Physics of the Solid State, 2022, Vol. 64, No. 10

04,14

Structure formation and depolarization relaxation processes in porous piezoactive polyvinylidene fluoride films

© D.I. Gerasimov[1], I.S. Kuryndin[1], V.K. Lavrentyev[1], E.A. Volgina[2], D.E. Temnov[2], G.K. Elyashevich[1]

[1] Institute of Macromolecular Compounds, Russian Academy of Sciences,
St. Petersburg, Russia
[2] Herzen State Pedagogical University of Russia,
St. Petersburg, Russia
E-mail: dmitrygerasimov1997@gmail.com

Received May 26, 2022
Revised May 26, 2022
Accepted May 30, 2022

Piezoactive porous polyvinylidene fluoride films prepared in the process based on melt extrusion with subsequent isometric annealing, uniaxial extension and thermal fixation have been studied. It was shown that two competing orientation processes -polymorphous transition of non-polar α-phase into polar piezoactive β-phase and formation of porous structure - occur during the uniaxial extension of annealed films. It has been established that orientation degree of extruded films is the key factor determining the efficiency of both processes. Thermally stimulated depolarization method was used to investigate the dipole relaxation in oriented films, and activation energy of these processes was found. The films were polarized using corona discharge and high-voltage contact methods, both, and the dependence of piezoelectric modulus on the polarization conditions has been obtained. The maximum value of piezoelectric modulus $d_{31} = 30.1$ pC/N was achieved by polarization of films in corona discharge method.

Keywords: polyvinylidene fluoride, porous films, supramolecular structure, piezoelectric properties, polarization, relaxation processes.

DOI: 10.21883/PSS.2022.10.54232.389

1. Introduction

At present, electroactive polymer compounds and materials based on them for use in various fields as nanogenerators [1–3], tactile sensors [4–5] and separators in chemical current sources [6–7] are of great scientific and technological interest. Among the well-known polymers, polyvinylidene fluoride (PVDF) holds a special place due to the combination of high pyro-, ferro- and piezoelectric characteristics [8] with good mechanical properties [9] and high chemical resistance. The physicochemical and functional properties of PVDF are significantly influenced by the polymorphic composition of the polymer, its degree of crystallinity, supramolecular structure and degree of orientation [10].

PVDF is a polymorphic amorphous-crystalline polymer, and its crystal structure is represented by the following chain conformations: α, β, δ, γ [11]. Under PVDF melt crystalization, a stable non-polar α-phase is formed, which is characterized by the TGTG' configuration, as a result of which the dipoles of the monomer units are directed oppositely to each other, which leads to zero total dipole moment of the unit cell. Polymer chains in the crystalline β-phase have a polar TTTT-conformation, with the largest total dipole moment, and it is the formation of such a structure that provides high piezoelectric characteristics of materials based on PVDF.

Polymorphic α–β transition can be initiated under mechanical efforts (stretching, bending) or polarization in a high-voltage field [12]. A common method for producing PVDF films is to form them from dimethylformamide [13] or dimethyl sulfoxide solutions [14]. In high-tech and environmentally friendly processes, PVDF films can be obtained without toxic solvents and additives, using melt polymer extrusion. Subsequent uniaxial extension of extruded samples at elevated temperatures is an effective method for obtaining piezoactive PVDF films, since molecular chains are stretched, which leads to the orientation of the dipoles in the direction of the drawing. The result of this process depends on the degree and rate of stretching of the films, as well as on the temperature, which affects the mobility of the molecular chains.

To obtaine the pronounced piezoelectric properties, it is necessary to carry out polarization of films, in which the orientation of ferroelectric domains occurs. Two methods of processing PVDF films are widely used: high-voltage contact polarization and polarization in the corona discharge field, and the processing performed at an elevated temperature ($50-90^\circ$C). The crystalline structure, the polymorphic composition of the samples and the conditions of their polarization have a significant impact on the electroactive properties of PVDF films, including the piezomodulus (d_{31}). The polarized state of the samples can be investigated by the thermostimulated depolarization method (TSD), which is sensitive to changes in structure and polymorphic composition. This method gives the possibility to systematic ally study the polarization process of PVDF films, to establish the influence of the supramolecular structure on the efficiency of the polarization process and to determine the quantitative characteristics of relaxation phenomena. Since today there is no unified theory of the nature of the ongoing depolarization processes, their study in PVDF films in the range of polarization temperatures is an important task both from a scientific and practical point of view.

