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EXPERIMENTAL METHODS FOR STUDYING THE INFLUENCE ON PIEZOELECTRIC PROPERTIES OF POLYMERS

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Presents a description and justification for the choice of experimental methods used to study the electrophysical properties of the P(VDF-TFE) copolymer. A description of the experimental equipment used is also provided. Consisted of studying the relationship between the processes of formation of the electret and piezoelectric state in P(VDF-TFE) polymer films to clarify the charge relaxation model, as well as identifying factors that improve the piezoelectric characteristics of the material under study [6-9].

Keywords: Piezoelectric properties of P(VDF-TrFE)-vinylidene fluoride-tetrafluoroethylene, coronoelectret state, piezoelectric properties, copolymer

Studying the electrophysical properties of polymers involves investigating their electrical conductivity, dielectric properties, and other electrical characteristics. Various experimental methods are employed to understand these properties. Here are some common techniques: Measures the response of a material to an applied AC voltage across a range of frequencies, Characterizing electrical properties, such as conductivity and dielectric constant, as a function of frequency, Measures the dielectric response of a material to an applied electric field over a range of frequencies, Provides information about molecular motions, relaxation processes, and conductivity in polymers, Measures the resistivity of a thin film or a bulk material by applying a current through four equidistant points and measuring the voltage drop, Determines electrical conductivity, especially in thin polymer films, Applies a magnetic field perpendicular to the direction of current flow to measure the charge carriers' mobility and concentration, Provides information about the type and concentration of charge carriers in a polymer, Measures the electrical conductivity of a material by applying a known voltage and measuring the resulting current, Quantifies the ability of a polymer to conduct electricity, Applies a potential sweep to a working electrode to study redox processes and charge storage in polymers, Used for studying electrochemical properties, such as capacitance and charge/discharge behavior, Measures the current released when charges trapped in a polymer are thermally activated, Provides information about charge carrier traps and mobility in polymers, Applies a pulsed magnetic field gradient to measure molecular mobility and diffusion in polymers, Studies the mobility of charged species within the polymer matrix, Measures changes in electrical conductivity induced by light illumination, Investigates the photoresponsive behavior of polymers and their potential use in optoelectronic devices, Helps characterize the piezoelectric and ferroelectric properties of polymers [1-5].

Understanding and mitigating the impact of these electrophysical processes is crucial in power engineering to ensure the reliability, safety, and efficiency of electrical systems. Engineers employ various measures such as proper insulation design, surge protection devices, and monitoring systems to manage the effects of electrical discharges in power engineering objects: Polymers possess varying dielectric properties, which affect their ability to store electric energy. The dielectric strength determines how much voltage a material can withstand before breakdown. High dielectric strength is desirable for capacitors and insulating materials in energy systems to prevent electrical breakdown; In some cases, polymers can exhibit electric conductivity, especially when doped or modified with conductive additives. Controlling the conductivity of polymers allows their use in applications such as organic electronics, sensors, and energy storage devices like batteries.; When subjected to electric gas discharge, polymers may exhibit several behaviors. They can experience degradation due to the formation of free radicals or breakdown products, affecting their longevity and reliability in energy systems. Additionally, discharge in polymers can lead to the emission of light, known as electroluminescence, which has applications in lighting technologies; Polymers are often used as insulating materials in high-voltage systems[1-6]. However, under certain conditions, they can experience corona discharge, where localized ionization occurs:

Managing corona discharge is crucial as it can lead to energy losses, material degradation, and even equipment failure in power transmission systems; Utilizing electric gas discharge, plasma treatment can modify the surface properties of polymers. This treatment can enhance adhesion, wettability, and other surface characteristics, enabling improved performance in energy-related applications like solar cells or fuel cells. Understanding and controlling these electrophysical properties are crucial for optimizing the performance and reliability of polymers in various energy sectors, including electrical insulation, energy storage, power transmission, and renewable energy technologies. The dielectric properties of polymers were described according to Maxwell's model. The values of the real parts of the effective complex dielectric constant $\varepsilon'_{eff}(f)$ and electrical conductivity $\sigma'_{eff}(f)$ of the samples were determined from the relations[3].

$$\varepsilon'_{eff}(f) = \frac{C(f) \cdot l}{\varepsilon_0 \cdot S}; \quad \sigma'_{eff}(f) = \frac{l}{R(f) \cdot S} \quad (1)$$

where $C(f)$ and $R(f)$ – capacitance and resistance of the sample on alternating current at frequency f of the external electric field, l and S – thickness and cross-sectional area of the sample, $\varepsilon_0 = 8.854 \cdot 10^{-12}$ F/m – dielectric constant[2-5].

