

Features of polarization switching in printed films of polyvinylidene fluoride and its copolymer of poly(vinylidene fluoride-trifluoroethylene)

Alexander V. Solnyshkin¹, Nikita V. Vostrov¹, Sergey I. Gudkov^{1,2}

¹ Tver State University, 33 Zhelyabova Str., Tver 170100, Russian Federation

² Institute for Theoretical and Applied Electromagnetics of Russian Academy of Sciences, 13-6 Izhorskaya Str., Moscow 125412, Russian Federation

Corresponding author: Alexander V. Solnyshkin (a.solnyshkin@mail.ru)

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Abstract

The paper studies the processes of spontaneous polarization switching in PVDF and P(VDF-TrFE) polymer films produced by 4D printing. The samples were synthesized by the direct ink writing technology. It was found that polarization reversal in PVDF samples is not observed in alternating fields less than 70 MV/m, and in P(VDF-TrFE) samples – in fields less than 35 MV/m. This phenomenon is associated, firstly, with the large mass of the objects being repolarized, which is determined by the mass of the entire polymer chain, and, secondly, with a strong dipole-dipole interaction between adjacent polymer chains of the crystalline phase of the polymer. An increase in the electric field above the specified values leads to a sharp increase in the residual polarization values and the appearance of saturated dielectric hysteresis loops. The coercive field of the P(VDF-TrFE) copolymer films is two times smaller than the corresponding value for PVDF films (38 and 80 MV/m, respectively). At the same time, the residual polarization value for the copolymer films is slightly lower than for PVDF films (30 and 35 $\mu\text{C}/\text{m}^2$, respectively). The hysteresis loops were modeled according to the Preisach model. This model is based on the assumption that all lamellar crystals in the polymer have the same spontaneous polarization, each crystal has its own value of the coercive field and a rectangular dielectric hysteresis loop. The simulation showed that the average coercive field of the lamellar crystals of the PVDF polymer film is 91 MV/m, and for the P(VDF-TrFE) copolymer sample – 46 MV/m. The dispersion characterizing the distributions of the coercive and internal fields has a value of 16 MV/m for the PVDF polymer and 14 MV/m for the P(VDF-TrFE) copolymer.

Keywords

ferroelectric polymer, additive technologies, 4D printing, 3D printing, spontaneous polarization, dielectric hysteresis

1. Introduction

Polyvinylidene fluoride (PVDF) and its copolymer with trifluoroethylene (P(VDF-TrFE)) are important ferroelec-

tric materials [1, 2]. One of the advantages of polymer ferroelectrics compared to inorganic ones is their flexibility that can be used to fabricate structures on both hard and flexible substrates of arbitrary shape. These materials

are promising due to the growing demand for functional flexible elements of modern microelectronics [3–6]. Because of their attractive electrical properties and polymer structure, structures based on them can be used to create sensors, self-charging batteries, non-volatile memory, energy transducers etc. [7–11]. To produce functional devices based on ferroelectric polymer films, ones of the most promising methods for manufacturing are additive technologies [12–16]. Three-dimensional (3D) printing has a number of technological advantages compared to traditional methods of polymer films manufacturing, in particular low cost, relatively high production speed, high efficiency, the ability to create complex shapes, including the ability to apply a ferroelectric polymer to flexible substrates and substrates of non-standard shapes [17–18]. Moreover, these advantages can be realized without any loss of quality of the polymers properties such as mechanical, electrical, thermal etc. In this work, the processes of polarization reversal in ferroelectric polymer films PVDF and P(VDF-TrFE) produced by 4D printing were studied and analyzed. The 4-th dimension was applied to traditional 3D printing by external influences (like to electric field) that change the properties of polymers.

