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Effect of Orientation Stretching Rate on Piezoelectric Properties in Corona Electrets Based on Vinylidene Fluoride–Tetrafluoroethylene Copolymer

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In this paper, the effect of the orientational stretching rate on the piezoelectric properties and structure of the vinylidene fluoride–tetrafluoroethylene P(VDF-TFE) copolymer was studied. A relationship in the formation of the electret and piezoelectric states in P(VDF-TFE) has been established. The parameters of electrically active defects involved in the polarization process and determining the stability of the electret and, as a consequence, the piezoelectric states in P(VDF-TFE) are calculated.

Keywords: electret state, polyvinylidene fluoride, tetrafluoroethylene, piezoelectric effect, thermal activation spectroscopy.

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1. Introduction

Polymer films based on polyvinylidene fluoride (PVDF) are known primarily due to their ferroelectric properties. In 1969 the pyro- and piezoelectric properties were discovered in this polymer [1]. This has opened up wide opportunities for the use of this material in electroacoustic transducers, in particular, in hydrophones [2,3].

PVDF — semi-crystalline polymer with a degree of crystallinity 50–70%, which exhibits polymorphism: its crystal phase has five conformations: α-, β-, γ-, δ- and ε-phases [4]. However, there are certain difficulties in manufacturing a piezoactive film from a PVDF homopolymer associated with a high coercive field of the order of 10^8 V/m [5]. Therefore, in the future, the attention of researchers switched to PVDF copolymers with trifluoroethylene P(VDF-TrFE) and tetrafluoroethylene P(VDF-TFE) having a lower magnitude of the coercive field [6–8].

One of the most common ways to create a piezoelectric state in PVDF-based films is the polarization of the film in the corona discharge field at elevated temperature. The popularity of this method is due to the fact that with corona polarization, higher field values are achieved (compared to contact polarization) [9–11]. At the same time, an electret state [12,13] is also formed in the PVDF along with the piezoelectric state.

It is known that for the formation of a piezoelectric state in PVDF and copolymers based on it, preliminary orientation stretching of polymer films (most often at elevated temperature) is a prerequisite [14,15]. This is due to the fact that during orientation stretching of films, the non-polar α-phase is able to transition into the polar β-phase, which has piezoelectric properties. As a rule, polymer films P(VDF-TFE) is pulled with the degree of stretching $n = 3-5$ [16,17]. At the same time, usually the stretching rate of polymer films is not paid much attention.

In this regard, the purpose of this work was to study the effect of the rate of preliminary orientation stretching of polymer films P(VDF-TFE) on their electret and piezoelectric properties.

2. Samples and research methods

Polymer films P(VDF-TFE) were studied in the work of the F2ME trademark (Plastpolymer, Russia) with the ratio of monomeric units 70 : 30 (VDF/TFE), elongated at a temperature of 115°C with different stretching rate: $\nu = 5$, 30, 50, 100 and 200%/min (% shows the stretching size compared to the original length). A further increase in the stretching rate leads to mechanical damage to the polymer films. The degree of stretching for all samples was the same and was $n = 3.5$. The thickness of all the studied films was 100 μm.

The measurement of the piezoelectric coefficient d_{33} was carried out by a quasi-static method using the device D33 Meter (the SinoCera company). The study of the structure of polymer films was carried out using an IR-Fourier spectrometer FSM 1202 using the method of disturbed total internal reflection. To study the processes of accumulation and relaxation of charges occurring in P(VDF-TFE) during polarization, methods of thermal activation spectroscopy were used (method of short-circuit thermally stimulated currents (short-circuit TSC)), and also a direct measurement of the surface potential. The short-circuit TSC measurements were carried out at the Setaram TSC II installation, the

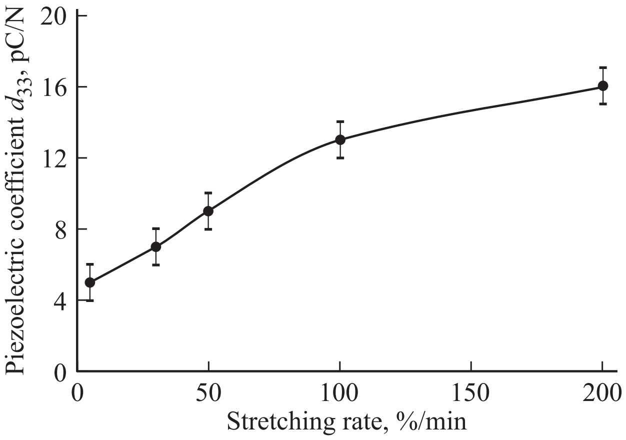

Figure 1. Dependence of the piezoelectric coefficient d_{33} of the copolymer P(VDF-TFE) from the pre-stretching rate.

surface potential was measured using an electrostatic field parameter meter IPEP-1.

