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## RHEOLOGICAL PARAMETERS' EFFECT ON THE ELECTRET PROPERTIES OF POLYVINYLIDENE FLUORIDE

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It is known that polymer films based on a copolymer of polyvinylidene fluoride and tetrafluoroethylene P(VDF-TFE) have piezoelectric properties, and these properties appear only after preliminary stretching of the films. The polar crystalline  $\beta$ -phase of the copolymer is responsible for the piezoelectric properties in the P(VDF-TFE), the percentage of this phase in the polymer can vary. In this work, we have studied the influence of the orientational stretching rate on the stability of the electret, and, as a consequence, the piezoelectric state. The influence of rheological parameters on the polymer structure and the parameters of electrically active defects responsible for polarization processes is shown.

**Keywords:** electret state, polyvinylidene fluoride, tetrafluoroethylene, piezoelectric effect, thermostimulated spectroscopy

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## ВЛИЯНИЕ РЕОЛОГИЧЕСКИХ ПАРАМЕТРОВ НА ЭЛЕКТРЕТНЫЕ СВОЙСТВА ПОЛИВИНИЛИДЕНФТОРИДА

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Известно, что полимерные пленки на основе сополимера поливинилиденфторида и тетрафторэтилена П(ВДФ-ТФЭ) обладают пьезоэлектрическими свойствами, причем эти свойства проявляются лишь после предварительной вытяжки пленок. За пьезоэлектрические свойства в П(ВДФ-ТФЭ) отвечает полярная кристаллическая  $\beta$ -фаза сополимера, процентное содержание которой в полимере может варьироваться. В данной работе исследовано воздействие скорости ориентационной вытяжки на стабильность электретного, и, как следствие, пьезоэлектрического состояния. Показано влияние реологических параметров на структуру данного полимера и параметры электрически активных дефектов, ответственных за процессы поляризации.

**Ключевые слова:** электретное состояние, поливинилиденфторид, тетрафторэтилен, пьезоэффект, термостимулированная спектроскопия

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## Introduction

The piezoelectric properties of polyvinylidene fluoride (PVDF) and copolymers based on it are used in various piezoelectric elements [1 – 3]. Piezoelectric properties of PVDF were observed for the first time in 1969 by H. Kawai [4]. Even then, it became clear to researchers that piezoelectric properties of PVDF films appear only after their preliminary stretching. Since there are certain difficulties in the production of dielectric films with piezoelectric properties from a PVDF homopolymer associated with a high coercive field of about  $10^8$  V/m (this is two orders of magnitude higher than that of piezoceramics) [5], there are usually used piezoelectric polymers with a lower coercive field based on vinylidene fluoride copolymers with trifluoroethylene (VDF-TrFE) and vinylidene fluoride with tetrafluoroethylene (VDF-TFE), which also have piezoelectric properties after stretching several times in comparison with the original length [6 – 9].

In this work, we have studied thermally stimulated depolarization currents in P(VDF-TFE) films manufactured at different rates of preliminary stretching and electreted in a negative corona discharge field.

It should be noted that prior to this, no proper attention was paid to the effect of the rate of preliminary stretching on charge relaxation in P(VDF-TFE) films.

## Samples and research methods

The subjects of inquiry were copolymers P(VDF-TFE) of the F2ME trademark with different rates of preliminary stretching. The pre-stretching rate (percentage increase in length per minute) was 5, 30, 50 and 200. The samples were examined by IR spectroscopy using the attenuated total reflection (ATR) on the FT-IR spectrometer FSM-1202 to determine the degree of crystallinity.

We also studied the thermally stimulated depolarization currents in P(VDF-TFE) films, in which the corona-electret state was created. The corona-electret state was created as follows: the samples were heated to a temperature of about  $70^\circ\text{C}$ , placed in positive or negative corona discharge (field of about 1 MV/cm) and held at an

elevated temperature for 10 min, then the samples were cooled down in the corona discharge field to room temperature. After that, the depolarization currents were measured in the films using a Setaram TSC II device; measurements were carried out in the linear heating mode at two heating rates:  $6^\circ\text{C}/\text{min}$  and  $9^\circ\text{C}/\text{min}$ .

