the poling process: 1 – 3 s, 2 – 7 s, 3 – 100 s, 4 – 150 s, 5 – 250 s, 6 – 350 s, 7 – 450 s, 8 – 750 s, 9 – 1000 s, 10 – 1510 s, 11 – 2000 s.

Fig. 2 – Evolution of the polarization profile in PVDF during polarization reversal in the field of 60 MV·m⁻¹ after initial poling and short-circuiting. The stage number corresponded to different times from onset of the switching: 1 – 0 s, 2 – 0.2 s, 3 – 0.5 s, 4 – 1 s, 5 – 5 s, 6 – 50 s, 7 – 200 s, 8 – 500 s, 9 – 1000 s, 10 – 1500 s, 11 – 2000 s.

At the same time, an oppositely directed polarization was formed to the right and to the left from this section. Strong polarization was again formed near the positive electrode. It should be noted that the switching of polarization was faster than its formation during initial poling. Comparison of the polarization profiles after several reversals had shown that almost identical profiles were formed after the even number of reversals. In the case of the odd number, the profiles were also identical, except for the profile after first poling, when there was still no reversed polarization zone near the negative electrode.
Thus, the profile was determined by whether the number of polarization reversals was either even, or odd. In both cases, the polarization distribution was non-uniform and asymmetrical. The residual polarization in the peak zone was almost 1.5 times higher than after initial poling.

The main polarization maximum, regardless of the phase parity, was always near the positive electrode in the last experiment, and the magnitude of this maximum was almost 1.5 times greater in the case of the even number of polarization reversals than in the case of the odd number of the reversals. The time of the quasi-stationary state formation decreased with the increase in the number of reversals from 2000 s during initial poling to 250-500 s during the reversals.

3.2 Poling in Strong Fields and the Subsequent Polarization Reversal

In the case of strong fields (160 MV·m⁻¹), as can be seen from Fig. 3, the polarization was much more homogenous than in the case of the middle fields.

![Fig. 3 – Evolution of the polarization profile in a PVDF film poled at 3 kV when a voltage of the opposite polarity and different magnitude was applied. Stages: 1 – initial state, 2 – 1.2 kV, 3 – 1.6 kV, 4 – 2.0 kV, 5 – 2.4 kV, 6 – 2.8 kV, 7 – 3.2 kV.](image)

The polarization homogeneity appeared even during initial poling. When the voltage polarity was changed, a symmetrical switching of the polarization took place. By applying a voltage of the opposite polarity and increasing it in small steps, it was possible to completely depolarize the sample. The field at which this occurred corresponded to 50 MV·m⁻¹. Namely this value can be considered as the true coercive field for PVDF.

The main features of poling and polarization switching in the strong field were as follows:

1. The polarization in the sample volume was uniform and symmetric with respect to the central section;
2. There was no difference in the profile shape and the magnitude of the polarization at different polarities of the polarizing voltage;
3. Polarization easily switched over the entire volume, and full depolarization was possible;
4. The homogeneity of polarization persisted not only in the strong field, but also in the middle field.

The effect of "formatting" in the strong field that we observed was important for practice, since the uniform polarization can be obtained at any field including coercive one. This makes it possible, if necessary, to change the magnitude and sign of the polarization over a wide range from zero to saturation that cannot be achieved without the specified formatting.

3.3 An Attempt to Improve the Non-uniformity of Polarization

It follows from Fig. 1 and Fig. 2 that the polarization is non-uniform in the case of average fields (60 MV·m⁻¹) at any voltage polarity. The resulting bimorph structure is formed independently of the direction of the external switching field. At the same time, a uniform polarization is formed during poling in the strong field of 160 MV·m⁻¹ and remained uniform after any change in the magnitude and sign of the voltage up to complete depolarization.

![Fig. 4 – Evolution of the polarization profile in PVDF after voltage increase from 1.2 kV (initial poling) to 3.2 kV in steps of 0.2 kV. The duration of each voltage application was 50 s.](image)

In this connection, it was of interest to investigate the behavior in the strong field of the films initially electrified in the middle field. If the initial polarization inhomogeneity was due to not sufficiently strong poling field, then the homogeneity of the polarization should be improved after subsequent application of the strong field. However, we have found that the polarization did not become uniform under the action of the strong field (Fig. 4).

