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Piezoelectric force microscopy for investigation the effect of electrical breakdown on the electrophysical properties of ferroelectric PVDF films

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The effect of electrical breakdown on the electrophysical properties of PVDF films was investigated. The electrical strength of the material was determined before and after polarization. The piezoelectric coefficient d_{33} was measured using the quasi-static Berkelinecourt method. It was found that for unpolarized films after breakdown, the d_{33} values were nonzero, indicating local polarization in the pre-breakdown region. Using piezo response force microscopy (PFM), the morphology of the film surface was studied after electrical breakdown. Vertical and lateral piezoelectric response distribution signals were obtained. The values of local piezoelectric coefficients d_{33} were calculated in the vicinity and at a distance from the breakdown point.

Keywords: ferroelectricity, piezoelectric force microscopy, polymer ferroelectrics, electrical breakdown, flexible electronics, smart materials.

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1. Introduction

Ferroelectric films of polyvinylidene fluoride (PVDF) and its copolymers have high values of pyro- and piezoelectric response, chemical and thermal stability, and proven biocompatibility, therefore they are of great interest as materials for flexible electronics and biomedicine [1–4].

To create devices based on PVDF and its copolymers, films are oriented and then polarized using a corona or glow discharge [5], as well as the contact method. Regardless of the polarization method, in order to achieve the required values of effective piezoelectric effects, the material must have a high electrical strength, which limits the magnitude of the polarizing field, indicating the threshold values of the electric field strength at which the breakdown of the material occurs [6].

Electrical breakdown is a critical phenomenon that can lead to irreversible changes in the structure and properties of ferroelectric materials. The study of this process makes it possible to identify the mechanisms of degradation of PVDF films, which is important for the development of protection methods and improvement of their operational characteristics.

Due to the fact that current trends in microelectronics and nanotechnology generally require the creation of materials capable of operating at high electric fields and under extreme conditions [7], the study of the effect of electrical breakdown on the piezoelectric properties of PVDF can contribute to the development of materials with improved characteristics. The high electrical strength of ferroelectric polymers, for example, allows for the level of an exciting electric field in PVDF-based electroacoustic transducers (EAT) at $1-2$ an order of magnitude larger than ceramics, which creates the prerequisites for the creation of radiating EAT for sonar based on such polymers [8]. The sensitivity of PVDF-based EAT operating in the longitudinal mode is $1-50\,\mu$V/Pa according to literature data [9]. Compared to piezoceramics, PVDF-based devices have a wider frequency range (1 Hz$-$10 MHz), and PZT (1 kHz$-$1 MHz) [9].

PVDF and vinylidene fluoride-based copolymers are characterized by the presence of four polymorphic modifications that differ in the packing of macromolecules in the unit cell of the crystallite [10], and, as a result, have excellent ferroelectric properties. In addition, differences are also observed in the magnitude of the electrical strength [11]. The paraelectric α-phase has a nonpolar conformation of TGTG, showing an intermediate value of electrical strength; the ferroactive β-phase, which is of the greatest interest for practical use, has a polar conformation -TT- with the lowest value of dielectric strength, which is explained by the presence of residual polarization; γ-phase has -T_3GT_3G-conformation with the highest value of electrical strength [11].

Despite the fact that there are currently many papers devoted to the study of the electrical strength of PVDF and its copolymers [4,10–12], there is practically no data in the literature on the influence of temperature, phase composition, and domain structure on the mechanisms of electrical breakdown. The detailed mechanisms of reducing the electrical strength of PVDF at elevated temperatures have not been sufficiently studied (for example, the role of thermal degradation or structural changes). Electrical breakdown in PVDF is associated with the formation of conductive channels and local overheating of the material, which, in turn, lead to changes in the structural, morphological and ferroelectric properties of the polymer; however, there is insufficient research on such changes. In this regard, studying the effect of electrical breakdown on the domain structure and, as a result, on the magnitude of the piezoelectric response of PVDF and its copolymers at various temperatures will help partially eliminate this gap.

For visualizing changes in the domain structure in the field of electrical breakdown and measuring local piezoelectric effects, piezoelectric response force microscopy (PFM) is optimally suited, which has long established itself as an important tool for studying local piezoelectric properties of materials at the nanoscale [13–17], allowing studying the influence of external influences on material properties. For instance, the polarization switching process in curved thin films of a copolymer of vinylidene fluoride with trifluoroethylene (P(VDF-TrFE)) and the movement of domain walls in the presence of a compression gradient created under the tip of a cantilever are studied in Ref. [14]. The piezoelectric response force microscopy method is used in Ref. [16] to calculate piezoelectric coefficients d_{33} for PVDF and P(VDF-TrFE) films. Previously, the domain structure of the VDF copolymer with tetrafluoroethylene [17] was characterized by PFM methods.