## Experimental results and their discussion

**IR spectroscopy.** Fig. 1 shows the IR transmission spectra obtained using the ATR method for copolymer P(VDF-TFE) with pre-stretching rates (in % per min): of 5, 30, and 200. To determine the degree of crystallinity of PVDF, we studied the conformationally dependent band at  $840\text{ cm}^{-1}$  (crystalline phase,  $\alpha$  peak in Fig. 1) and the conformationally independent band at  $876\text{ cm}^{-1}$  (amorphous phase,  $\beta$  peak in Fig. 1). Since there are no bands corresponding to the  $\alpha$  phase for copolymers of VDF with TFE, the ratio of the intensities of these bands characterizes the degree of crystallinity of the polymer. By calculating the peak area ratio, it was obtained that the degree of crystallinity of the copolymer increased slightly from 49 % to 57 % as the stretching rate increased. Thus, it can be concluded that an increase in the stretching rate leads to a slight increase in the proportion of the crystalline  $\beta$  phase responsible for the piezoelectric properties of P(VDF-TFE). It should be noted that the quality of a piezoelectric element is determined not only by the magnitude of its piezoelectric modulus, but also by its stability.

**Thermally stimulated depolarization currents.** Fig. 2 shows a comparison of the curves of the depolarization currents P(VDF-TFE) with a preliminary stretching rate of 50 %/min electreted in the field of a positive and negative corona discharge (heating rate was  $6^\circ\text{C}/\text{min}$ ).

The curves show two closely located peaks, the magnitude and temperature position of which strongly depend on the polarity of the corona electrode. It should be noted that for other rates of preliminary stretching, the result was similar, i.e., the peak on the curve for negative polarity of the corona electrode was higher in magnitude and shifted along the temperature axis position compared with the peak for the positive polarity

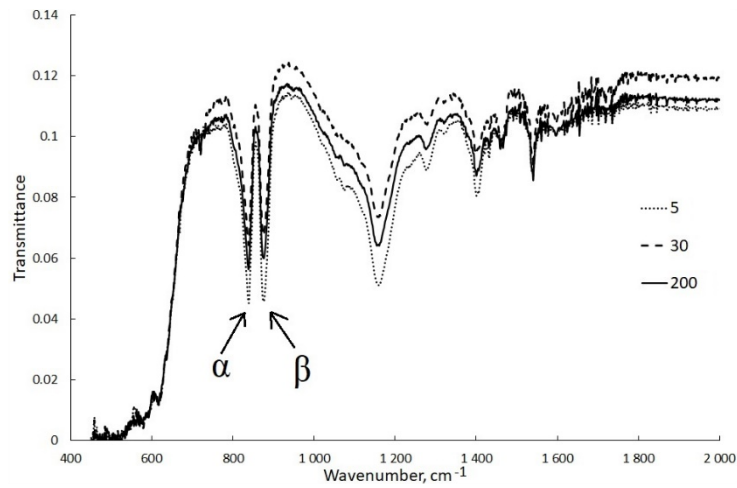


Fig. 1. ATR-IR spectra in copolymer P(VDF-TFE) for different rates of preliminary stretching (in % per min)

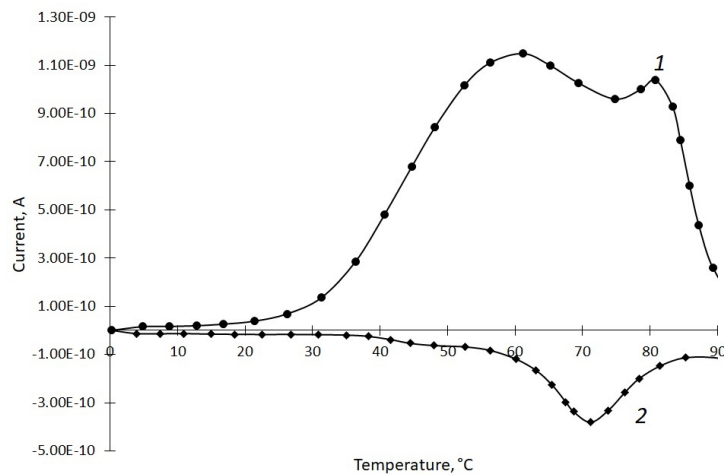


Fig. 2. Thermally stimulated depolarization currents in the P(VDF-TFE) with a preliminary stretching rate of 50 %/min, electreted in the field of the negative (1) and positive (2) corona discharges

