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A study of charge relaxation in corona electrets based on P(VDF-TFE) copolymer

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Abstract. Using the method of thermally stimulated depolarization currents, this paper explains the polarization in the field of corona discharge of polyvinylidene fluoride-tetrafluoroethylene (P(VDF-TFE)) copolymer films. It has been determined that to achieve the best electret properties of PVDF, polarization must be carried out in the field of negative corona discharge. It was found that the studied objects have two types of polar structures different in the activation energy and the frequency factor. Using a mix of traditional and numerical methods to analyze the peaks of the thermally stimulated depolarization currents, the parameters of the polar structures of both types found in P(VDF-TFE) were determined.

Keywords: electret state, polyvinylidene fluoride, tetrafluoroethylene, piezoelectric effect, TSD spectroscopy, weak regularization method

Introduction

Polymer films based on polyvinylidene fluoride (PVDF) and its copolymers with trifluoroethylene P(VDF-TrFE) and tetrafluoroethylene P(VDF-TFE) are widely used in electroacoustic transducers (in particular, in hydrophones) due to their piezoelectric properties (Aguilar et al. 2021; Martins et al. 2019).

PVDF is a semicrystalline polymer. The crystalline phase exhibits polymorphism and exists in five different crystalline modifications: α-, β-, γ-, δ- and ε-phases (Begum et al. 2018). The polar β-phase has piezoelectric properties (Kalimuldina et al. 2020). However, researchers still do not share a common ground regarding the nature of piezoelectricity in PVDF.

One of the most common ways to create a piezoelectric state in PVDF-based films is polarization in corona discharge field at an elevated temperature. The popularity of this method is due to the fact that corona polarization (compared to contact polarization) results in higher field values (Sukumaran et al. 2021). In this case, in addition to the piezoelectric state, an electret state is also formed in PVDF (Wang et al. 2016).

The reported study investigated the formation of the electret state in P(VDF-TFE) films.

Samples and research methods

The object of the study was a P(VDF-TFE) copolymer film (F2ME, 20 μm thick, mechanically stretched). A piezoelectric state was created in the samples using corona discharge field under special polarization conditions: the sample was placed in corona discharge field for 10 min (keeping the temperature constant) and then cooled to room temperature in this field. It is known that the magnitude of the electric field strength to form a piezoelectric state in PVDF is 1.2 MV/cm (Mahadeva et al. 2013). The value of the polarization temperature varied from 50 °C to 80 °C.

To study the accumulation of charges and relaxation occurring in P(VDF-TFE) during polarization, the method of thermally stimulated depolarization currents (TSD) was used. TSD measurements were carried out on a TSC II installation by Setaram.

Experimental results and discussion

Fig. 1 shows TSD curves in P(VDF-TFE) films polarized in the fields of negative and positive corona discharges (in both cases the polarization temperature was 70 °C).

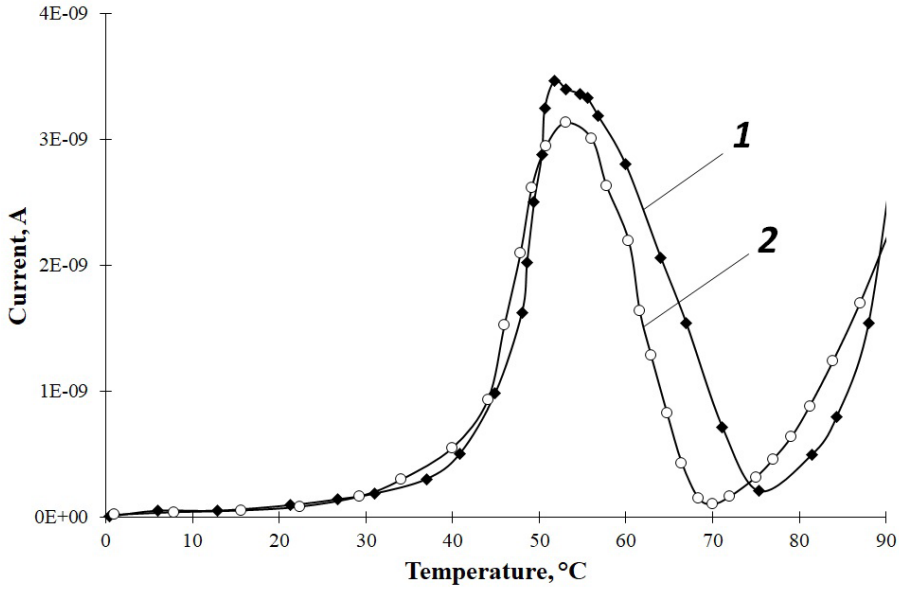

Fig. 1. Thermally stimulated depolarization currents in P(VDF-TFE) films polarized in the field of negative (1) and positive (2) corona discharge (polarization temperature is 70 °C)

TSD curves in Fig. 1 show a peak that is identical in its temperature position (about 50 °C) for both corona electrode polarities. However, the beginning and nature of an increase in current above 70 °C strongly depends on the corona electrode polarity: for positive polarity, the increase begins earlier and is less steep than for the negative polarity.