Previously, in a number of works, it was shown that porous films exhibit high piezoelectric characteristics, since the higher (compared to dense samples) specific surface of such materials contributes to an increase in the density of the electric charge and, accordingly, the growth of piezomodulus [15]. In the studies [16–18] highly porous PVDF films were obtained in a process based on melt processing which included a number of orientation efforts stages. At the same time, it is known that such process allow polymorphic transformations into PVDF. The ability to impart various properties in a single process is an attractive prospect for the development of new polyfunctional materials based on this polymer.

The aim of the work was to obtain piezoactive porous PVDF films, characterize their supramolecular structure, determine the conditions for the realization of an effective polymorphic $\alpha-\beta$ transition, as well as study the effect of the polarization method on the piezoresponse of samples and analyze the processes of dipole relaxation in the materials under study. The development of methods for obtaining PVDF films with variable functional properties — porosity and piezoactivity — will significantly expand the fields of their practical applications.

2. Objects and methods

To obtain the films, commercial PVDF grades Kynar-720 (Atofina Chemicals, USA), a molecular mass $M_w = 190000\,\mathrm{g\cdot mol^{-1}}$ and a melting point 168°C were used. Film formation was carried out by extrusion of PVDF melt through a slit die on a laboratory line (Scamia, France). The temperature of the extrusion head was 200°C. The orientation efforts applied to the polymer melt were characterized by the melt draw ratio λ:

$$\lambda = S \cdot \rho \cdot l/m, \tag{1}$$

where S — die area, ρ — density of the extruded film ($1.78\,\mathrm{g/cm^3}$), l and m — the length and mass of the sample, respectively.

The porous films preparation process consisted of a number of subsequent stages, and included annealing of extruded films under isometric conditions, uniaxial extention of annealed films and thermal stabilization of stretched samples [19].

Annealing of the extruded films was carried out for 4 hours at a temperature of $T = 167^\circ$C close to the melting point of the polymer. Annealed films were extended in air in the orientation direction: first at room („cold“ drawing), then at elevated temperatures („hot“ drawing). The degree of „cold“ drawing (ε_1) varied from 1.3 to 1.9 times, „hot“ drawing 1.4 times (ε_2) was carried out at a temperature of $T = 100^\circ$C. In the process of extension, the formation of a porous structure occurred, visually fixed by the whitening of the samples. The total degree of drawing was calculated by the formula: $\varepsilon_\Sigma = \varepsilon_1 \cdot \varepsilon_2$.

To give stability to the formed structure after extension, the films were thermofixed for 1 hour at a temperature of $T = 100^\circ$C.

The fraction of the sample volume occupied by the pores was characterized by a overall porosity (P), which was determined by the gravimetric method and calculated using the formula

$$P = [(\rho - \rho_0)/\rho] \cdot 100\%, \tag{2}$$

where ρ and ρ_0 — the density of the extruded and porous film, respectively.

The polymorphic composition of PVDF films was investigated by wide-angle X-ray scattering (WAXS) using meridional reflexes at $2\theta = 39^\circ$ and 35°, related to crystallites of α- and β-forms, respectively. The orientation factor (f_c) was determined by the WAXS method on a DRON 2.0 diffractometer (Bourevestnik, Russia) using Cu$K\alpha$-radiation. To calculate f_c, diffraction azimuthal curves of the intensity of the plane (110) were used

$$f_c = (3 \cdot \cos^2\varphi - 1)/2, \tag{3}$$

where φ — the angle between the direction of the orientation of the films and the molecular chain.

Determination of the degree of crystallinity of PVDF films was carried out by the WAXS method by the ratio of the areas of the peaks of the crystalline phase and the area of the amorphous halo.

Relaxation processes in polarized samples were studied by thermally stimulated depolarization in the temperature range from 0−70°C in a helium atmosphere at the TSC II set (Setaram, France). The values of depolarization currents were measured using a Keithley electrometer with a resolution of 10^{-16} A. Before the experiment, the PVDF films were polarized at 40°C in a field of 100 V/mm for 2 minutes, then sharply cooled in an electric field. The TSD spectra were obtained in a short-circuited state at linear heating rates of 3, 6 and 9°C/min. To quantitatively describe relaxation processes, a method based on the theory of activated states of Eirring, was used according to the equation

$$\tau(T) = \frac{h}{kT} \exp\left(\frac{\Delta H}{RT}\right) \exp\left(-\frac{\Delta S}{R}\right), \tag{4}$$

where τ — characteristic relaxation time, k — Boltzmann constant, h — Planck constant, ΔH and ΔS — enthalpy and entropy of activated states, respectively. Plotting a graph corresponding to equation (4) in Arrhenius coordinates $\ln(1/\tau T) \sim 1/T$ allows us to calculate enthalpy and entropy, as well as the activation energy of $E_a = \Delta H - T\Delta S$.