The present work is aimed at studying the effect of electrical breakdown on the ferroelectric properties of PVDF, including changes in morphology, the nature and magnitude of the piezoelectric response in the near-hole region.

2. Materials and methods

2.1. Description of materials

Ferroelectric films of PVDF homopolymer (PolyK, Pennsylvania, USA) were studied in this work. The films were obtained by extrusion from a melt. The thickness of the studied samples was 28 μm. Some of the films were pre-polarized by the contact method for 180 s at a temperature of 80 °C and a polarization field strength of $E_p = 300$ MV/m. The piezoelectric coefficients d_{33} after polarization were 17 pC/N. The polarization was carried out using overhead aluminum electrodes with a diameter of 3 mm and a thickness of 0.25 mm. The studied samples were subjected to electrical breakdown at three temperatures, 30, 50, and 70 °C, away from the Curie point. The temperature of the ferroelectric to paraelectric phase transition for PVDF is 120 °C [10]. The selected temperatures correspond to the operating range of PVDF film-based devices.

2.2. Study of the structure and phase composition of the material

The degree of crystallinity and phase composition of the material were determined using differential scanning calorimetry (DSC) on a NETZSCH DSC 204F1 Phoenix device (NETZSCH-Gerätebau GmbH, Selb, Germany) with a heating rate of 2 K/min in an argon medium. The degree of crystallinity was calculated using a simplified formula:

$$\chi_c = \frac{\Delta H_\mathrm{m}}{\Delta H_\mathrm{m}^{\varnothing}} \tag{1}$$

where ΔH_m is the enthalpy of melting of the film, and $\Delta H_\mathrm{m}^{\varnothing}$ is the enthalpy of melting of a completely crystalline material, which is 104.5 J/K [18,19]

2.3. Method of measuring electrical strength

Electrical strength was measured using an experimental bench in accordance with GOST 6433.3-71 „Electrical insulating solid materials“. The experiments were carried out in a heated aluminum bath filled with petroleum jelly oil. The test bench is schematically shown in Figure 1. The same test bench was used for contact polarization of films.

The values of the breakdown field E_b at each temperature were obtained using the two-parameter Weibull model [4,10,12,20], according to which a statistical set of a large number of values E_b (in the experiment, the breakdown was measured at least 10 points) can be described by the function

$$F(x) = 1 - \exp\left[-\left(\frac{x}{\alpha}\right)^{\beta_\mathrm{b}}\right], \tag{2}$$

where x is the current value E_b, α is some characteristic field at which at least 63.2 % of the tested samples are broken down; parameter β_b characterizes the variance of the value E_b relative to the average value.

2.4. Piezoelectric response force microscopy

Ferroelectric properties and morphological changes of the samples after electrical breakdown were studied by scanning probe microscopy (SPM) using an NTEGRA Prima atomic force microscope (NT-MDT SI, Zelenograd, Russia) using cantilevers with platinum conductive coating FMG01/Pt (Tipsnano, Tallinn, Estonia). The experimental data was processed using the Gwiddion software 2.63 (Czech Metrology Institute, Czech Republic).

The measurements were carried out at three points: at the boundary of the near-hole area, at a distance of 225 μm from the breakdown point, at a distance of 1.2 mm or more from the breakdown point.

The topography of the film surface was obtained using SPM, the values of RMS roughness were calculated, and height profiles were constructed near and away from the breakdown area.

