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# The role of polar relaxers in the formation of the piezoelectric state in the vinylidene fluoride-tetrafluoroethylene copolymer

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***Abstract.*** In this work, the corona electret and piezoelectric states of vinylidene fluoride-tetrafluoroethylene (P(VDF-TFE)) copolymer films were studied to determine the correlation between these states. Previously, it was determined that in the objects under study there are two types of polar structures that differ in the values of activation energy and frequency factor. A detailed description of the application of a numerical method for processing experimental curves of thermally stimulated short-circuit currents, the Tikhonov method of weak regularization, which makes it possible to determine the parameters of polar structures of both types, is given. It is shown that the key role in the formation of the piezoelectric state in P(VDF-TFE) is played by polar structures with a lower activation energy.

***Keywords:*** electret state, polyvinylidene fluoride, thermally activation spectroscopy, Tikhonov's weak regularization method, piezoelectric effect

## Introduction

At present, the study of polymeric piezoelectric materials is of great interest. The most common representative of this class of materials is polyvinylidene fluoride (PVDF) and its copolymers with trifluoroethylene (P(VDF-TrFE)) and tetrafluoroethylene (P(VDF-TFE)) (Kalimuldina et al. 2020; Kunming et al. 2021; Lee et al. 2016). Interest in the study of these materials is due, on the one hand, to the wide possibilities of their application (in electroacoustics, medicine, biology, etc.) (Ma et al. 2005; Ribeiro et al. 2015) and, on the other hand, to the lack of a common opinion among researchers about the nature of the piezoelectric effect in these materials. Therefore, a variety of research in this area continues—both in order to find an explanation for the nature of the piezoelectric effect and in order to achieve the best piezoelectric characteristics of PVDF.

It is known that the crystalline phase of PVDF can exist in five different modifications, of which the polar β-phase is of the greatest interest because of its piezoelectric properties (Singh et al. 2018). Since in order to impart piezoelectric properties to polymeric materials based on PVDF their preliminary polarization is necessary (one of the most common methods is polarization in the field of a corona discharge), as a rule, an electret (corona electret) state is formed in these polymer films along with the piezoelectric state (Park 2021).

The purpose of this study was to investigate the correlation between the corona electret and piezoelectric states in the P(VDF-TFE) copolymer.

## Samples and research methods

In this work, the P(VDF-TFE) copolymer films (F2ME trademark) with a thickness of 20 μm were studied. The polarized state was created in the samples using the corona discharge field in two ways. The first method is the traditional method of polarization in the field of a corona discharge: the sample is placed in the field of a corona discharge (with a negative polarity of the corona electrode, since it was experimentally found that the value of the surface potential turns out to be much higher during polarization in a negative corona), kept in it for 10 min (polarization temperature is 80 °C), and then cooled to room temperature in the same field. However, this method is associated with a high probability of electrical breakdowns at elevated temperatures, which, in turn, leads to mechanical damage to polymer films. The second polarization method, proposed earlier in (Sotova et al. 2022), consists in polarization in the field of a negative corona discharge at room temperature for 10 minutes, and then (without an applied field, in the open circuit mode) the sample is heated to 80 °C and cooled to room temperature.

The processes of relaxation of the corona electret state in P(VDF-TFE) were studied by the method of thermally stimulated short-circuit currents (TSC) using the experimental equipment TSC II from Setaram. The piezoelectric modulus $d_{33}$ was measured by a quasi-static method using a D33meter instrument.

## Experimental results and discussion

With the polarization of P(VDF-TFE) polymer films by the traditional method, it is possible to achieve values of the piezoelectric modulus $d_{33}$ = 26 ± 1 pC/N. It is important to note that the obtained value of the piezoelectric modulus is not only sufficiently high (for polymeric piezoelectrics) but also has good stability (to verify this statement, the sample was held in a thermostat at the temperature of 70 °C for 2.5 hours).

Fig. 1 shows the TSC curves measured in P(VDF-TFE) polymer films traditionally polarized in a negative corona discharge field for various linear heating rates $\beta$ (6 and 9 °C/min) during current measurement.