To obtain piezoactive PVDF films, polarization was carried out by two methods — high-voltage contact polarization and polarization in the corona discharge field. When

Table 1. Orientation factor (f_c) and degree of crystallinity (χ) of extruded and annealed films

Melt draw ratio, λ	Orientation factor, f_c		Degree of crystallinity, χ, %	
	Extruded	Annealed	Extruded	Annealed
15	0.46	0.58	41.7	62.0
29	0.56	0.64	42.5	64.2
44	0.61	0.70	43.1	65.3
76	0.69	0.78	44.5	65.1

polarized by an electric field, the eutectic alloy Ga–In–Sn was used as contact electrodes. The electric field strength ranged from 50 to 90 kV/mm. The films were polarized for 1.5 hours at elevated temperatures (50–90°C) in a high-voltage field and then cooled to room temperature in an electric field.

Corona discharge polarization was carried out using a brush electrode (cathode) and a cylindrical drum rotating at a speed of 4 rpm, at a field strength of 120 kV/mm. The samples were polarized for 5 min at a temperature of 70°C and then cooled to room temperature while maintaining the field.

Piezomodulus d_{31} was measured using the potentiostat P-30 (Elins, Russia) according to the resulting potential difference when applying a mechanical load (5H) in the direction of film orientation.

3. Results and discussion

3.1. Structure transformations in the process of obtaining porous PVDF films

When tensile forces are applied to the melt at the stage of extrusion, a crystal structure formed in the films and the degree of orientation depends on the melt draw ratio λ. The results of the research showed that at low values of $\lambda < 20$ in the crystal phase of the samples, a weakly oriented spherolite structure prevails, at $\lambda > 20$ — oriented lamellar structure [20]. With an increase in the melt draw ratio, the degree of orientation of the films grows, which is confirmed by the obtained values of orientation factors (Table 1).

Isometric annealing leads to a significant increase in the degree of crystallinity of samples due to the involvement of chains of macromolecules from amorphous and near-crystalline regions into crystallites (Table 1). As a result of the restructuring of the structure in the stressed state of the sample when fixing its dimensions, the proportion of stressed tie chains connecting the lamellas increases, and the so-called „hard-elastic“ state — the ability to large reversible deformations with a high modulus of elasticity [21] is achieved. As can be seen in Table 1, with the growth of λ there is a tendency to increase both the degree of crystallinity and the orientation factor for both extruded and annealed films.

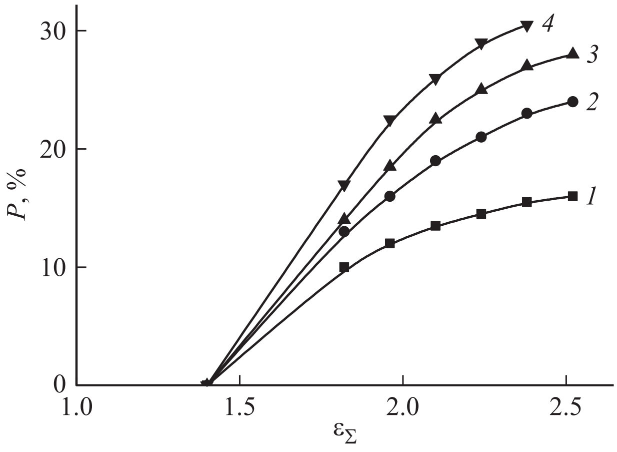

Figure 1. The dependence of the overall porosity on the total degree of extension for PVDF films formed at $\lambda = 15$ (*1*), 29 (*2*), 44 (*3*) and 76 (*4*).

Uniaxial extension initiates in these films the processes of both pore formation and polymorphic $\alpha-\beta$ transition, the efficiency of which significantly depends on the initial crystal structure and tensile conditions. The formation of voids (pores) occurs as a result of the moving apart and bending of the lamellae. Films start losing transparency due to the scattering of light on the walls of the pores. As the degree of extension increases, there is an increase in the number and size of pores. As can be seen in Fig. 1, the efficiency of pore formation increases with the melt draw ratio. The maximum value of overall porosity was reached for the sample with $\lambda = 76$ and $\varepsilon_\Sigma = 2.38$ and was 28%.