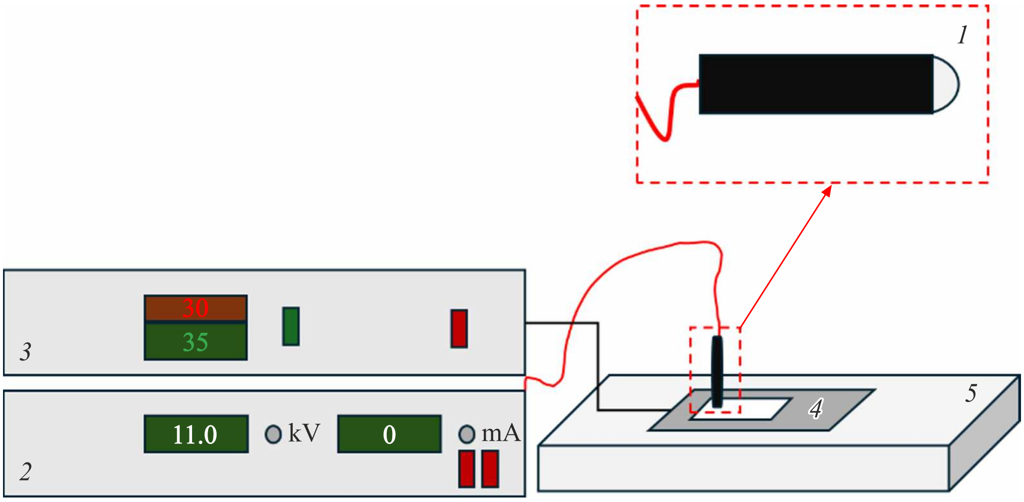

Figure 1. Experimental test bench for measuring electrical strength: *1* — high voltage electrode; *2* — voltage unit; *3* — temperature control unit; *4* — vaseline oil bath; *5* — heating table.

Maps of the distribution of vertical and lateral piezoelectric response signals were obtained in the PFM mode, and the values of local piezoelectric effects d_{33} were calculated. Conducting cantilevers HA_HR/Pt (NT-MDT SI, Zelenograd, Russia) were used to measure local piezoelectric effects with a stiffness constant of 17 N/m.

Local piezoelectric coefficients were determined by direct measurement of deformation when applying an alternating voltage from 0 to 10 V at a fixed frequency of 890 kHz. The measurements were carried out at two points: near the breakdown area and away from it. The piezoelectric effect values d_{33} were calculated from the Mag1n signal:

$$d_{33}^{*} = \frac{\mathrm{Mag}1n}{U \cdot Q}, \tag{3}$$

where U is the voltage applied during scanning (V), Q is the quality factor, and the signal Mag $1n$ corresponds to the deformation of the sample (pm).

Monocrystalline lithium niobate with known values of $d_{33} = 18$ pm/V was selected as the calibration sample.

2.5. Measurement of piezoelectric coefficients

The values of the macroscopic piezoelectric effects d_{33} were measured by the quasi-static Berlincourt method using the d_{33} YE2730A meter (Sinocera Piezotronics, INC., China).

3. Results and discussion

The structural properties of the samples before and after polarization were characterized using differential scanning calorimetry. Figure 2 shows the DSC curves of the initial and contact polarized films.

The DSC data shows differences in the structure of the samples before and after polarization. The degree of crystallinity, calculated by the formula (1), for an unpolarized film was 51 %, and it was 49 % for a polarized film. In this case, for an unpolarized film, a peak at 116.7 °C is present on the curve of the first heating, corresponding to the melting of secondary crystallites [21], which also contributes to the overall degree of crystallinity and disappears after polarization.

Both films are characterized by peaks corresponding to the α-phase (168.9 °C) and β-phase (165.9 °C). However, the curve of the first heating of the unpolarized film also contains a peak of the γphase (172.8 °C), which also disappears during polarization. The crystallites in the γ-conformation are also polar, but have worse ferroelectric properties compared to the β-phase. Consequently, a decrease in the proportion of the γ-phase after contact polarization may indicate an improvement in the ferroelectric properties of the material.

Based on the shape of the peaks, it can be concluded that the sample has a more perfect crystallite structure after polarization.

The values of the electrical strength of PVDF films before and after polarization are calculated using the two-parameter Weibull model (Figure 3). The electrical strength of unpolarized films turned out to be slightly higher over the entire temperature range, which may also indicate a more perfect crystal structure of the material.

Table 1 shows the results of contact polarization of films, as well as the values of electrical strength depending on the temperature of electrical breakdown T_{b}.

As can be seen from the data in Table 1, after electrical breakdown, the piezoelectric effects d_{33} turn out to be nonzero for both polarized and previously unpolarized films. At the same time, the values of the initial piezoelectric effects of the polarized film are slightly higher than the values after breakdown.