Apparently, when the film is polarized in the field of corona discharge, the homocharge (positive or negative) is captured by deep near-surface traps. The homocharge itself does not contribute to the piezoelectric state in P(VDF-TFE), however, in the resulting internal electric field of the homocharge, the oriented state of the polar structures (present in the piezoelectric β-phase of PVDF) is maintained, which is essential for maintaining the piezoelectric state. On the TSD curves, the misorientation of the polar structures is shown as a peak near 50 °C (therefore, its temperature position does not depend on the polarity of the corona electrode), and the release of the homocharge from deep surface traps is shown as an increase in current at above 70 °C.

It is possible to estimate the value of the homocharge activation energy by the initial rise method (Gorokhovatskiy, Bordovskiy 1991). The obtained value is (1.90 ± 0.09) eV for negative electrode polarity and (1.20 ± 0.06) eV for positive electrode polarity. Thus, the trap depth for a negative homocharge is greater than for a positive one, and to achieve the best electret properties of PVDF, polarization must be carried out in the field of negative corona discharge.

Fig. 2 shows TSD curves in P(VDF-TFE) films polarized in the field of negative corona discharge at different polarization temperatures. It can be seen from the obtained data that at a low polarization temperature (50–60 °C), the TSD curves exhibit one peak in the region of 50 °C, and with an increase in the polarization temperature (70 °C and 80 °C), the curves show two strongly overlapping peaks (at around 40–70 °C).

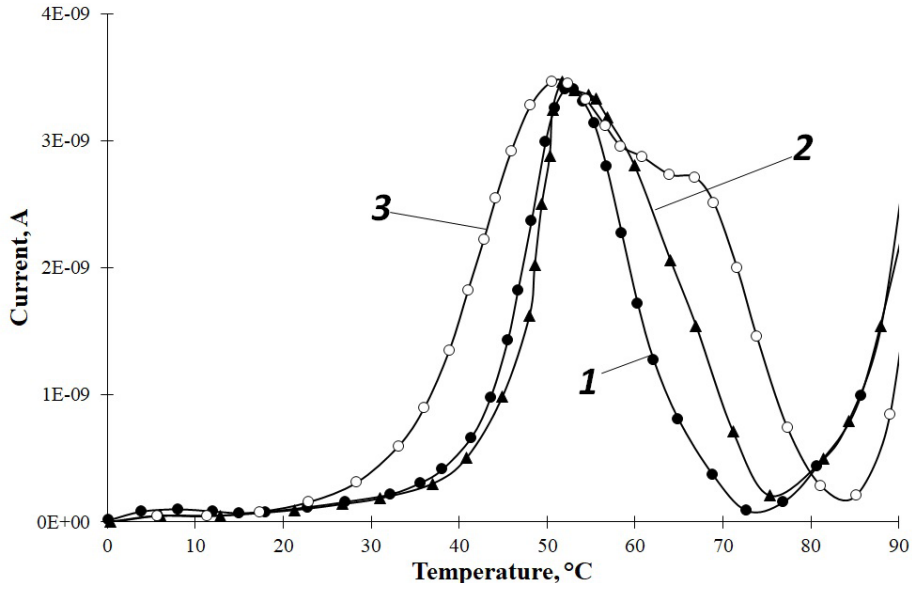

Fig. 2. Thermally stimulated depolarization currents in P(VDF-TFE) films polarized in the field of negative corona discharge at different polarization temperatures: 50 °C (1), 70 °C (2), and 80 °C (3)

Apparently, there are two kinds of polar structures in P(VDF-TFE) with different activation energies. During polarization in the field of corona discharge at a temperature of 50–70 °C, in the internal electric field of a homocharge, polar structures of only one type are oriented (with a lower activation energy shown as the current peak at around 50 °C). An increase in the polarization temperature to 80 °C leads to the orientation of both types of polar structures shown as the appearance of two strongly overlapping peaks on the TSD curves (in the temperature range from 40 °C to 70 °C).