Studies by X-ray diffraction have shown that both extruded and annealed samples have a set of reflections related exclusively to the α-phase of PVDF. At the same time, the porous samples obtained by subsequent uniaxial extension of the annealed films contain crystallites of α- and β-modifications in their crystal structure, and the lower the values λ at the extrusion stage, the more efficient the polymorphic transition occurs and the higher the content of piezoactive β-crystallites in porous films. This result is explained by the fact that a less ordered spherolite structure formed at low melt draw ratio is more favourable for structural transformations under the extension than a more perfect lamellar structure formed at high λ. At the same time, it was previously shown [22] that the higher the value of λ at the extrusion stage, the greater the porosity was reached in the obtained piezoactive samples. Thus, pore

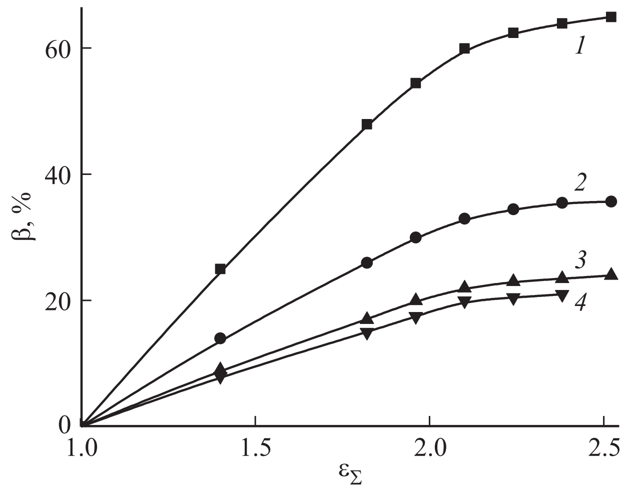

Figure 2. The dependence of the content of β-phase on the total degree of extension for porous films formed at the melt draw ratio of 15 (*1*), 29 (*2*), 44 (*3*) and 76 (*4*).

formation and $\alpha{-}\beta$-transition during uniaxial extension are competing processes, and the dominance of each of them is determined by the conditions for the structure formation of the original (extruded) films.

The achieved fraction of β-phase in porous films also depends on the value of the orientational effort during extension. As can be seen in Fig. 2, with an increase in the total degree of drawing, the content of the polar β-phase first increases, then its growth slows down and reaches a constant value. The maximum content value of β-phase of 67% was reached for a sample formed at $\lambda = 15$ and subjected to a uniaxial extension to $\varepsilon_\Sigma = 2.66$.

The obtained results make it possible to choose the conditions of the sample structure formation process that provide the required combination of functional characteristics of oriented PVDF films — porosity and piezoactivity.

3.2. Depolarization processes under heating of oriented PVDF films

To realize the essential piezoelectric properties in PVDF films, it is necessary to carry out the orientation of the dipoles, which can be reached by polarizing the samples. An important role in the efficiency of the polarization process is played by dipole mobility, which can be greatly complicated by the high orientation of the PVDF films. To increase the efficiency of polarization and, as a consequence, to enlarge the piezomodulus, it is necessary to investigate the effect of the processing parameters (λ and ε_Σ) on the dipole mobility of the samples. Dipole mobility can be studied by thermally stimulated depolarization. This method makes it possible to analyze the depolarization phenomena observed in PVDF films and quantify them.

For PVDF, two relaxation processes registred by the TSD method [23] are typical: the first is observed at a temperature close to the glass transition temperature of the PVDF ($T_g = -40°\mathrm{C}$), the second proceeds at temperatures of 20–70°C, at which polarization of the samples is usually carried out. The nature of relaxation processes in this temperature range is associated with the reorientation of dipoles, relaxation of ferroelectric polarization and/or migration of bulk charge [24].

Figure 3 shows the TSD curves for PVDF films obtained at different melt draw ratio λ and the same total degree of extension $\varepsilon_\Sigma = 2.1$. As can be seen in the figure, the intensity of the peak of the TSD and its temperature position significantly depends on the value of λ, which has a significant impact on the structure of the samples under study. The intensity of the peak is presumably related to the crystallite content of the polar piezoactive β-phase and their ability to polarize. The position of the maximum of the TSD curve is due to the overall porosity of the films, which makes it possible for charges to drain along the pore surface. An increase in overall porosity leads to a shift in the maximum to the region of lower temperatures.