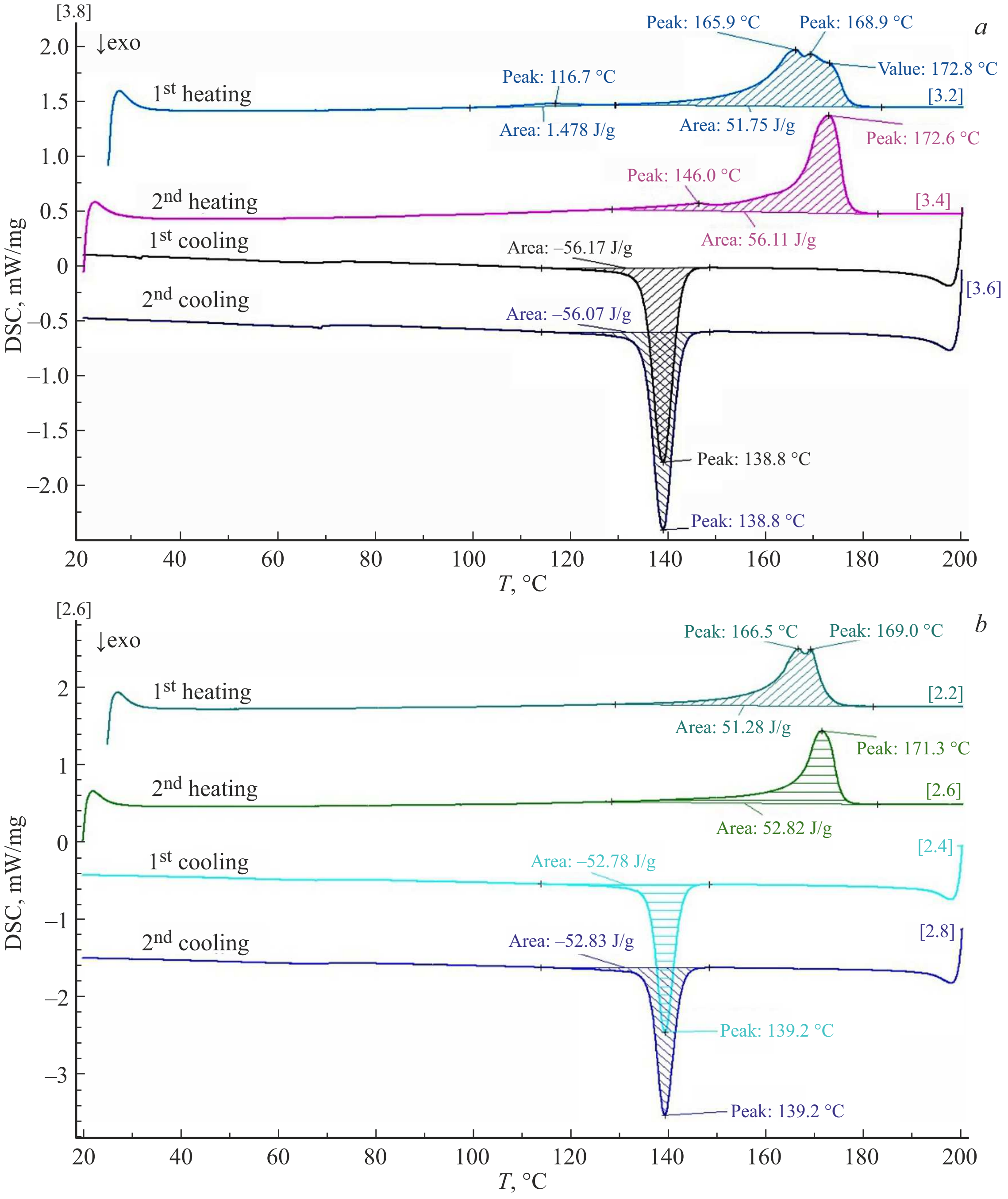

Figure 2. DSC curves for *a*) unpolarized and *b*) polarized PVDF films.

Table 1. Electrophysical properties of PVDF films before and after electrical breakdown

№	T_b, °C	E_b, MV/m	d_{33} before the breakdown, pC/N	d_{33} after the breakdown, pC/N
Polarized film				
1	30	450	17	15
2	50	430	17	16
3	70	480	17	15
Unpolarized film				
4	30	488	0	16
5	50	520	0	13
6	70	490	0	11