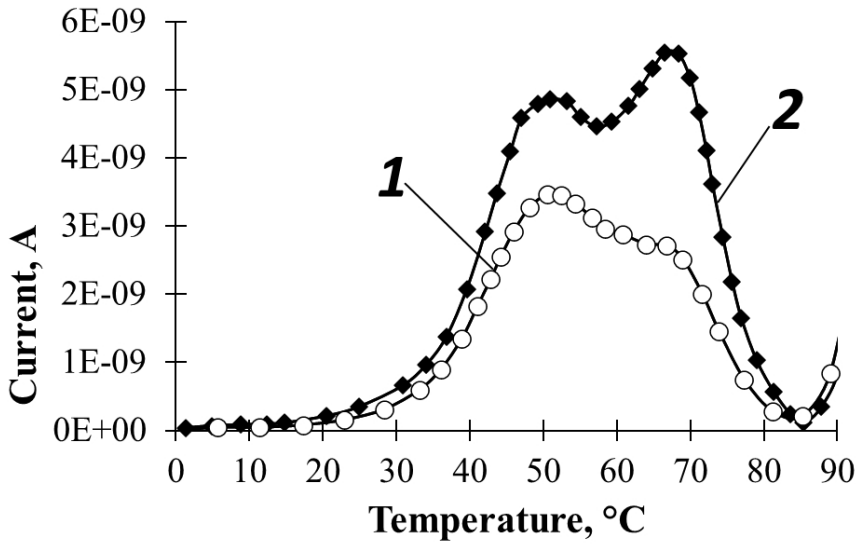


Fig. 1. TSC in P(VDF-TFE) films polarized in the field of a negative corona discharge at different linear heating rates (polarization temperature 80 °C): 1—linear heating rate β = 6 °C/min; 2—linear heating rate β = 9 °C/min

The TSC curves show two strongly overlapping peaks. Previously, a model of the P(VDF–TFE) polarization mechanism was proposed in (Gorokhovatsky et al. 2022): when the films are polarized in the field of a corona discharge, the negative homocharge is captured by deep near-surface traps. In the internal field of the homocharge, the orientation (and, importantly, the retention of the oriented state) of polar structures occurring in the composition of the ferroelectric phase of PVDF occurs (Kalimuldina et al. 2020). Two closely spaced peaks in Fig. 1 correspond to the processes of disorientation of polar structures (of two kinds), and the increase in the current above 85 °C is determined by the release of the homocharge from the traps.

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There are several ways to process experimental TST curves to calculate the parameters of relaxers (activation energy $W$ and frequency factor $\omega$). One of the simplest and most common methods is the method of varying the heating rate, which is based on the dependence of the position of the TSC maximum on the heating rate: the higher the rate, the higher the temperature of the current peak maximum (Gorokhovatsky, Bordovskiy 1991). Knowing the temperature positions of the current maximum at various heating rates, it is possible to calculate the value of the activation energy and the frequency factor.

However, in this case, the method of varying the heating rate cannot be applied, since with an increase in the heating rate, the amplitude of the current maxima increases (both low-temperature and high-temperature peaks), but no shift to the region of high temperatures is observed. Apparently, this is due to the strong overlap of two closely spaced peaks.

To calculate the parameters of polar structures of both kinds, it makes sense to use Tikhonov's numerical method of weak regularization (Gorokhovatsky et al. 2018; 2022). For the experimental temperature dependence of the current, the activation energy distribution function *G(W)* is found, which is an inverse problem. The restoration of the distribution function for the activation energy *G(W)* is possible only in the case of a previously known value of the frequency factor. Since the frequency factor is not known in advance, a certain value of the frequency factor is chosen and the numerically reconstructed energy spectra are compared for two different heating rates of the same sample (ceteris paribus). In the case of a correctly chosen value of the frequency factor, the energy spectra (at least, the maxima of the distribution functions) should not differ for different heating rates. The difference in the reconstructed energy spectra indicates the need to select a different value of the frequency factor.

Figs. 2 and 3 show the reconstructed distribution functions for activation energy *G(W)*.