3. Experimental results and discussion

3.1. The piezoelectric coefficient d_{33} measurement

In the samples, an electret (and piezoelectric) state was created under the action of a corona discharge field. The sample was placed in a corona discharge field at a temperature of 80°C, kept for 10 min (maintaining a constant temperature), and then cooled to room temperature in the field. To achieve the best electret characteristics, the polarization of the samples was carried out in the negative corona discharge field [18]. After polarization, the piezoelectric coefficient d_{33} was measured in P(VDF-TFE). Fig. 1 shows the dependence of the piezoelectric coefficient d_{33} in P(VDF-TFE) from stretching rate. Despite the same stretching coefficient for all samples, a significant (several times) increase in the value of the piezoelectric coefficient d_{33} was observed with an increase in the stretching rate. Among the studied samples, the best piezoelectric characteristics were shown by polymer films P(VDF-TFE), pre-orientationally elongated at a rate of $\nu = 200$%/min.

Preliminary studies have shown that the value of the obtained piezoelectric coefficient d_{33} varies slightly over several months (under the condition of storage of polymer films at room temperature). In the future, an additional study of the time and temperature stability of the piezoelectric coefficient d_{33} in P(VDF-TFE) is planned.

3.2. IR spectroscopy data

Since the orientation stretching leads to the transition of the nonpolar α-phase to the polar β-phase, the structure of all samples was investigated by the method of IR-Fourier spectroscopy. Fig. 2 shows a comparison of the IR spectra of P(VDF-TFE) at different stretching rates ($\nu = 5$, 50 and 200%/min).

Degree of crystallinity P(VDF-TFE), calculated using Fourier spectroscopy, depending on the rate of stretching

The stretching rate P(VDF-TFE) ν, %/min	Film Thickness P(VDF-TFE), μm	Crystallinity Degree, %
5	102 ± 1	49 ± 1
30	103 ± 1	51 ± 1
50	100 ± 1	52 ± 1
100	101 ± 1	54 ± 1
200	100 ± 1	57 ± 1

The IR spectroscopy data showed that qualitatively the spectra for all stretching rates are identical, i.e. the rate of orientation stretching does not affect the molecular composition of the studied samples. At the same time, characteristic bands corresponding to the crystal α-phase ($1278\,\mathrm{cm}^{-1}$) [19] are not observed on the spectra for all stretching rates, and there are only bands corresponding to β-phase ($842\,\mathrm{cm}^{-1}$) [20,21]. Thus, in all the studied samples, the crystal fraction consists only of β-phase. At the same time, with an increase in the stretching rate, the degree of crystallinity increases from 49 to 57% (table), which may partially explain the increase in the piezoelectric coefficient d_{33} with an increase in the rate of orientation stretching. However, the resulting significant change in the piezoelectric coefficient d_{33} (by more than 3 times) cannot be determined only by a change in the degree of crystallinity.

3.3. Thermal activation spectroscopy data

To explain the obtained dependence of the piezoelectric characteristics P(VDF-TFE) from the rate of the orientation stretching the previously proposed model of the polarization mechanism in the corona discharge field at elevated temperature [22] was used. According to the model, during polarization, a homocharge is captured by deep near-surface traps, in the internal electric field of which the orientation and retention of the oriented state of the polar structures present in the β-phase. At the same time, the homocharge itself does not contribute to the piezoelectric state. The piezoelectric state is formed due to the orientation and retention of the oriented state of polar structures in the field of a this charge.

The results of the study of short-circuit TSC in P(VDF-TFE) with different pre-stretching rates are shown in Fig. 3.