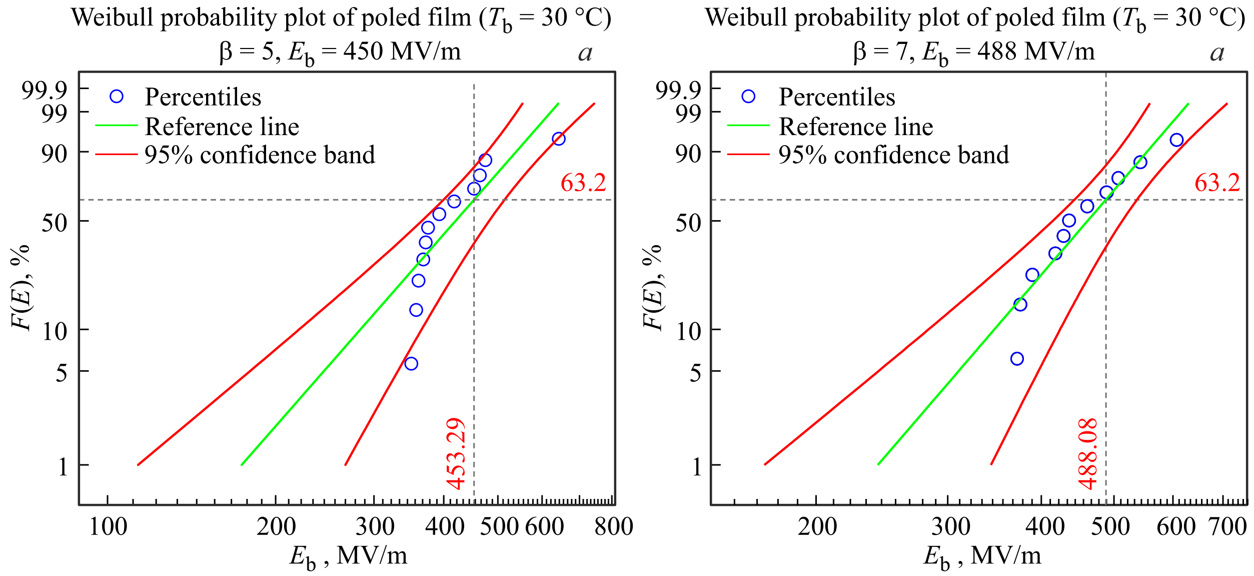

Figure 3. Measurement of electrical strength using the two-parameter Weibull model *a*) polarized and *b*) unpolarized PVDF films.

Table 2. Scanning probe microscopy data

№	RMS, nm			*h*, nm			Profile period, µm		
	0 mm*	0.225 nm	1.2 mm	0 µm	0.225 mm	1.2 mm	0 mm	0.225 mm	1.2 mm
Polarized film									
1	27	50	15	24	18	19	5	11	8
2	29	29	18	20	14	17	6	7	8
3	10	10	11	19	18	16	7	8	6
Unpolarized film									
4	28	29	22	20	19	22	8	7	17
5	28	17	18	22	19	23	6	4	5
6	36	37	26	17	20	16	6	9	9

Note. * distance from the breakdown point.

The sensitivity of the EAT (M_v), which characterizes the ratio of the output electrical signal to the acoustic pressure, is calculated as follows when operating in longitudinal mode [22]:

$$M_v = g_{33}t, \tag{4}$$

where g_{33} is the piezoelectric coefficient, t is the film thickness (28 µm).

The piezoelectric coefficients g_{33} and d_{33} are related by the ratio

$$g_{33} = \frac{d_{33}}{\varepsilon_0 \varepsilon'} \tag{5}$$

where ε_0 is the electrical constant equal to $8.85 \cdot 10^{-12}$ F/m, ε' is the actual part of the dielectric constant, the value of which, according to the datasheet data, for this polymer is 12.

Let's substitute in (5) the average measured values d_{33} — 16 pC/N, then we obtain that the coefficient $g_{33} = 0.15$ Vm/N. Therefore, the sensitivity of the EAT based on the studied film, according to (4), is 4.2 µV/PA, which is consistent with the literature data [9].

Morphological changes after electrical breakdown have been studied using SPM methods in the PFM mode. It is revealed that the size of the near-hole locally polarized region averages 225 µm. Destruction of the material is observed at the boundary of the breakdown area near the hole. The RMS roughness of the film increases after electrical breakdown. These patterns are valid for both polarized and previously unpolarized samples.

Table 2 shows the morphological characteristics of the films after breakdown, including the RMS values of surface roughness, the profile height h, and the profile period calculated using the refined Fourier transform.

As can be seen from the data in Table 2, the structure characteristic of extrusion films changes near the breakdown area, the average profile height increases from 19 nm for the area far from the breakdown point to 24 nm for the area