2. Experimental

The polymer PVDF and copolymer P(VDF-TrFE) 72/28 films were produced using 4D printing technology based on a kinematic of 3D printer with fused deposition of polymer solution (like to ink jet printing). The solutions used for printing were prepared by dissolving ferroelectric polymer granules in a dimethyl sulfoxide/acetone mixture (80% / 20%). Magnetic stirring the solution was carried out at a temperature of 100 °C until the polymer granules were completely dissolved. Then, the 3D printer cartridges were filled with the resulting solution. The films were printed on heated and pre-cleaned aluminum plates. After printing, the samples were kept at a tempera-

ture of 100 °C for 1–2 h to evaporate the solvent completely. As a result of the 3D printing process, films with a thickness of 15–25 μm were obtained.

The film polarization process was carried out in a corona discharge field. For polarizing, polymer film printed on metal substrate was placed on a heater surface. The film and substrate were heated up to about 100 °C. At the same time, the aluminum substrate was the bottom electrode that was grounded. A needle as the upper electrode was placed at a distance of 50 mm from the film surface. The potential difference between the upper and bottom electrodes was 15 kV.

To study the switching processes of electrical polarization, aluminium circular electrodes with diameters 10 mm were deposited on the free surface of the films through a metal shadow mask by thermal sputtering to make metal-copolymer-metal configuration.

The polarization reversal in the PVDF polymer and P(VDF-TrFE) copolymer films was studied on the base of the analysis of dielectric hysteresis loops recorded using the Sawyer–Tower method. An alternating electric field with frequency of 50 Hz and amplitude up to $1.2 \cdot 10^8 \text{ V/m}$. During the measurements, the samples were immersed in silicone oil because of the high electric fields used in the experiment that were corresponded in order of magnitude to the breakdown fields.

3. Experimental results

The results of the study of the polarization switching processes of PVDF films produced by the 4D printing method are shown in Fig. 1. When the electric field applied to PVDF films does not exceed 70 MV/m, the ferroelectric loops in the samples are not observed. PVDF film exhibits the properties of a linear dielectrics that does not possess ferroelectric properties. The dependence of polarization (P) on the strength of the alternating electric field (E) is linear (Fig. 1a).

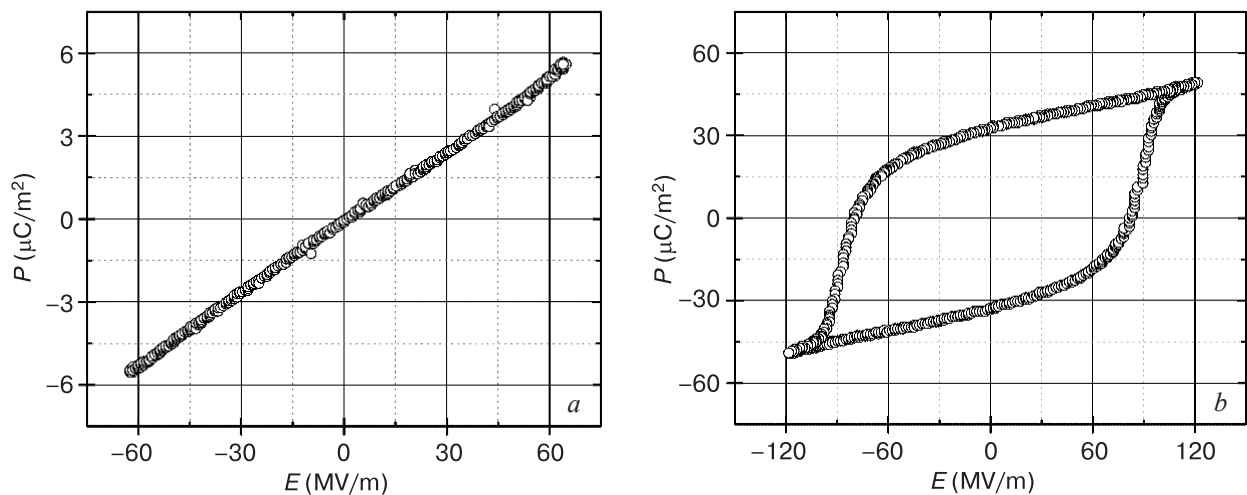


Figure 1. Dependence of polarization on the external alternating electric field (a) and the dielectric hysteresis loop (b) for PVDF films manufactured by 4D printing

On the base of the oscillogram shown in Fig. 1a, the dielectric susceptibility (χ) of the PVDF film was calculated using the formula:

$$\chi = \frac{P}{\varepsilon_0 E}, \quad (1)$$

where ε_0 is the electric constant (the vacuum permittivity). The value of χ for the PVDF samples is 9.8 that corresponds to the low-frequency relative permittivity of 10.2 determined by standard dielectric analyzers or impedance meters.