Fig. 3 shows that at the lowest stretching rate ($\nu = 5$%/min), only one low-temperature peak was observed in the region of 55°C. Earlier in [22] it was experimentally shown that in P(VDF-TFE) there are two varieties of polar structures with different activation energies. When polymer films are polarized at a pre-stretching rate of

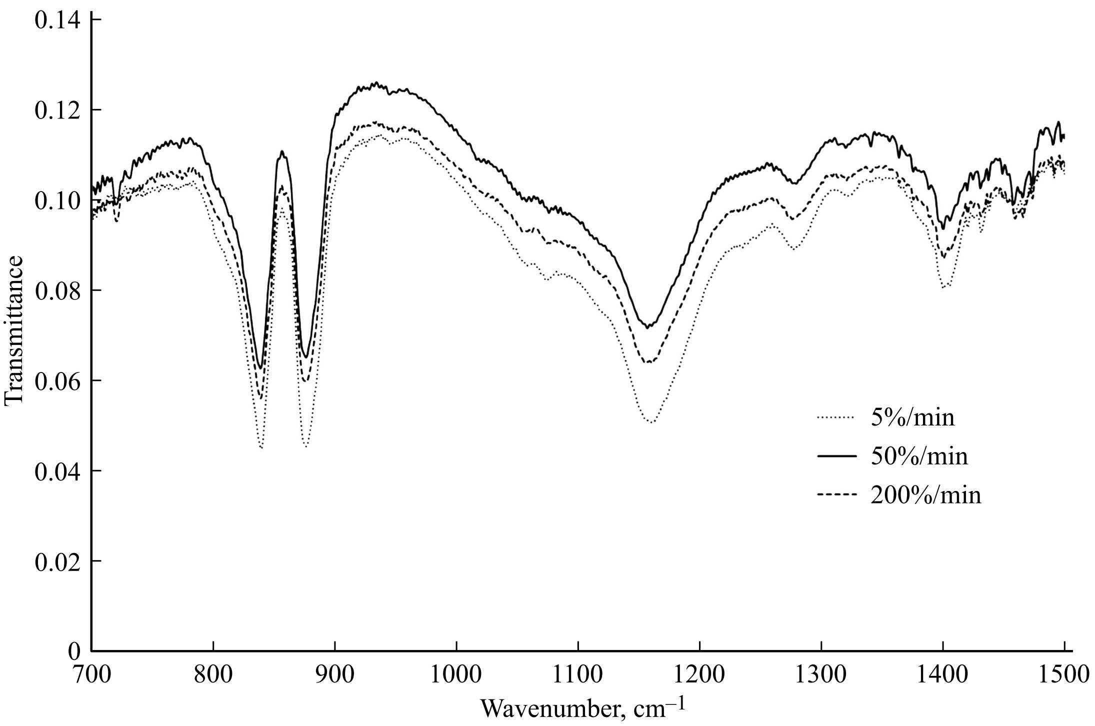

Figure 2. IR transmission spectra P(VDF-TFE) with stretching rates $\nu = 5$, 50 and 200%/min in the range of wave numbers from 500 to 1700 cm^{-1}.

$\nu = 5$%/min, only a small number of polar structures with a lower activation energy are oriented. The calculated parameters of these polar structures are: activation energy $E_{\text{act}} = 0.83 \pm 0.04$ eV, frequency factor 10^{10} s^{-1} (accurate to half a decade).

With an increase in the stretching rate from $\nu = 30$ to $\nu = 200$%/min, two closely spaced peaks were observed on the current curves, the magnitude and area of which increase with increasing stretching rate. At the same time, the temperature position of both peaks does not depend on the stretching rate. Thus, an increase in the stretching rate leads to the orientation of polar structures of both varieties; and with an increase in the stretching rate, the number of oriented polar structures increases. The parameters of polar structures with greater activation energy are: $E_{\text{act}} = 0.90 \pm 0.04$ eV, frequency factor 10^{11} s^{-1} (with precision to half a decade). Thus, polar structures differ not only in the value of E_{act}, but also in the value of the frequency factor.