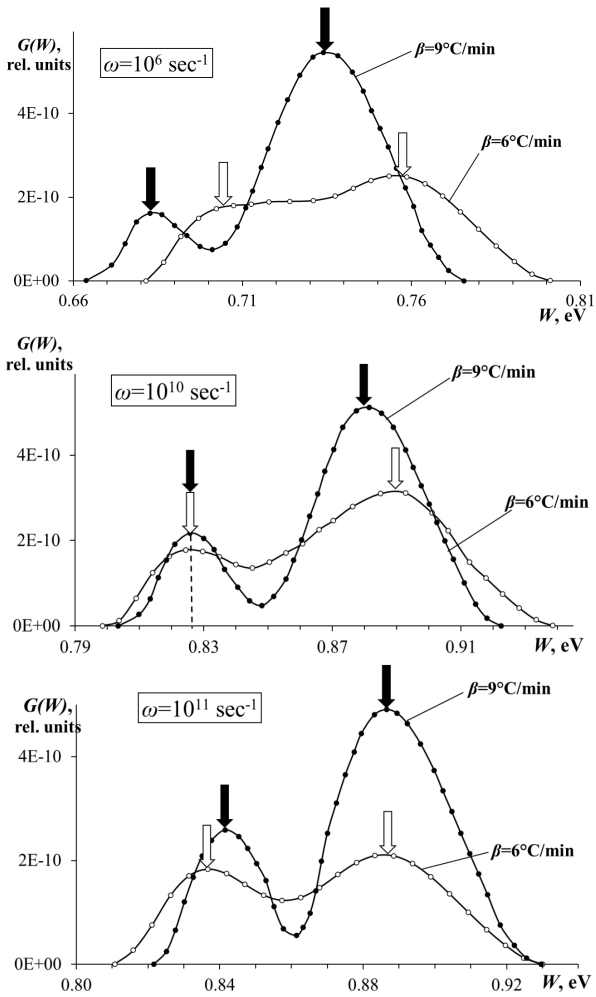


Fig. 2. Versions of the activation energy distribution functions G(W) for the P(VDF-TFE) copolymer polarized at a temperature of 80 °C in the field of a negative corona discharge for different linear heating rates. Calculation of activation energy and frequency factor for polar structures with lower activation energy