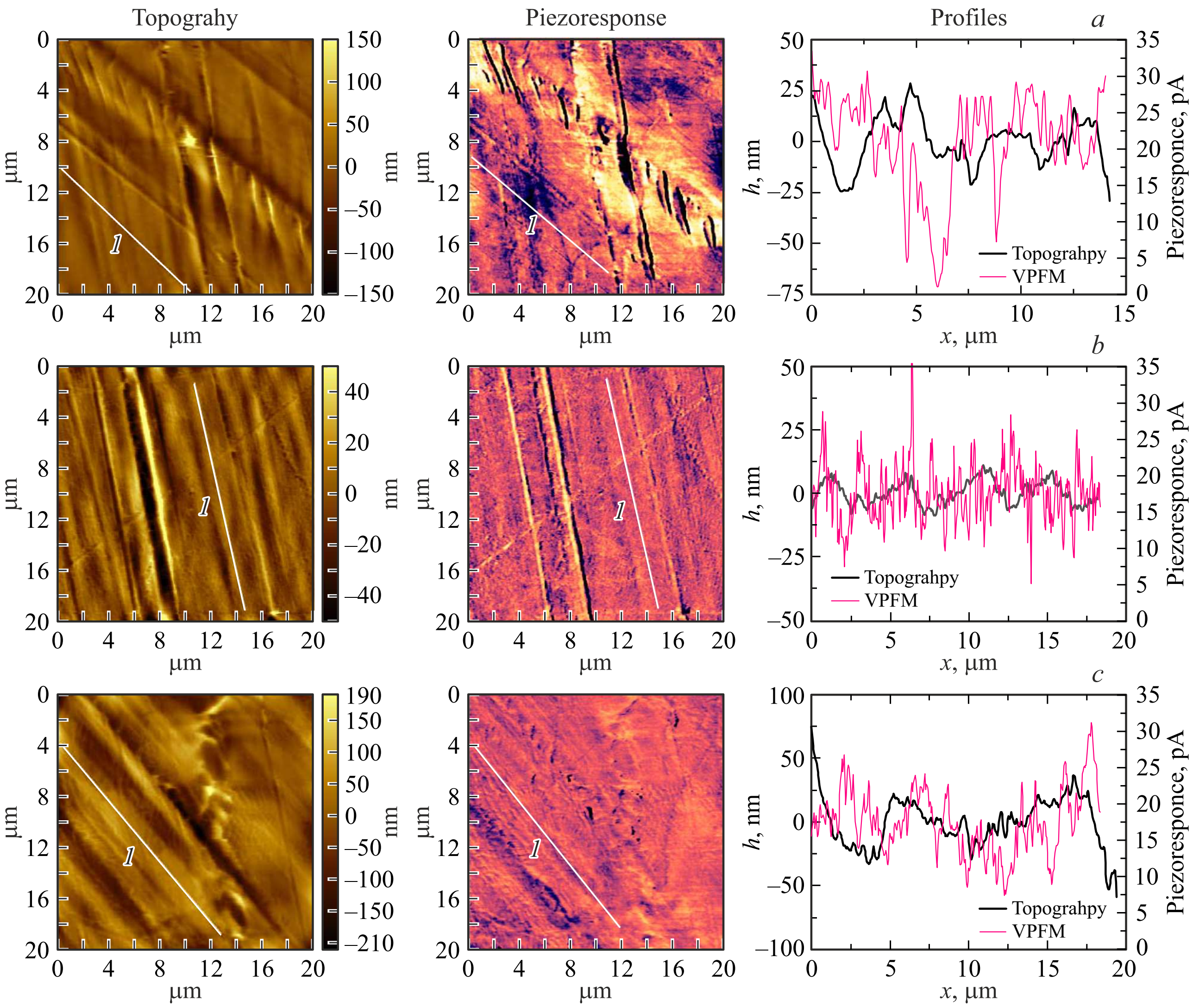

Figure 4. Force microscopy data for a polarized PVDF film subjected to electrical breakdown at 30 °C: *a*) location near the breakdown point, *b*) location at a distance of 225 μ from the breakdown point, *c*) a point away from the breakdown point.

near the breakdown, the film becomes more heterogeneous, which correlates with the magnitude of the RMS roughness.

The non-monotonic dependence of the surface profile roughness on the distance from the breakdown point can be related to both the film heterogeneity and the geometry of the high-voltage electrode and local overheating of the film during electrical breakdown.

The polymer domain structure was studied using piezoelectric response force microscopy. Figure 4 shows the topography of the film surface and vertical piezoelectric response signals. The size of ferroelectric domains was estimated by plotting the profiles of topography and vertical piezoelectric response for three points at different distances from the breakdown site.

For instance, for the topography profile, the period calculated using the refined Fourier transform was 8 μm, and it was 2 μm for the vertical piezoelectric response signal (Figure 4, *c*). This means that the dimensions of the ferroelectric domains on the surface of the films are smaller than the lateral dimensions of the roughness. It can be assumed that the size of the domains is significantly affected by the magnitude of the dipole interactions.

The average sizes of ferroelectric domains ξ and lateral roughness sizes were calculated to refine the data obtained using the autocorrelation function.

$$\langle C(r)\rangle = A\cdot\exp\left[-\left(\frac{r}{\langle\xi\rangle}\right)^{2h}\right], \qquad (6)$$

where A is a constant, r is the distance from the central peak (nm), determined from the image of the autocorrelation function, ξ is the average value of the domain size (nm), h $(0 < h < 1)$ — parameter [23].