Applying the electric field $E > 70$ MV/m to the printed PVDF film leads to the appearance of a ferroelectric hysteresis loop (Fig. 1b) typical for ferroelectric materials. Based on the hysteresis loop measurements, the magnitudes of the remnant polarization (P_r) and coercive field (E_C) were determined as $35 \mu\text{C}/\text{m}^2$ and 80 MV/m, respectively. These correspond to typical values for PVDF films that are equal to 30 – $75 \mu\text{C}/\text{m}^2$ for the remnant polarization and 50 – 120 MV/m for the coercive field [19–21]. The dielectric susceptibility found from the slope of the linear sections of the hysteresis loop at the high electric field has a value of 15.6. This value exceeds the dielectric susceptibility found earlier for PVDF film, since it is determined by the increased magnitude of induced polarization in fields significantly exceeding the coercive field.

Polarization switching processes were also studied for P(VDF-TrFE) copolymer films manufactured by 4D printing. In alternating electric fields up to 35 MV/m, polarization reversal in P(VDF-TrFE) films is not observed, as well as in PVDF films. This is indicated by the linear dependence of polarization on the electric field strength, shown in Fig. 2a. Calculation of the dielectric susceptibility using Eq. (1) showed that $\chi \approx 10.2$. This value approximately coincides with the χ parameter determined by the standard technique that gives dielectric susceptibility of 9.5.

The electric field above 35 MV/m applied to the P(VDF-TrFE) film results in the appearance of a

ferroelectric hysteresis loop. It should be noted that the strength of such an electric field is 2 times lower than the corresponding value for PVDF films. The oscillogram of the ferroelectric hysteresis loop for the P(VDF-TrFE) copolymer film manufactured by the 4D printing method is shown in Fig. 2b. The remnant polarization value determined on the base of the hysteresis loop measurements is equal to $30 \mu\text{C}/\text{m}^2$. This value is slightly lower than P_r of PVDF films. The coercive field found from the hysteresis loop is equal to 38 MV/m, which is approximately 2 times lower than E_C of PVDF films. The values of the remnant polarization and coercive field agree with the literature data for P(VDF-TrFE) films: the remnant polarization varies from 40 to $110 \mu\text{C}/\text{m}^2$ and the range of coercive field is 24 – 55 MV/m [22]. The dielectric susceptibility determined from the slope of the linear sections of the ferroelectric loop is equal to 18. This value is larger than the dielectric susceptibility in low fields found earlier, since it is due to induced polarization in the very high electric fields. A decrease in the electric field strength leads to the appearance of partial hysteresis loops, which degenerate into a straight line at $E < 25$ MV/m.

Based on the oscillograms of the ferroelectric hysteresis loops, the dependences of the remnant polarization on the amplitude of the external electric field were plotted (Fig. 3). The arrows indicate the directions of change in the amplitude of the electric field with increasing (forward run) and decreasing (reverse run).