The experiments were carried out on fresh PVDF films placed in the field of 60 MV·m⁻¹. As can be seen from Fig. 1 and Fig. 2, the spatial distribution of the polarization was non-uniform. Then without stopping measurements of the polarization profile, the voltage was increased in steps of 200 V up to 3.2 kV, i.e. to the values creating strong fields, several times higher than the coercive value $E_c$. However, as seen in Fig. 4, the increase in the field strength did not result in the expected improvement of the polarization homogeneity.
Only the magnitude of the maximum increased, while the non-uniform character of the polarization distribution remained unchanged.

Thus, for obtaining a uniform residual polarization, it is necessary to take into account under what conditions the sample was polarized for the first time.

If initial poling was carried out in a strong field, then the residual polarization was uniform. If the first charging was carried out in medium or weak fields, the inhomogeneity of the polarization cannot be eliminated by further application of a strong field.

The discovered effect was important for selecting proper parameters of initial poling. For obtaining the homogeneous distribution of polarization in the samples with already formed inhomogeneity, we performed a complete thermal depolarization of the sample by annealing it in the short-circuited state at a temperature of 160°C for two hours. After cooling, the sample was re-electrified by applying the strong field and it showed a uniform distribution of the polarization.

4. DISCUSSION

Polarization in PVDF consists of three parts. Firstly, it is reversible capacitive component $P_{cap}$ that disappears in a very short time after disconnecting the external voltage [7-9]. Secondly, it is also reversible component $P_e$ ascribed to the amorphous phase [9], and thirdly it is a switchable ferroelectric polarization $P_{fe}$ remaining in the short-circuited sample, if the depolarizing field is compensated. Therefore,

$$ P = P_{cap} + P_{fe} + P_{re} $$  \hspace{1cm} (1)

The reversible (capacitive) polarization component depended on the field strength and the permittivity

$$ P_{cap} = \varepsilon_o (\varepsilon - 1) E $$  \hspace{1cm} (2)

Assuming $\varepsilon = 16$ [10] and taking into account that $\varepsilon_o = 8.85 \times 10^{-12}$ F m$^{-1}$ and $E = 60$ MV m$^{-1}$ in the case of the middle field, we obtained $P_{cap} = 0.79 \mu$C cm$^{-2}$.

It was shown in [9] that in PVDF, in addition to the capacitive $P_{cap}$ and ferroelectric $P_{fe}$ components of polarization, there was also an additional reversible $P_{re}$ component, the presence of which was associated with the dipole polarization in the amorphous phase of the polymer. The relationship between the polarization components can be established by analyzing the evolution of the polarization profile after switching off the voltage and short-circuiting the sample. At the initial stage of poling in the middle field, all three components of the polarization were present. However, the ferroelectric component was very weak since the field was close to the coercive value.

Polarization became non-uniform (Fig. 1) indicating appearance of the inhomogeneous distribution of the field strength with its weakening near the negative electrode and strengthening near the positive electrode. According to the Poisson equation, the inhomogeneous polarization of this kind was possible only in presence of excess negative charges in the region of the field and polarization inhomogeneity.

$$ \varepsilon_o \frac{\partial E(x,t)}{\partial x} = \rho(x,t) - \frac{\partial P(x,t)}{\partial x}, $$  \hspace{1cm} (3)

where $\rho(x,t)$ was the volume density of the real excess charge. Since the applied voltage remained constant ($U_0 = \text{const}$), the normalization condition was fulfilled

$$ \int_0^x E(x,t)dx = U_0 $$  \hspace{1cm} (4)

$P_{max} = 3.31 \mu$C cm$^{-2}$ (Fig. 1) at the point of maximum polarization. After the short-circuiting, the reversible components $P_{cap}$ and $P_e$ disappeared and only the ferroelectric component remained, i.e. $P_{fe} = P_{re}$, with $P_{fe} = 1.71 \mu$C cm$^{-2}$ (see Fig. 2). The process of the polarization formation was rather slow, so the experiment time was much longer than the Maxwell relaxation time

$$ \tau_M = \frac{\varepsilon_o E}{g} \approx 5 \text{ s}, $$  \hspace{1cm} (5)

where $g = 3 \times 10^{-11}$ S m$^{-1}$ [7-9] was the intrinsic conductivity of PVDF. The capacitive component of the polarization was $P_{cap} = 0.79 \mu$C cm$^{-2}$ according to (2). Then, the reversible component of the polarization was equal to $P_{re} = P - P_{cap} = 0.81 \mu$C cm$^{-2}$.