The conclusion made about the effect of the content of β-phase on the intensity of the peak of the TSD is confirmed by the data presented in Fig. 4. As shown in Fig. 2, for samples formed at $\lambda = 15$, with an increase in orientation efforts at the uniaxial extension stage (ε_Σ), the of the polar

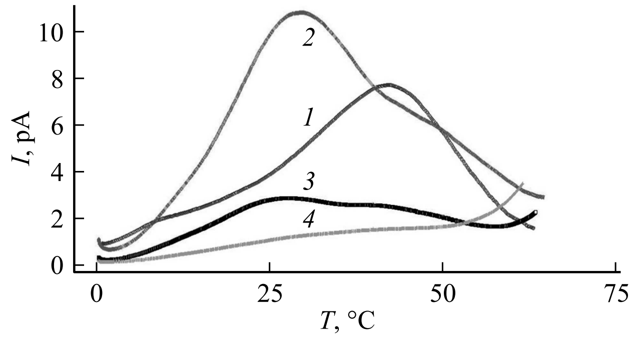

Figure 3. TSD curves for films formed at $\lambda = 15$ (*1*), 29 (*2*), 44 (*3*) and 76 (*4*); total degree of extension $\varepsilon_\Sigma = 2.1$.

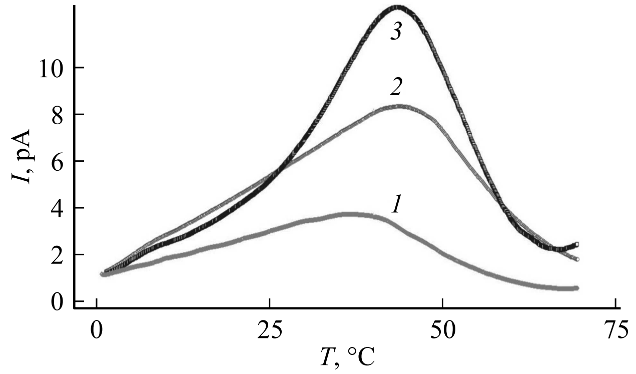

Figure 4. TSD curves for films obtained with the melt draw ratio $\lambda = 15$ and the total degree of extension: $\varepsilon_\Sigma = 1.82$ (*1*), 2.1 (*2*), 2.38 (*3*).

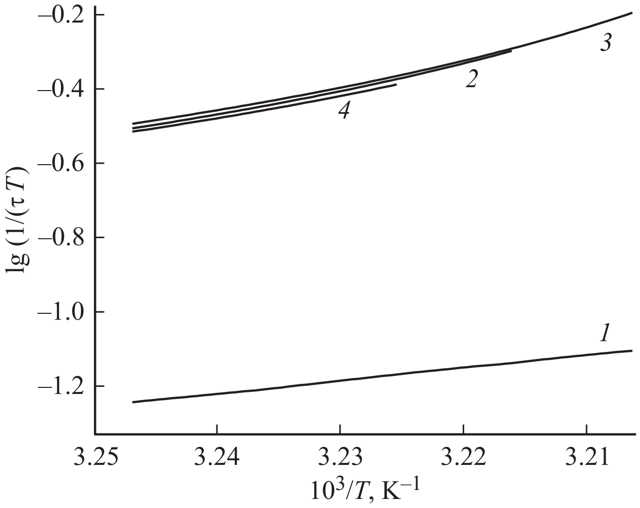

Figure 5. Determination of the parameters of relaxation processes for PVDF films obtained at $\lambda = 29$ and $\varepsilon_\Sigma = 1.82$ (*1*), 2.1 (*2*), 2.38 (*3*) and 2.66 (*4*).

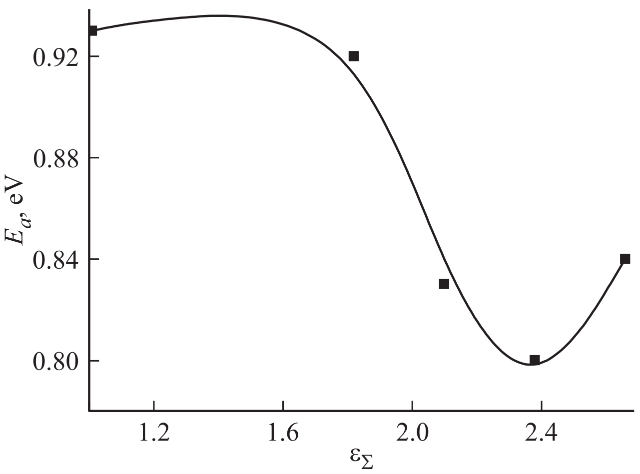

Figure 6. Activation energy dependence E_a on the total degree of extension ε_Σ for porous film (extrusion at $\lambda = 29$).