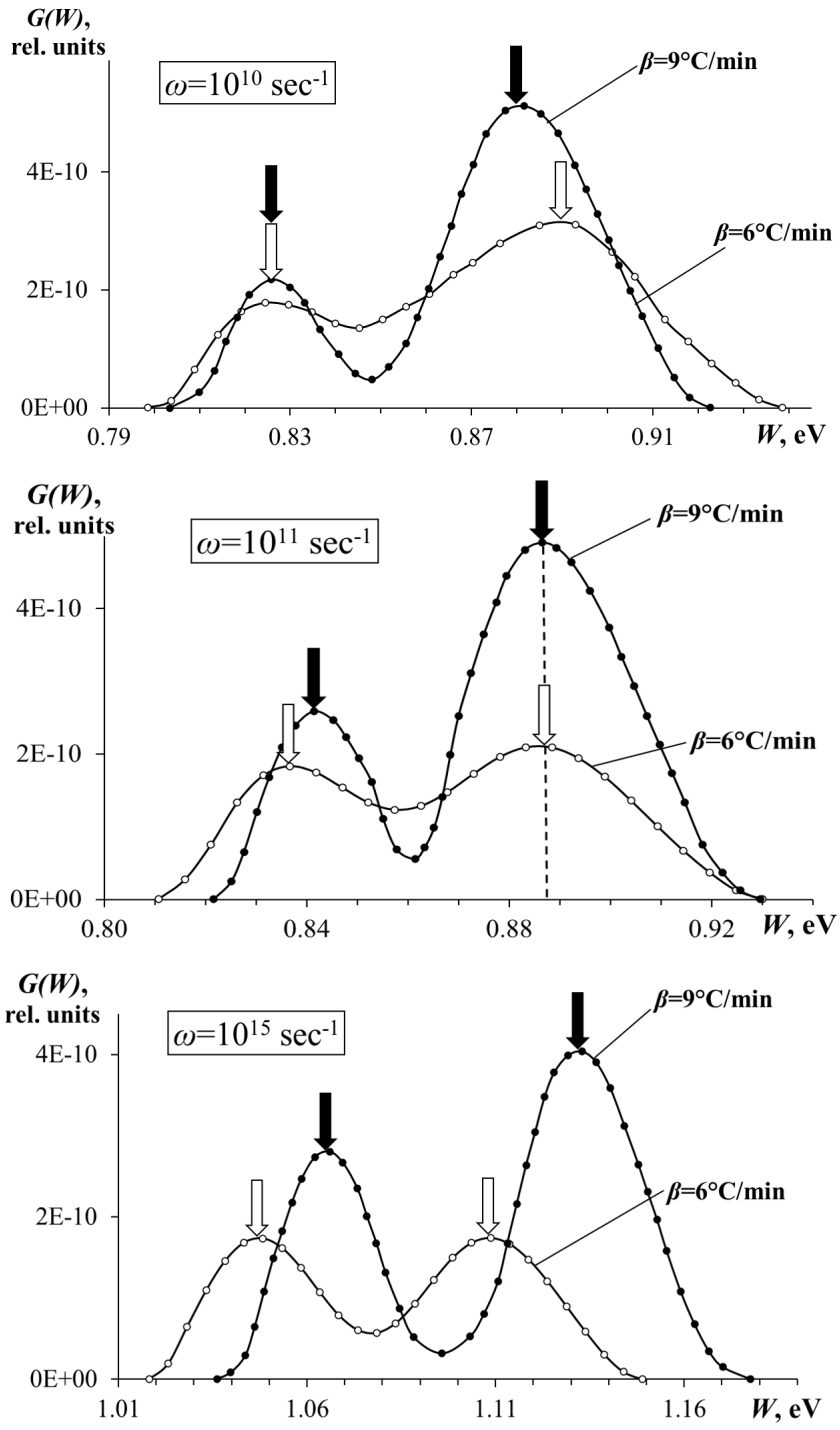


Fig. 3. Versions of the activation energy distribution functions G(W) for the P(VDF-TFE) copolymer polarized at a temperature of 80 °C in the field of a negative corona discharge for different linear heating rates. Calculation of activation energy and frequency factor for polar structures with higher activation energy

Fig. 2 shows that, according to Tikhonov's method of weak regularization, the parameters of polar structures with a lower activation energy are determined as $W$ = 0.83 ± 0.04 eV, $\omega = 10^{10}$ sec$^{-1}$ (with an accuracy of half a decade). According to Fig. 3, the parameters of polar structures with higher activation energy have the following values: $W$ = 0.89 ± 0.04 eV, $\omega = 10^{11}$ sec$^{-1}$ (accurate to half a decade). Thus, the polar structures in P(VDF-TFE) differ not only in the value of the activation energy but also in the value of the frequency factor (Gorokhovatsky et al. 2022).

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Another method of polarization, proposed by us in (Sotova et al. 2022), consists in polarization in the field of a negative corona discharge at room temperature for 10 minutes with further heating (the sample is in the open circuit mode, without an applied external electric field) to a temperature of 80 °C and cooling up to room temperature. The values of the piezoelectric modulus $d_{33}$ obtained with this method of polarization reach 22 ± 1 pC/N and are also characterized by good temperature stability.

Fig. 4 shows the TSC curves of P(VDF-TFE) polymer films polarized by the proposed method, measured at two different heating rates.