Since the reversible polarization, most likely, was due to the dipole structure of the amorphous phase, it can be taken into account by introducing the effective permittivity including all reversible processes

$$ \varepsilon_{eff} = \frac{P_{cap} + P_{re}}{\varepsilon_o E} = 20.2. $$  \hspace{1cm} (6)

The obtained value is of the same order as used by von Seggern and Fedosov [7] ($\varepsilon_{eff} = 19.6$) in calculating the two-stage formation of the ferroelectric polarization in PVDF.

It is known from the theory of injection currents [11] that the field strength near the injecting electrode is very small or zero. However, just the injection of charges cannot explain the presence of a 5-6 μm thick region with almost zero field and polarization. Obviously, there was another phenomenon leading to the field and polarization decrease with time near the negative electrode.

It is known that during formation of the ferroelectric polarization in PVDF, the effective conductivity decreases [7]. Therefore, we can assume that the conductivity of the polarized part of the sample was much smaller than that of the non-polarized portion. Then the total applied voltage $U_0$ was divided between non-polarized and polarized parts as between two series-connected resistors. The voltage, and consequently the field strength are small at the non-polarized part, but it is increased at the polarized part. This division of voltage together with the current injection could contribute to the formation of polarization inhomogeneity.

When the localization of injected charges occurred at the boundary between polarized and non-polarized regions in accordance with the Poisson equation (3), the charged layer formed an obstacle for penetrating other
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charges from non-polarized region to the polarized one.

The explained phenomenon led to formation of the three-layer structure, schematically shown in Fig. 5.

![Fig. 5](image)

In the region adjacent to the negative electrode, a high concentration of injected charges was observed, as well as the high conductivity, the low field and a very small polarization. At the boundary between non-polarized and polarized regions, a layer of the localized negative charge was formed. Within this layer, the polarization increased sharply from zero to the maximum value. In the third zone, the uniform field, the small effective conductivity, and the uniform polarization were observed.

When the sample was short-circuited after ending of poling, the average field became zero. At the same time, the direction of the field vector \( E_1 \) in the non-polarized part of the sample (Fig. 6) became such that excess non-localized injected charges from the first zone were "blown out" through the electrode that was negative during poling. The field at all points of the sample became zero with the time constant equal to the Maxwell relaxation time (5), as shown in Fig. 6. Finally \( E(x, t) = 0 \) everywhere, while the excess charges remained localized at the slope of the polarization curve in accordance with Poisson's equation (3).

The obtained results corresponded to the model that assumed an important role of the space charge and injection of charge carriers from electrodes in the formation of polarized zones in PVDF. The concept of the close interrelation between trapped charges and the ferroelectric polarization in PVDF was suggested and proved in several publications [7-10]. Experimental data indicated that in the case of widely used Al electrodes, the level of injection from the negative metal electrode was higher than from the positive electrode. It was also possible that the mobility of injected negative carriers was higher than that of the positive carriers. Own intrinsic carriers in PVDF played a secondary role in this case.

In the case of the short-circuiting after completing of poling, the field in the peak region supported the residual polarization, while near the negative electrode the charges moved in the opposite direction to injected charges until the field in all points of the volume became zero (Fig. 6). The trapped charges remained only on slopes of the polarization peak.

The massive trapping of injected charges at the boundary of the polarized region started immediately as soon as the strong polarization zone appeared. This charged layer divided the volume into two parts. In the first part, adjacent to the negative electrode, there was no strong polarization, and the concentration of free injected carriers was rather high. This predetermined

![Fig. 6](image)
the high apparent conductivity and, accordingly, the weakened field in this zone during poling. At the same time, the polarized region was separated from the injecting electrode by a layer of trapped charge carriers, and its apparent conductivity became significantly smaller than in the first zone. This phenomenon can be considered as the Maxwell-Wagner effect induced by the inhomogeneous polarization. The polarized region did not expand with time; and the polarization value increased there. Phenomenologically, the trapping of charges and formation of three zones was manifested by the decrease of the charging current under the constant voltage, and in decreasing of the effective conductivity.

When the polarity of the applied voltage was switched to the opposite, the negative charge carriers were again injected, but from the opposite electrode. As a result, the strong field was located where the residual polarization was previously zero leading to formation of the strong polarization of the new direction in this region (Fig. 3). The field weakened in the former area of the residual polarization location due to injection of the negative carriers and presence of the negative space charge. Therefore, the full switching of polarization did not occur in this region, so a part of the residual polarization of the former direction remained. In the zone of the negative space charge localization (8-15 µm), the direction and magnitude of the polarization gradient did not change. This indicated that the negative charges trapped during initial poling remained at the same place, despite that the total polarization reversed its direction. This unusual phenomenon was in complete agreement with the Poisson equation for the case of the zero field. It was also possible that the previously trapped carriers were delocalized and re-trapped again without significant changes in the spatial location of the localization sites.