β-phase increases, and, as a consequence, the intensity of TSD peak increases.

Based on the data obtained, it can be concluded that the nature of the observed relaxation process is associated with the mobility of dipoles, which is significantly influenced by the orientational order in the structure of the polymer.

The dependence of the relaxation time (τ) on the temperature in Arrhenius coordinates allows us to calculate the value of the activation energy E_a of relaxation processes. The linear dependence of $\lg(1/\tau T)$ on $1000/T$ (Fig. 5) is typical for local forms of molecular mobility, when the process of reorientation of dipoles is determined only by intramolecular interactions and can be characterized over the whole temperature range by a single value of E_a. This value was calculated using the formula 4. As can be seen in Fig. 6, for the film obtained at $\lambda = 29$, the dependence E_a of the total degree of extension (the point $\varepsilon_\Sigma = 1$ corresponds to the annealed film) has a minimum at $\varepsilon_\Sigma = 2.38$, i.e., at a given degree of extension, a structure is formed that is optimal for subsequent polarization in terms of the combination of the content of the piezoactive β-phase and the orientation of the polymer chains.

Table 2. Activation energies E_a (eV) for porous PVDF films

λ	ε_Σ				
	*	1.82	2.1	2.38	2.66
15	0.94	0.94	0.93	0.92	0.93
29	0.93	0.92	0.83	0.80	0.88
44	0.93	0.84	0.80	0.92	0.95
76	0.92	0.96	0.97	–	–

Note: * corresponds to annealed PVDF films.

For all the studied samples, the activation energy of the relaxation processes of the dipoles was determined and its values are given in Table 2.

As can be seen in Table 2 with an increase in λ, there is a shift in the minimum activation energy towards lower values of extension degrees. This is due to the fact that in films formed at low λ, the original structure is weakly oriented, and it retains the mobility of dipoles even with large degrees of extension. Thus, the position of the minimum E_a allows us to determine the parameters of the process of obtaining PVDF films, which provides the highest values of piezomodulus.

3.3. Piezoelectric characteristics of oriented PVDF films

A necessary condition for the implementation of piezoactivity in PVDF films is their polarization. In this paper two methods were used to polarize the samples: high-voltage polarization and polarization in the corona discharge field. The piezoresponse value is characterized by piezoelectric coefficients d_{ij} (pC/N), where i — the direction of the polarization axis in the material; j — the direction of the applied mechanical force. The influence of the method and conditions of polarization on piezomodulus d_{31} in PVDF films was investigated at variation of processing parameters (λ and ε_Σ).

3.3.1. High-voltage contact polarization

High-voltage contact polarization was carried out at various temperatures (T_{pol}) and electric field strength values (E_{pol}). The results obtained are presented in Fig. 7. The maximum strength of the electric field is limited by the breakdown voltage, which in turn depends on the polarization temperature and the overall porosity of the films. It was shown that piezomodulus grows with increasing content of β-phase, field strength and polarization temperature. The highest value of the piezomodulus was