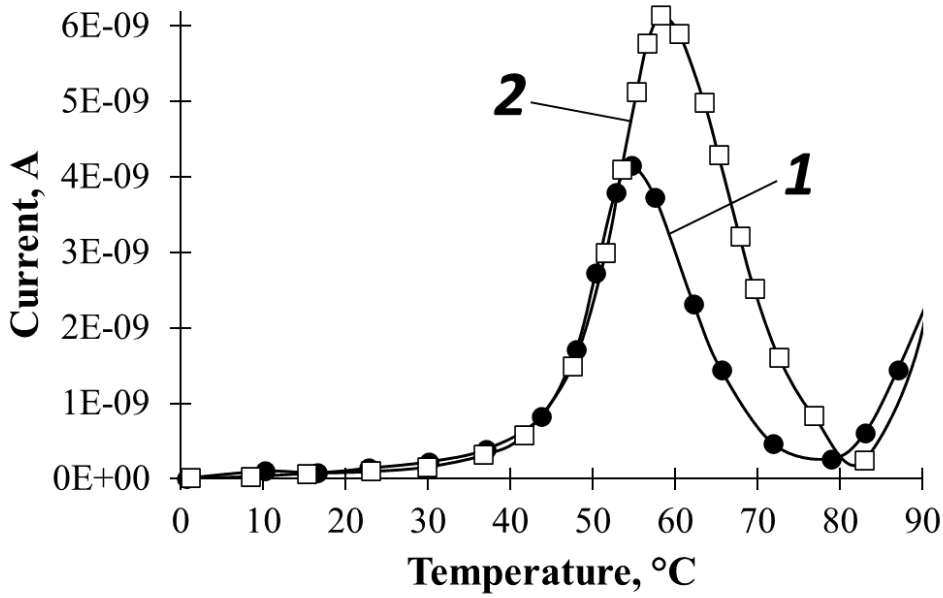


Fig. 4. TSC in P(VDF-TFE) copolymer films polarized at room temperature, depending on the linear heating rate (heating temperature after polarization is 80 °C): 1—linear heating rate β = 6 °C/min; 2—linear heating rate β = 9 °C/min

On the TSC curves in Fig. 4 there is one peak which is similar in its temperature position and magnitude to the low-temperature peak in Fig.1. Since it was previously concluded that the low-temperature peak in Fig. 1 is due to the misorientation of polar structures with lower activation energy, then we can assume that in this case the peak shown in Fig. 4 is due to the same process. The dependence of the TSC curves on the heating rate in this case has a traditional form: with an increase in the heating rate, the temperature position and the maximum of the current peak increase. The application in this case of the method of varying the heating rate gives the value of the activation energy $W$ = 0.82 ± 0.03 eV, the frequency factor $\omega = 10^{10}$ sec$^{-1}$ (with an accuracy of half a decade). The obtained values are in good agreement with the results calculated in the case of the traditional polarization method, which confirms that the peak in Fig. 4 is due to the misorientation of polar structures with lower activation energy.

Thus, during polarization in the field of a corona discharge at room temperature, the homocharge is captured by deep near-surface traps, and subsequent heating in the open circuit mode without an applied field leads to the orientation of polar structures (with lower activation energy) in the formed internal field of the homocharge. In this case, the resulting homocharge field turns out to be insufficient for the orientation of polar structures with higher activation energy. Apparently, the field of oriented polar structures with lower activation energy partially shields the homocharge field, thereby reducing it.

Comparison of the values of the piezoelectric modulus $d_{33}$ (22 ± 1 pC/N) obtained using polarization in the field of a negative corona discharge at room temperature with the value of the piezoelectric modulus obtained by the traditional method of polarization in the field of a corona discharge at elevated temperature (26 ± 1 pC/N) allows us to conclude that the orientation of polar structures with lower activation energy is sufficient to create a stable piezoelectric state. The orientation of polar structures with higher activation energy only slightly increases the value of the piezoelectric modulus $d_{33}$ and has little effect on its stability.

## Conclusions

A high and stable value of the piezoelectric modulus $d_{33}$ in P(VDF-TFE) polymer films can be achieved using a corona discharge field in various ways. It is possible to use the traditional technique and carry out polarization at an elevated temperature, as a result of which deep near-surface traps capture a homocharge, in the internal electric field of which the orientation and retention of the oriented state of polar structures occur. According to the TSC data, in this case, at least two kinds of polar structures are observed, which differ in their values of the activation energy $W$ and the frequency factor $\omega$. The numerical method of Tikhonov's weak regularization made it possible to determine the parameters of these relaxators: for polar structures with lower activation energy $W = 0.83 \pm 0.04$ eV, $\omega = 10^{10}$ sec$^{-1}$ (with an accuracy of half a decade); for polar structures with higher activation energy $W = 0.89 \pm 0.04$ eV, $\omega = 10^{11}$ sec$^{-1}$ (accurate to half a decade).

Another method of polarization in the field of a corona discharge is polarization at room temperature (which significantly reduces the probability of electrical breakdown) followed by heating and cooling (in open circuit mode, without an applied field). In this case, the homocharge is also captured by deep near-surface traps, but the resulting internal field of the homocharge is sufficient only for the orientation of polar structures with a lower activation energy, while the orientation of polar structures with a higher activation energy does not occur. Meanwhile, the piezoelectric modulus $d_{33}$ obtained in this case, in terms of its value and temperature stability, is not inferior to the piezoelectric modulus obtained by the traditional polarization method. This allows us to conclude that the stability of the piezoelectric state in P(VDF-TFE) is associated with the orientation of polar structures with lower activation energy.

## Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

## Author Contributions

The authors have made an equal contribution to the paper.

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