For example, for an unpolarized film, the average lateral roughness size was 341 nm, and the size of ferroelectric domains calculated from the autocorrelation function was

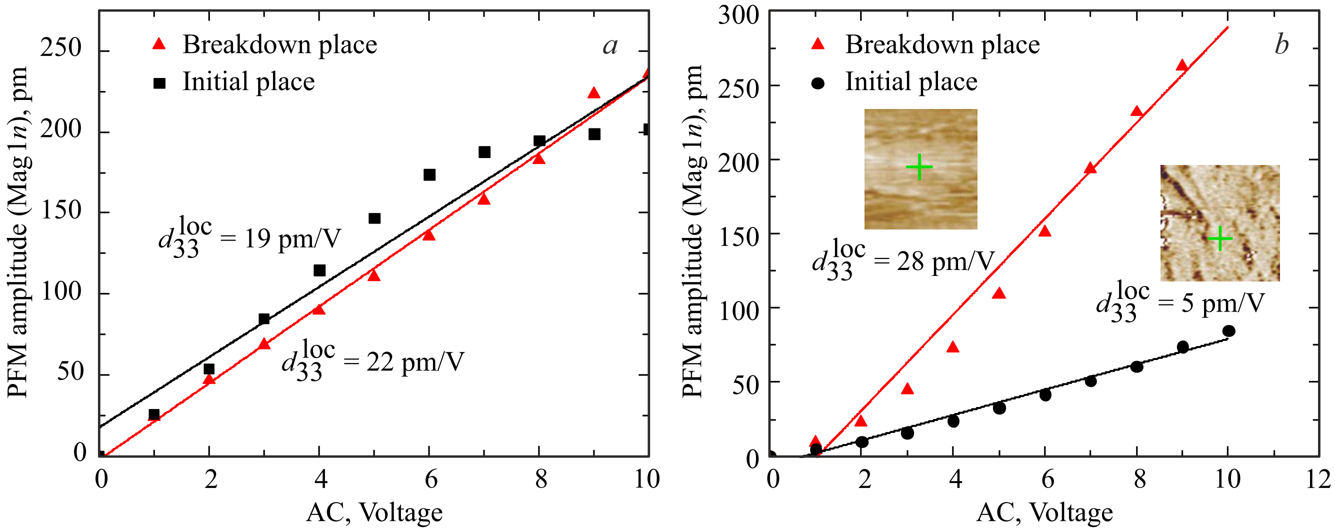

Figure 5. Measurement of local piezoelectric effects from PFM data near the breakdown point and in the distance: *a*) polarized film, *b*) unpolarized film.

Table 3. Piezoelectric response force microscopy data

№	d_{33}^{loc}, pm/V		Domain size ξ, nm		
	0 mm*	1.2 mm	0 mm	0.225 mm	1.2 mm
Polarized film					
1	16	15	113	62	83
2	15	12	85	99	63
3	14	11	168	151	99
Non-polarized film					
4	24	3	165	60	99
5	14	5	46	70	100
6	13	4	60	138	114

Note. * distance from the breakdown point.

165 nm. The result obtained is consistent with the literature data [24].

The values of local piezoelectric effects are provided in Table 3 and Figure 5.

In the case of an unpolarized film, it can be seen that with distance from the breakdown point, the piezoelectric effect decreases from 28 to 5 pm/V, which indicates the polarized state of the film only in the near-breakdown region. In this case, the macroscopic piezoelectric effects measured by the Berlincourt method for the area separated from the breakdown site are zero. The data obtained indicate the presence of spontaneous polarization of the film (Ps), which is compensated for the entire sample volume due to the disordered arrangement of ferroelectric domains.

Moreover, the piezoelectric effect d_{33} drops from 15 to 13 pC/N with an increase in the temperature at which the breakdown occurred, which may indicate a decrease in the influence of local polarization. At the same time, it was previously noted that the temperature of contact polarization in the region of 20–100 °C does not significantly affect the magnitude of the piezoelectric effects of PVDF films (unlike other VDF copolymers). This may be due to local overheating of the borehole area.

4. Conclusion

The effect of electrical breakdown on the electrophysical properties of ferroelectric polymer PVDF films in the temperature range from 30 to 70 °C before and after polarization has been studied. It was found that electrical breakdown leads to local polarization of the material in the region up to 250 μm from the breakdown point. This may be due to the geometry of the high-voltage electrode, which had the shape of a sphere, which caused the electric field to decrease away from the center of the electrode and, accordingly, the breakdown point. The values of local piezoelectric effects d_{33} near and away from the breakdown point were measured using piezoelectric response force microscopy. It is revealed that for unpolarized films, the piezoelectric effects are nonzero near the breakdown point (25 pm/V) and decrease to almost zero (4 pm/V) at a distance from the breakdown region. In addition, with an increase in the temperature at which the breakdown occurred, the values of the piezoelectric effect d_{33} decrease, which may indicate a decrease in the influence of local polarization.