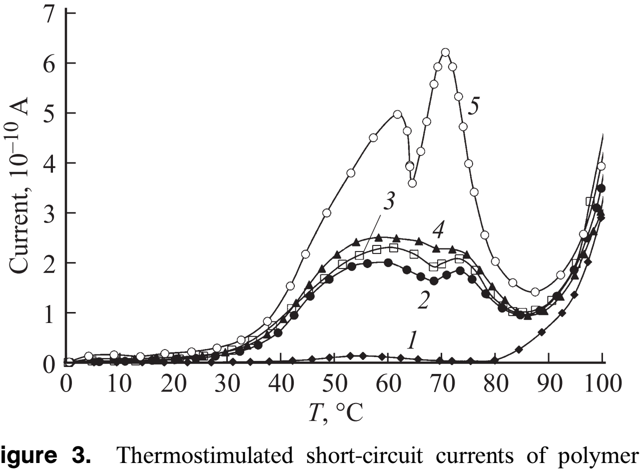

Figure 3. Thermostimulated short-circuit currents of polymer films P(VDF-TFE) electretted in the negative corona discharge field, having different rates of preliminary orientation stretching ν: 5%/min (*1*); 30%/min (*2*); 50%/min (*3*); 100%/min (*4*); 200%/min (*5*). (polarization temperature 80°C, linear heating rate 6°C/min).

The increase in the number of oriented polar structures with an increase in the stretching rate is due to an increase in the internal field of the homocharge. An estimate of the activation energy of this process (manifested as an increase in current above 80°C in Fig. 3) gives the same value $E_{\text{act}} = 1.9 \pm 0.09$ eV for all stretching rates. In this case, the increase in the internal field of the homocharge is associated with an increase in the concentration of traps capturing the homocharge.

To verify this assumption, the value of surface potential of P(VDF-TFE) films with different stretching rates was measured immediately after the polarization of the films. (Fig. 4).

It can be seen that the value of the surface potential increases with an increase in the stretching rate, i.e., the homocharge field increases. Thus, with an increase in the stretching rate in polymer films P(VDF-TFE) the number of traps for the homocharge capable of capturing charge carriers increases, which, in turn, leads to an increase in the internal field of the homocharge. At $\nu = 5$%/min, the

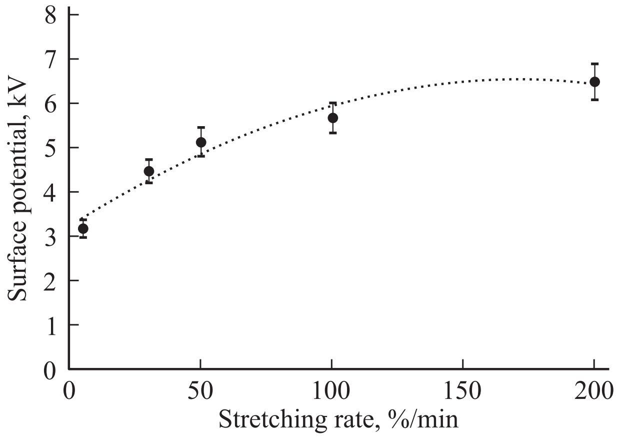

Figure 4. The value of the surface potential of copolymer films P(VDF-TFE) polarized in the field of negative corona discharge (polarization temperature 80°C), depending on the orientation stretching rate.

homocharge field is small, and only a small number of polar structures with a lower activation energy are oriented in it, and the orientation of polar structures with a higher activation energy does not occur at all. At $\nu = 30\%/\mathrm{min}$ and above, the number of defects (traps) formed is already sufficient to form a homocharge field in which the orientation of polar structures of both varieties occurs. At $\nu = 200\%/\mathrm{min}$, the homocharge field is the largest, and the number of oriented polar structures reaches a maximum (in the investigated range of stretching rates). It is important to note that it is the presence of a component associated with the orientation of polar structures that determines the stability of the electret state, and, accordingly, the stability of the piezoelectric state. An increase in the stretching rate leads to an increase in this component, and, as a consequence, to an improvement in the stability of the electret and piezoelectric properties of the studied copolymer P(VDF-TFE).

4. Conclusion

In this paper, the influence of the rate of orientation stretching on the piezoelectric properties of P(VDF-TFE) is revealed: with an increase in the stretching rate in the range $\nu = 5-200\%/\mathrm{min}$ the value of the piezoelectric coefficient d_{33} grows and reaches a value of 16 pC/N at the stretching rate $\nu = 200\%/\mathrm{min}$.

Using the results obtained by thermal activation spectroscopy methods, a possible explanation was proposed for the dependence of electret and piezoelectric properties on the rate of preliminary orientation stretching: with an increase in the stretching rate, the number of structural defects acting as traps for charge carriers increases, and, as a consequence, the internal field of the homocharge increases, which, in turn, leads to improve the electret and piezoelectric properties of P(VDF-TFE).

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Conflict of interest

The authors declare that they have no conflict of interest.

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