of the corona electrode. This difference suggests that these peaks are associated with the relaxation of the homocharge, i.e., with the release of charge carriers from deep subsurface traps. Such traps can be caused, for example, by various defects in the structure of polymer films. Apparently, the number and depth of traps for positive and negative charge carriers are different: for negative charge carriers the traps are deeper and their number is greater. This result is consistent with literature data [10].

The dependence of the depolarization currents in the P(VDF-TFE) electreted in the field

of the negative corona discharge on the rate of preliminary stretching is shown in Fig. 3 (heating rate was 6°C/min). It can be seen that the high-temperature peak increases in magnitude and shifts to the region of higher temperatures with an increase in the stretching rate. Since we concluded earlier that this peak is associated with the release of charge carriers from traps, which, in turn, are caused by structural defects, it can be assumed that with a faster orientation of polymer films, the number of polymer chain defects increases, which means that the number of traps also increases.

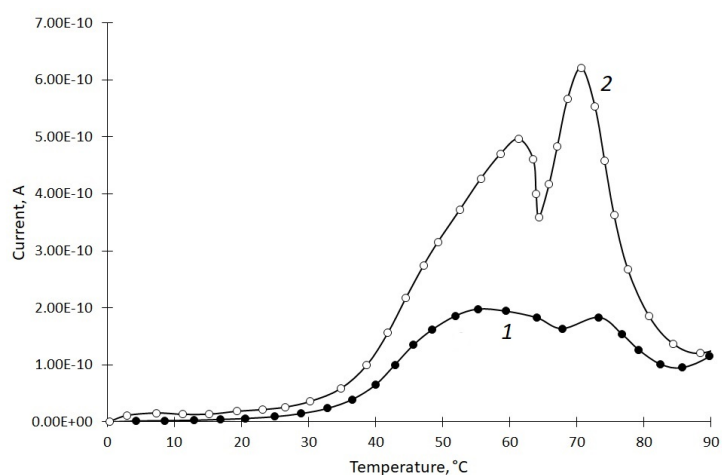


Fig. 3. Depolarization currents in the P(VDF-TFE) electreted in the field of the negative corona discharge at two values of a preliminary stretching rate (%/min): 30 (1) and 200 (2)

Using the method of varying the samples heating rate, the parameters of the traps (activation energy and frequency factor) for negative charge carriers were calculated. For this purpose, we measured the depolarization currents of the P(VDF-TFE) films with a preliminary stretching rate of 30 %/min, electreted in the field of the negative corona discharge, at two different heating rates (6 °C/min and 9 °C/min). The results are shown in Fig. 4, *a*. It is seen that with an increase in the heating rate, the peak increases in magnitude and shifts to the right along the temperature scale. This result is consistent with the theory of thermally stimulated depolarization currents. Calculations revealed that, in this case, the activation energy of traps for negative charge carriers is  $0.89 \pm 0.05$  eV, and the frequency factor is  $10^{12} \text{ s}^{-1}$  (with an accuracy of half a decade).

For the P(VDF-TFE) films with a preliminary stretching rate of 200%, electreted in the field of a negative corona discharge, the depolarization currents obtained for different heating rates are shown in Fig. 4, *b*. The chart also shows a shift in the peak towards higher temperatures with an increase in the heating rate from 6 °C/min to 9 °C/min. In this case, calculations give the following trap parameters: activation energy  $0.93 \pm 0.05$  eV, frequency factor  $10^{13} \text{ s}^{-1}$  (with an accuracy of half a decade). Thus, it can be

concluded that with an increase in the rate of preliminary stretching, the activation energy (depth) of traps for negative charge carriers slightly increases.