The noted effect can be used to create structures with an array of ordered locally polarized and unpolarized regions, for example, to develop electroacoustic transducers for sonar.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Organic Ferroelectric Materials and Applications / Ed. K. Asadi. Woodhead Publishing: Sawston, UK (2021).
[2] M.G. Broadhurst, G.T. Davis. Ferroelectrics **60**, *1*, 3 (1984).
[3] A. Vodyashkin, E. Koshevaya, M. Makeev, P. Kezimana. Biomater. Sci. **12**, *20*, 5164 (2024).
[4] V.V. Kochervinskii, O.V. Gradov, M.A. Gradova. Russ. Chem. Rev. **91**, *11*, RCR5037 (2022).
[5] B.A. Basov, K.T. Makarova, E.L. Buryanskaya, K.M. Moiseev, A.S. Osipkov, A.A. Maltsev. In: 2024 IEEE UFFC-JS (2024). Pp. 1–6.
[6] T.T. Wang, J.M. Herbert, A.M. Glass. The Applications of Ferroelectric Polymers. Springer, Netherlands (1988).
[7] Z. Gao, D. Min, L. Yang, Y. Duan, Q. Wu, S. Zhu, S. Qin. In: Int. Conf. Energy Storage and Intelligent Vehicles (ICEIV). Springer Nature, Singapore (2022). Pp. 1089–1107.
[8] Yu.A. Koryakin, S.A. Smirnov, G.V. Yakovlev. Korabel’naya gidroakusticheskaya tekhnika. Sostoyanie i aktual’nye problemy. Nauka, SPb (2004). p. 410. (in Russian).
[9] Q. Zhang, P.A. Lewin. Ferroelectrics **171**, *1*, 381 (1995).
[10] V.V. Kochervinskii. Russ. Chem. Rev. **65**, *10*, 865 (1996).
[11] P. Saxena, P. Shukla. Adv. Composites. Hybrid Mater. **4**, *1*, 8 (2021).
[12] R. Tao, J. Shi, M. Rafiee, A. Akbarzadeh, D. Therriault. Mater. Adv. **3**, *12*, 4851 (2022).
[13] V.V. Kochervinskii, I.A. Malyshkina, D.A. Kiselev, T.S. Ilina, N.V. Kozlova, N.A. Shmakova, A.A. Korlyukov, M.A. Gradova, S.A. Bedin. J. Appl. Polymer Sci. **137**, *41*, 49235 (2020).
[14] R. Cai, B. Nysten, Z. Hu, A.M. Jonas. Appl. Phys. Lett. **110**, *20*, 202901 (2017).
[15] N. Jia, Q. He, J. Sun, G. Xia, R. Song. Polymer Testing **57**, 302 (2017).
[16] S. Chen, X. Li, K. Yao, F.E.H. Tay, A. Kumar, K. Zeng. Polymer **53**, *6*, 1404 (2012).
[17] V.V. Kochervinskii, E.L. Buryanskaya, A.S. Osipkov, D.S. Ryzhenko, D.A. Kiselev, B.V. Lokshin, A.I. Zvyagina, G.A. Kirakosyan. Polymers **16**, *2*, 233 (2024).
[18] S. Satapathy, S. Pawar, P.K. Gupta, K.B.R. Varma. Bull. Mater. Sci. **34**, *4*, 727 (2011).
[19] L. Wu, Z. Jin, Y. Liu, H. Ning, X. Liu, Alamusi, N. Hu. Nanotechnol. Rev. **11**, *1*, 1386 (2022).
[20] C. Laurent, C. Chauvet, J. Berdala. IEEE Trans. Dielectrics and Electrical Insulation **1**, *1*, 160 (1994).
[21] M. Neidhöfer, F. Beaume, L. Ibos, A. Bernes, C. Lacabanne. Polymer **45**, *5*, 1679 (2004).
[22] F.V. Hunt. Electroacoustics. McGraw Hill (2014).
[23] R.C. Munoz, G. Vidal, M. Mulsow, J.G. Lisoni, C. Arenas, A. Concha, R. Esparza. Phys. Rev. **62**, *7*, 4686 (2000).
[24] V.V. Kochervinskii, D.A. Kiselev, M.D. Malinkovich, A.S. Pavlov, I.A. Malyshkina. Colloid. Polym. Sci. **293**, *2*, 533 (2015).

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