Thus, an asymmetric bimorph structure was formed after switching. The negatively charged layer, judging from the polarization gradients direction in the region of 8-15 µm, was retained and fixed in the bulk of the sample during all reversals. The presence of this layer explained more rapid formation of the polarization profile during switching in comparison to initial poling when this layer did not exist. The same layer prevented formation of the uniform polarization even in the case of strong fields.

The observed impossibility to improve the uniformity of the polarization profile by increasing the voltage applied to the films originally poled in the middle fields can be explained by the effect of the injected charges [11] and formation of the blocking layer consisted of the trapped charges. This layer prevented expansion of the polarized region even in rather strong field.

This feature is of the fundamental importance from scientific, methodological and practical points of view. Firstly, it clarifies the mechanism of the relationship between the polarization and the trapped space charge [7-9]. It would seem that a strong field three times larger than the coercive field should provide the uniform polarization regardless of the initial conditions.

However, it is not the case. The effect of the trapped charge is so significant that even strong fields were not able to suppress it. Secondly, while studying the switching and hysteresis phenomena in ferroelectric polymers, it was taken for granted to start from a weak field and to gradually increase it. That was how measurements were often performed at low frequencies [12]. Taking into account our data, it turned out that such measurements could produce inhomogeneous polarization, since its profile depended not only on the field value, but also on the prehistory of the sample.

If the sample was poled and switched in strong fields, the ferroelectric polarization was uniform and easily switchable over the entire volume. Even complete depolarization was possible in this case. These features can be explained by the fact that the polarized region in presence of the strong field rapidly occupies practically the entire volume leading to the blocking of the charge injection and motion. So, the polarization profile is not distorted. The processes of compensation and neutralization of the depolarizing field occur in this case either at the electrodes or near the surface, so that the entire bulk remained free of injected and trapped charges, which could disturb the uniformity of the field and polarization.

5. CONCLUSIONS

It has been shown that the polarization in PVDF is asymmetric after poling in the middle field close to the coercive value. The existing inhomogeneity of the polarization cannot be eliminated by subsequent application of even very strong fields, while during initial poling in strong fields, a uniform and easily switchable polarization was formed.

A model of the polarization profile formation has been developed that took into account the injection of charges from the negative electrode and creation of a stable layer of trapped negative charges at the boundary between polarized and non-polarized regions, the presence of which led to distortion of the polarization profile and to impossibility of its improvement. It has been shown why uniform polarization was formed in the strong field during initial poling.

The obtained results have a practical importance in design of piezo- and pyro- sensors and activators using the ferroelectric PVDF films, because they should be considered while selecting poling conditions.

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REFERENCES
10. Y. Wang, C. Xing, J. Guan, Y. Li, Polymers 9, 562 (2017)

Розподіл сегнетоелектричної поляризації в полівініліденфториді під час первинної електризації та при перемиканні поляризації

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Динаміка профілів поляризації в плівках полівініліденфториду (PVDF) вивчалася in situ методом покрокової зміни тиску. Показано, що при електризації і зворотному перемиканні в середніх полях формується істотно неоднорідний профіль поляризації з максимумом поляризації поблизу позитивного електрода. Однак первинна електризація зразків з великих полях приводила до формування однорідного профілю поляризації, який залишався однорідним при будь-якому згладжуванні через прикладене поле. Виявлено, що неможливо поліпшити однорідність поляризації в PVDF шляхом застосування сильних полів, якщо орігінальна електризація проводилася в слабких або середніх полях. Спостережувані особливості були пояснені моделью, яка передбачала інжекцію негативних зарядів і формування постійного блокуючого шару на кордоні між поляризованими і неполяризованими зонами. Отримані результати дозволяють враховувати при виборі умов електризації при проектуванні і виготовленні датчиків та виконавчих елементів на основі PVDF. Результати мають практичне значення в розробці п’єзо- і піросенсорів та активаторів з використанням сегнетоелектричних PVDF плівок, оскільки їх слід враховувати при виборі умов полірування.

Ключові слова: Сегнетоелектричні полімери; Розподіл поляризації; PVDF.