The curves in Fig. 3 also show a low-temperature peak (in the region of 50 – 60 °C), which is partially superimposed on the high-temperature peak (in the region of 75 °C). Since the growth of the low-temperature peak correlates with the growth of the high-temperature peak, we assume that the process in the region of 60 °C is associated with the reorientation of polar structures that are present in the amorphous phase. With an increase in the stretching rate, the value of the homocharge, as noted above, increases, which means that the field of this homocharge also increases, and therefore the reorientation of polar structures becomes more and more evident.

It should be noted that it is the presence of the component associated with the reorientation of polar structures present in the amorphous phase of P(VDF-TFE) that determines the stability of the electret state, and, accordingly, the stability of the piezoelectric state. The increase in the tensile rate leads to an increase in this component and, as might be expected, to an improvement in the stability of the electret and piezoelectric properties of the copolymer under study.

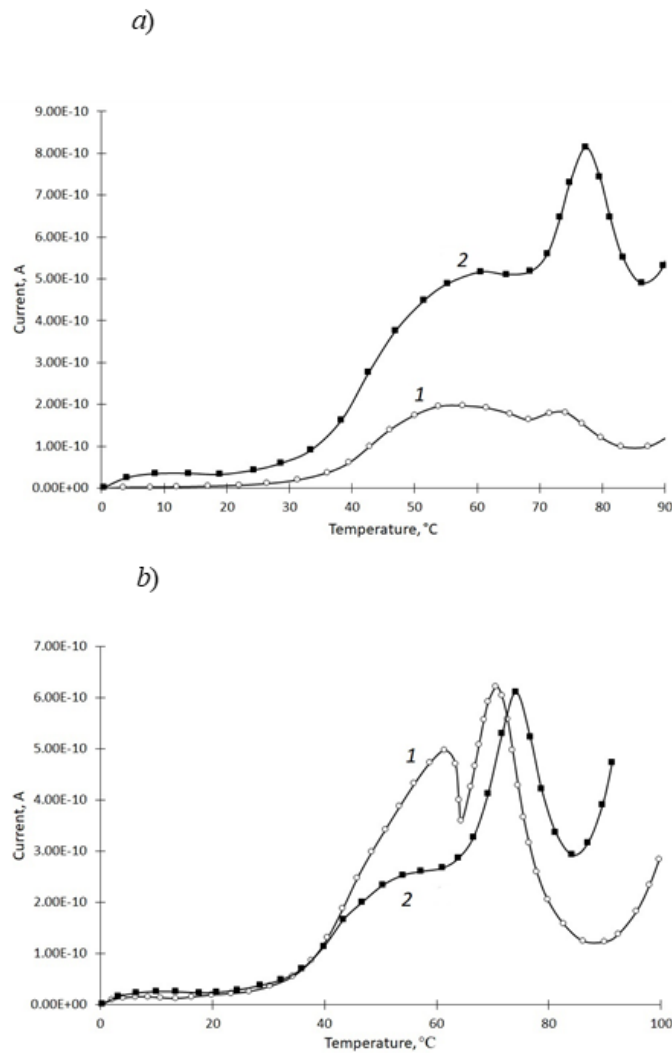


Fig. 4. Thermally stimulated depolarization currents in the P(VDF-TFE) with preliminary stretching rate of 30 %/min (a) and 200 %/min (b), electreted in the negative corona discharge field, for a heating rate of 6°C/min (1) and 9°C/min (2)

### Summary

IR spectroscopy data on the subjects of inquiry showed that with an increase in the stretching rate, the proportion of their ferroelectric  $\beta$ -phases increases. On the curves of thermally stimulated depolarization currents, two closely spaced peaks were found: a low-temperature one with a maximum in the region of 60°C and a high-temperature one with a maximum at 75°C. The high-temperature peak is associated with the release of charge carriers from deep near-surface traps, i.e., with relaxation of homocharge, the

value of which depends on the rate of preliminary stretching. The activation energy of the traps increases with an increase in the stretching rate from 0.89 eV to 0.93 eV. The low-temperature peak is due to the reorientation of polar structures that are present in the amorphous phase. As the stretching rate increases, i.e., with an increase in homocharge, the proportion of oriented polar structures also increases. The presence of a component associated with the reorientation of polar structures determines the stability of the electret and, consequently, the piezoelectric state.

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