As one can see from Fig. 3, at the field strength below 70 MV/m for PVDF films and 35 MV/m for P(VDF-TrFE) films, the remnant polarization is zero. Raising the electric field amplitude above these values leads to a fast increase in the remnant polarization values and a transition from the linear $P(E)$ dependence to a hysteresis one. In this case, nearly saturated ferroelectric hysteresis loops appear immediately. Such behavior differs from the typical switching processes of crystalline ferroelectrics, which are characterized by partial polarization switching in fields less than the coercive one and the presence

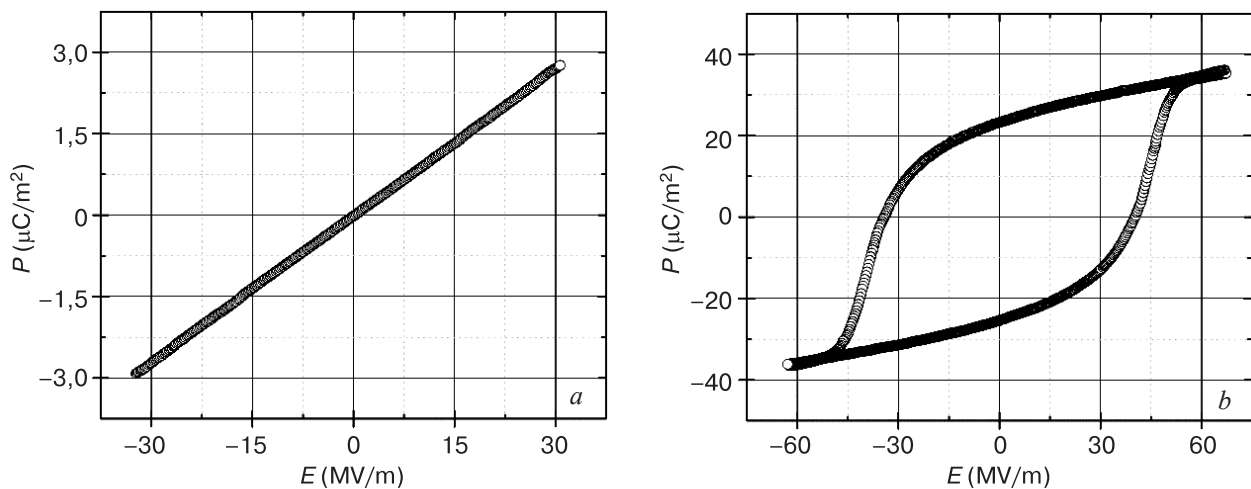


Figure 2. Dependence of polarization on the alternating electric field (a) and a characteristic dielectric hysteresis loop (b) for P(VDF-TrFE) films synthesized by 4D printing

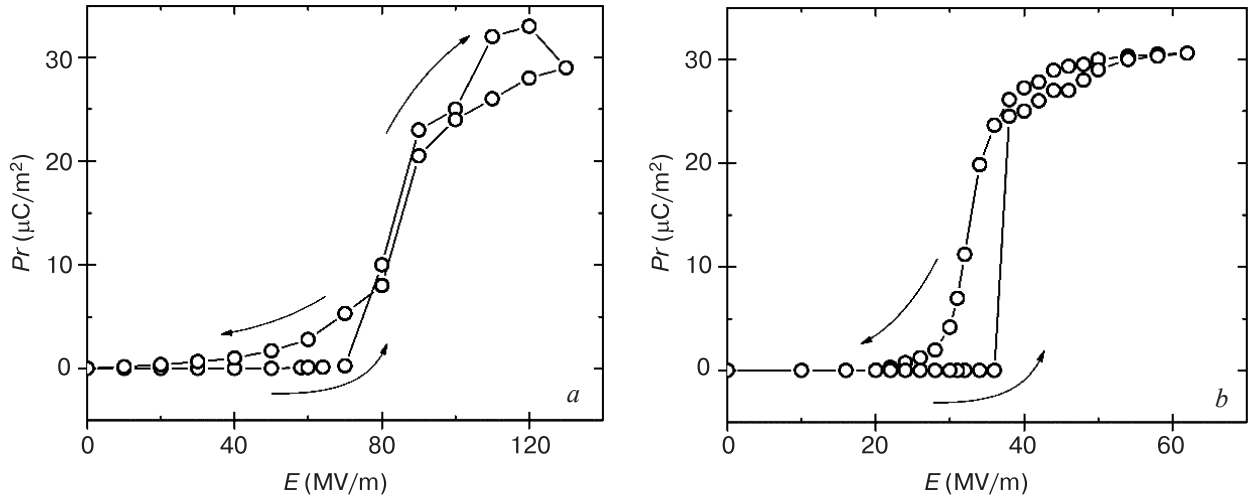


Figure 3. Dependences of remnant polarization on the external electric field for PVDF (a) and P(VDF-TrFE) (b) films