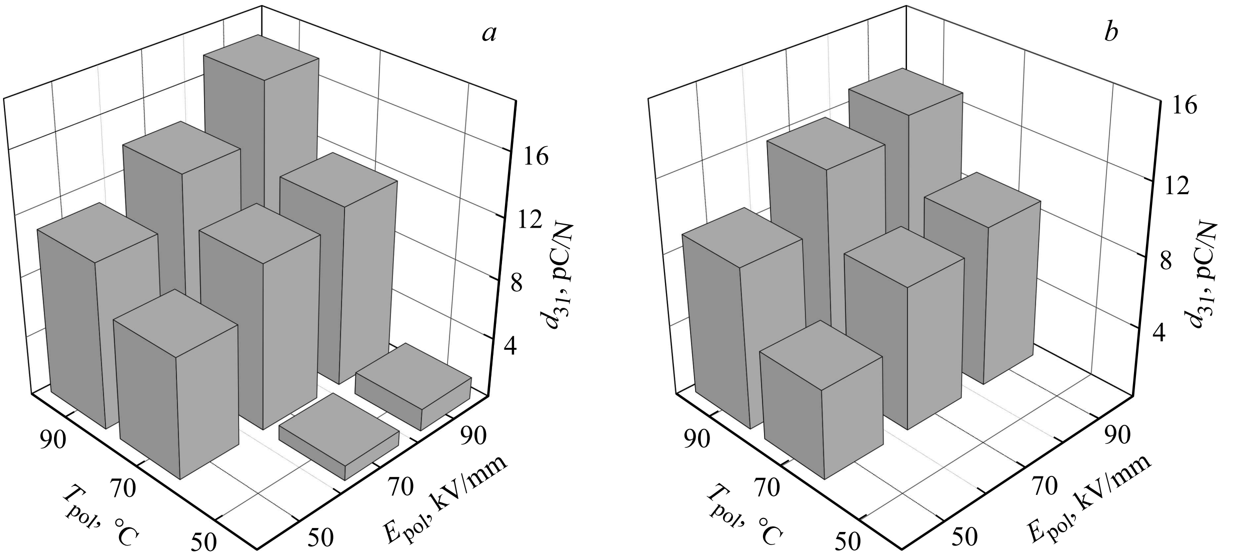

Figure 7. Dependence of the piezomodulus value on the electric field strength and polarization temperature for films obtained at $\lambda = 15$ (*a*) and 29 (*b*) and ($\varepsilon_\Sigma = 2.1$).

grows after polarization at a temperature of 90°C and an electric field strength of 90 kV/mm.

3.3.2. Polarization by corona discharge

When polarized by a corona discharge, the risk of electric breakdown is reduced, so it is possible to use high electric field strength, the maximum values of which are limited by the effects of charge drain. This method was used to polarize samples formed at $\lambda = 15$ and 29, for which there is an effective polymorphic α–β transition during the extension process. The results of measurements of the piezomodule of the samples, depending on the degree of total drawing, are presented in Fig. 8.

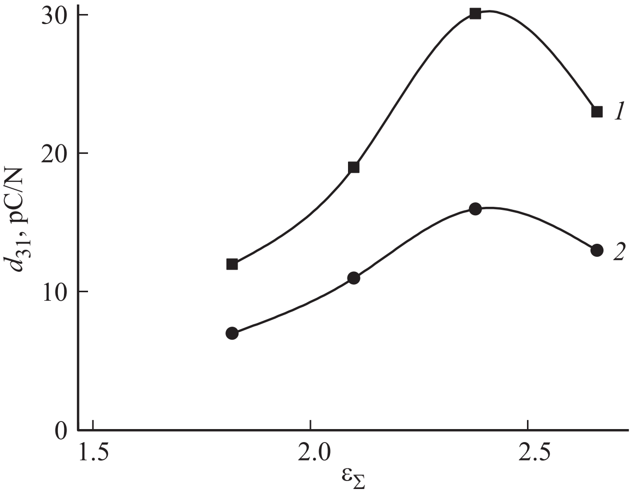

Figure 8. The dependence of the piezomodulus of PVDF films formed at $\lambda = 15$ (*1*) and 29 (*2*) on the total degree of extension ε_Σ.

As can be seen in Fig. 8, the effect of the total degree of extension on the value of the piezoelectric coefficient has a pronounced extreme dependence with a maximum at $\varepsilon_\Sigma = 2.38$. This result is consistent with the fact that the activation energy E_a (Fig. 6) has a minimum with a total degree of extension equal to 2.38. The presence of a maximum value of piezomodule d_{31} can be explained by two factors. On the one hand, with an increase in the total degree of extension, the content of the polar β-phase increases, which naturally leads to the growth of the piezomodulus. On the other hand, the mobility of the dipoles is influenced by the degree of orientation of the films. It is known [25] that in PVDF molecules dipoles are located perpendicular to the molecular chain, therefore, for more oriented structures, the rotation and orientation of dipoles along the polarization field are difficult, which leads to less efficient polarization and, accordingly, lower values of d_{31}. These difficulties are related to the fact that in a strongly oriented state, along with the rotation of the polar grouping, changes occur in the geometric location of the adjacent macromolecular chain. That is why the maximum piezoelectric coefficient is observed in films combining a high content of β-phase and a relatively small orientation of the polymer structure.

The results obtained show that polarization by corona discharge leads to for more efficient orientation of dipoles, since it is carried out at higher electric field strengths compared to high-voltage contact polarization.