The method of varying the heating rate was used to estimate the value of the activation energy and the frequency factor of polar structures with a lower activation energy (Gorokhovatskiy, Bordovskiy 1991). Table 1 shows the results of calculating the activation energy and the frequency factor (with an accuracy of half a decade) of polar structures present in the composition of P(VDF-TFE) polarized at different polarization temperatures.

Table 1. Values of the activation energy and frequency factor (with an accuracy of half a decade) of polar structures with a lower activation energy in P(VDF-TFE) films polarized at different polarization temperatures

Polarization temperature	Activation energy W, eV	Frequency factor ω, sec.$^{-1}$
50 °C	0.84 ± 0.03	10^{10}
70 °C	0.83 ± 0.03	10^{10}
80 °C	0.83 ± 0.03	10^{10}

Due to a too strong overlap of two closely spaced peaks, traditional methods for calculating the frequency factor and the activation energy are not effective enough for the estimation of these parameteres in the case of polar structures with a higher activation energy. In this case, Tikhonov's numerical method of weak regularization can be used (Gorokhovatsky et al. 2018). Based on the experimental temperature dependence of the TSD currents, it is possible, using numerical methods, to restore the distri-

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bution function of relaxing structures (in our case, polar structures) *G(W)* with respect to the activation energy. As a result, the obtained parameter values are W = (0.83 ± 0.04) eV, ω 10^{10} sec.$^{-1}$ for polar structures with lower activation energy and W = (0.89 ± 0.04) eV, $\omega = 10^{11}$ sec.$^{-1}$ for polar structures with higher activation energy (the frequency factor is determined with an accuracy of half a decade). It turns out that 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. Fig. 3 shows the distribution function of polar structures in P(VDF-TFE) *G(W)* in terms of activation energy for two types of polar structures (taking into account the difference in the value of the frequency factor).

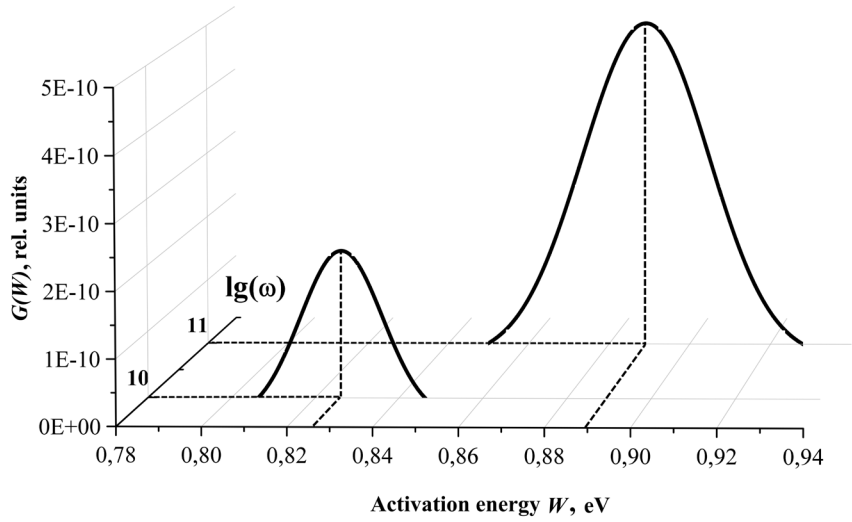

Fig. 3. The distribution function of polar structures in P(VDF-TFE) *G(W)* in terms of activation energy for the two types of polar structures (taking into account the difference in the value of the frequency factor)

Thus, the complex application of traditional methods for processing TSD current peaks and Tikhonov's numerical method of weak regularization made it possible to find the parameters of the polar structures of both types present in P(VDF-TFE).

Conclusions

Using thermal activation spectroscopy, the mechanism of polarization in P(VDF-TFE) copolymer films was identified: during polarization in the corona discharge field, deep near-surface traps capture a homocharge. In the internal homocharge electric field, the polar structures are oriented and their oriented state is maintained. An increase in the polarization temperature increases the contribution of dipoles with a higher activation energy (which is observed in the TSD curves as two strongly overlapping peaks). The activation energies of polar structures of two different types are (0.82 ± 0.03) eV and (0.89 ± 0.04) eV, frequency factors are 10^{10} sec. $^{-1}$ and 10^{11} sec.$^{-1}$ (accurate to half a decade). The depth of traps for positive and negative homocharge is different and amounts to (1.20 ± 0.09) eV and (1.90 ± 0.09) eV, respectively.

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 preparation of the text.

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