of partial hysteresis loops. In our case, a decrease in the electric field amplitude leads to a mismatch between the forward and reverse runs on the $Pr(E)$ dependences for PVDF and P(VDF-TrFE) films and the appearance of partial ferroelectric hysteresis loops in the certain limited range of fields.

Thus, in the fields lower than 70 and 35 MV/m applied to PVDF in P(VDF-TrFE) films respectively, no reorientation of dipole moments of polymer chains occurs. This is due to some reasons: firstly, the mass of an object with a dipole moment is large and is determined by the mass of the entire polymer chain, secondly, there is a strong dipole-dipole interaction between neighboring polymer chains of the crystalline β -phase of the polymer. Applying the electric fields above presented early to the printed films leads to intensive reorientation of dipoles and the appearance of ferroelectric hysteresis loops observed on the oscillograms.

4. Discussion

The experimental results are discussed within the framework of the Preisach model [23] developed for the analysis of hysteresis loops in ferromagnets and considered for the description of ferroelectric hysteresis firstly in [24]. This model assumes that all lamellar crystals of the β -phase in the polymer have the same spontaneous polarization (P_s), and the individual crystal has its own value of the coercive field strength (E_c) and a rectangular dielectric hysteresis loop. The effect of the environment in the polymer volume is described by the internal electric field (E_i), which can both weaken and enhance the effect of the external electric field. If the electric field strength applied to the sample exceeds the coercive and internal fields, then polarization reversal occurs and the

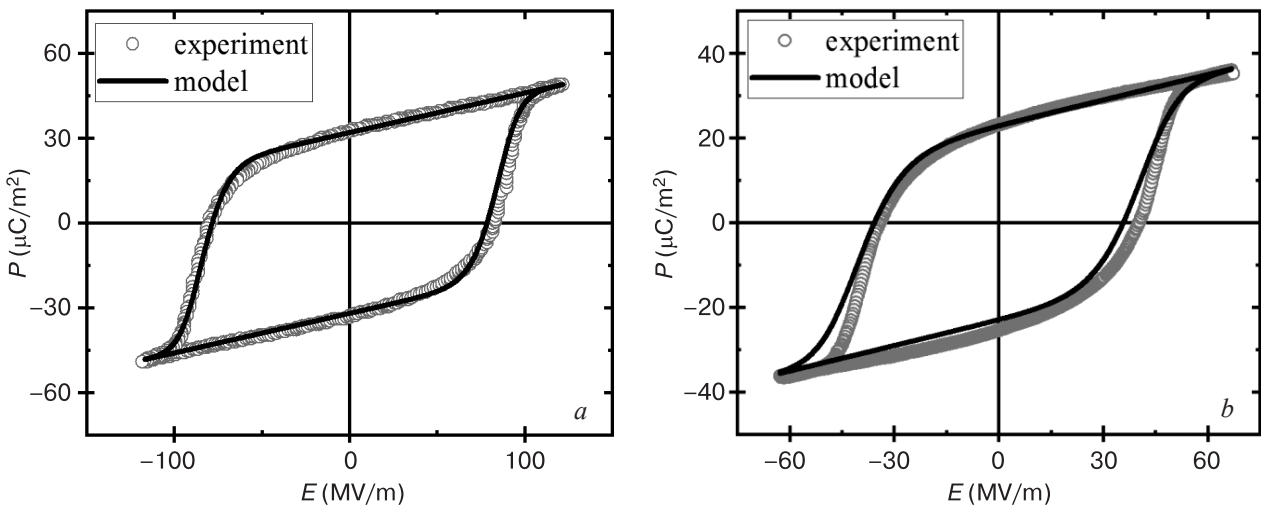


Figure 4. The result of theoretical calculation of dielectric hysteresis loops for PVDF (a) and P(VDF-TrFE) (b) films