4. Conclusion

A systematic study of the effect of the processing parameters of obtaining porous oriented PVDF films (melt draw ratio at the stage of extrusion and the total degree of extension at the stage of pore formation) and polymorphic transition to the formation of their structure (degree of crystallinity, orientation factor and content of polar β-phase) and piezoelectric properties (d_{31}) was carried out. The relaxation processes in the studied samples were analyzed by the TSD method, their activation energies, as well as the optimal conditions for obtaining PVDF films to achieve maximum piezoelectric characteristics, were determined. Comparative analysis of polarization conditions and methods showed that the highest value of the piezomodulus d_{31} is reached in samples that have undergone polarization in the corona discharge field and is 30.1 pC/N. The achieved values of piezomodulus d_{31} allow the use of the obtained piezoactive PVDF films in energy storage and conversion systems (nanogenerators, piezosensors, hydro-acoustic transducers).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] L. Yu, P. Zhou, D. Wu, L. Wang, L. Lin, D. Sun. Microsyst. Technol. **25**, 3151 (2019).

[2] K. Shi, B. Sun, X. Huang, P. Jiang. Nano Energy **52**, 153 (2018).

[3] F.R. Fan, W. Tang, Z.L. Wang. Adv. Mater. **28**, 4283 (2016).

[4] W. Deng, T. Yang, L. Jin, C. Yan, H. Huang, X. Chu, Z. Wang, D. Xiong, G. Tian, Y. Gao. Nano Energy **55**, 516 (2019).

[5] Y. Hu, W. Kang, Y. Fang, L. Xie, L. Qiu, T. Jin. Appl. Sci. **8**, 836 (2018).

[6] Al. Ahmad, U.R. Farooqui, N.A. Hamid. Polymer **142**, 330 (2018).

[7] L. Ahmadian-Alam, H. Mahdavi. Polym. Adv. Technol. **29**, *8*, 2287 (2018).

[8] E. Fukada, T. Furukawa. Ultrasonics **19**, 31 (1981).

[9] M. Jungin, MP. Hee, K. Eunjoo. J. Ind. Eng. Chem. **65**, 112 (2018).

[10] Ed. Basset. Development in Crystalline Polymers. Applied Science Publisher, London (1982). P. 195–261.

[11] A.J. Lovinger. Science **220**, *4602*, 1115 (1983).

[12] M.M. Nasef, H. Saidi, K.Z.M. Dahlan. J. Polym. Degrad. Stab. **75**, *1*, 85 (2002).

[13] X. He, K. Yao. Appl. Phys. Lett. **89**, *11*, 112909 (2006).

[14] S. Satapathy, S. Pawar, P.K. Gupta, K.B.R. Varma. Bull. Mater. Sci. **34**, *4*, 727 (2011).

[15] R. Gerhard-Multhaupt. Proceedings 11 th Int. Symp. Electr. **36**, (2002).

[16] C. Lei, B. Hu, R. Xu, Q. Cai, W. Shi. J. Appl. Polymer Sci. **131**, *7*, 40077 (2014).

[17] M. Shulin, G. Zhihao, W. Rongyan, T. Jie, M.Z. Jian. Polym. Adv. Technol. **32**, 2397 (2021).

[18] G.K. Elyashevich, D.I. Gerasimov, I.S. Kuryndin, V.K. Lavrentyev, E.Y. Rosova, M.E. Vylegzhanina. Coatings **12**, 51 (2022).

[19] G.K. Elyashevich, E.Yu. Rozova, E.A. Karpov. Patent of the Russian Federation № 2140936 (1997).

[20] D.I. Gerasimov, I.S. Kuryndin, V.K. Lavrentyev, D.E. Temnov, G.K. Elyashevich. AIP Conf. Proc. **2308**, 030001-1 (2020).

[21] I.Yu. Dmitriev, V. Bukošek, V.K. Lavrentyev, G.K. Elyashevich. Acta Chim. Slov. **54**, 784 (2007).

[22] G.K. Elyashevich, I.S. Kuryndin, I.Yu. Dmitriev, V.K. Lavrentyev, N.N. Saprykina, V. Bukošek. Chin. J. Polym. Sci. **37**, 1283 (2019).

[23] T. Yamada, T. Mizutani, M. Ieda. J. Phys. D **15**, 289 (1982).

[24] A.F. Butenko, A.E. Sergeeva, S.N. Fedosov. Fotoelektronika **15**, 77 (2006).

[25] N. Karasawa, W.A. Goddard. Macromolecules **28**, 6765 (1995).