dependence of the polarization on the external field can be written as

$$P(E) = \iint_{S^+} \mathbf{P}(E_C, E_i) dE_C dE_i - \iint_{S^-} \mathbf{P}(E_C, E_i) dE_C dE_i, \quad (2)$$

where $\mathbf{P}(E_C, E_i)$ is the Preisach function defining the normalized polarization, and S^+ and S^- mean that the integration is carried out over that part of the Preisach plane where the normalized spontaneous polarization is equal to +1 and −1, respectively. In our case of the PVDF and P(VDF-TrFE) films, we assume that the $\mathbf{P}(E_C, E_i)$ is distribution function of lamellar crystals by coercive and internal fields.

The calculation of the $P(E)$ dependence was carried out on the basis of the normalized Preisach function, which was described in detail in [25]

$$\begin{aligned} \rho(E_C, E_i, h, v) &= \frac{\mathbf{P}(E_C, E_i)}{P_S} = \\ &= \frac{1}{2v} \operatorname{sech}\left(\frac{E_C - h}{v}\right)^2 \left[1 - \tanh\left(\frac{E_C - h}{v}\right)\right] \times \\ &\times \frac{1}{2v} \operatorname{sech}\left(\frac{E_i + h}{v}\right)^2 \left[1 - \tanh\left(\frac{E_i + h}{v}\right)\right], \end{aligned} \quad (3)$$

where v is the dispersion parameter of the distribution by coercive and internal fields, h is the parameter that determines the maximum of this distribution and corresponds to the average coercive field

$$\begin{aligned} h(v) &= \\ &= v \ln \sqrt{1 - 2 \cosh^2\left(-\frac{E_C}{v}\right) + 10 \cosh\left(-\frac{E_C}{v}\right)} \times \\ &\times \sqrt{\cosh^2\left(-\frac{E_C}{v}\right) - 1}. \end{aligned} \quad (4)$$

The numerical calculation results of ferroelectric hysteresis loops based on the Preisach model for PVDF and P(VDF-TrFE) films are presented in Fig. 4.

For PVDF films (Fig. 4a), the best agreement between theoretical and experimental data is achieved with an average coercive field in lamellar crystals equal to

about 91 MV/m and a dispersion parameter characterizing the distribution of coercive and internal fields equal to 16 MV/m. For P(VDF-TrFE) films (Fig. 4b), the values of h and v are equal to 46 and 14 MV/m, respectively.

5. Conclusion

The study of switching processes in the ferroelectric polymer films produced by 4D printing showed that the application of alternating fields to the PVDF and P(VDF-TrFE) structures with a strength of less than 70 MV/m for PVDF and 35 MV/m, respectively, does not lead to polarization reversal of the samples. This is due to two factors: 1) the large mass of the switching polymer molecule, which has a dipole moment (the mass is determined by the mass of the whole of the polymer chain); 2) strong dipole-dipole interaction between neighboring the polymer chains of the crystalline β -phase of the PVDF and P(VDF-TrFE) films. An increase in the field strength above the values mentioned above causes polarization switching, which is typical for ferroelectric materials. In this case, the magnitude of the coercive field and residual polarization in PVDF films are greater than the corresponding values in P(VDF-TrFE) films.

Modeling of ferroelectric hysteresis loops on the base of the Preisach model showed that the average coercive field in lamellar crystals of the ferroelectric β -phase for the PVDF film is equal to 91 MV/m, and for the P(VDF-TrFE) film – 46 MV/m. The dispersion characterizing the distribution of coercive and internal fields is 16 MV/m for PVDF and 14 MV/m for P(VDF-TrFE). It should be noted that the average values of coercive fields in PVDF and P(VDF-TrFE) differ by two times approximately, which is experimentally observed. At the same time, the dispersion parameter h takes almost the same values for the PVDF and P(VDF-TrFE) films.

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