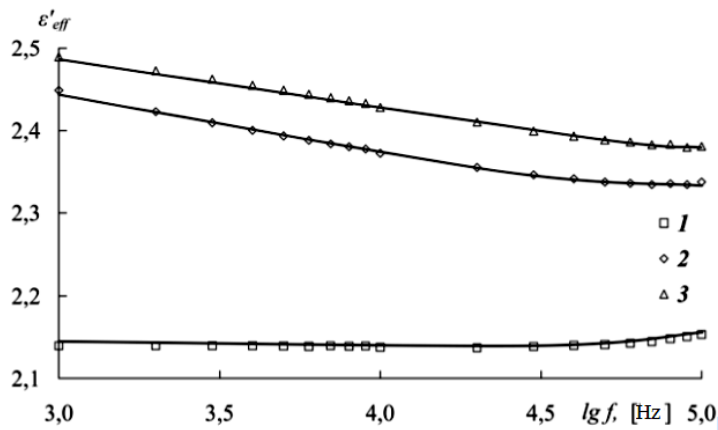


Figure 1- Frequency dependences of the real part of the complex dielectric constant of the original polymers: 1 – PS; 2 – PMMA; 3 – PVC [2-4].

The sharp increase in the value of the real part of the complex dielectric permittivity of PVC in the low-frequency region is obviously associated with Maxwell-Wagner losses caused by the movement of the space charge. This suggests that irradiation of PVC is accompanied by an increase in electrical conductivity. The studies carried out allow us to assert that changes in the values of the real parts of the complex dielectric constant and electrical conductivity of a material depend on the type of polymer and its irradiation dose. Frequency dependences of quantities indicate different degrees of mobility of structural elements exposed to radiation, which is one of the most effective modifiers of the electrical properties of materials.

Piezoactive PVDF has several advantages over piezoelectric crystals: flexibility, strength and the ability to be used in the form of thin films. Therefore, PVDF has found its wide application in electroacoustic transducers (in particular, in hydrophones). It is known that the addition of trifluoroethylene (P(VDF-TrFE)) and tetrafluoroethylene (P(VDF-TFE)) monomers to the PVDF polymer chain improves the piezoelectric properties of this polymer.

However, if the piezoelectric properties of P(VDF-TrFE) have been widely studied (usually foreign colleagues, for example, in [1-3]), much less is known about the P(VDF-TFE) copolymer, although it also has piezoelectric properties. Since in order for PVDF to have piezoelectric properties, preliminary polarization of the polymer films is necessary (as usually in the field of a corona discharge), often, in addition to the piezoelectric state, a corona-electret state is also formed in PVDF. At the same time, attempts continue to improve the piezoelectric characteristics of PVDF and copolymers based on it by changing the polarization conditions or the manufacturing conditions of polymer films. In connection with all of the above, It seems relevant to study the coronoelectret state and its effect on the piezoelectric properties in the P(VDF-TFE) copolymer.

It is shown that the combined use of experimental methods of thermal activation spectroscopy (in particular, thermally stimulated short-circuit currents

and thermally stimulated relaxation of surface potential), Fourier transform infrared spectroscopy, and a quasi-stationary method of measuring the piezoelectric modulus makes it possible to determine the nature of relaxation processes in polymer films, as well as to determine the key parameters of these processes. Methods of thermal activation spectroscopy - thermally stimulated short-circuit currents and thermally stimulated relaxation of surface potential - make it possible to study and determine the mechanisms of relaxation of the electret state. The integrated application of traditional and numerical methods for processing experimental data makes it possible to calculate the activation energy and frequency factor of electrically active defects. Using the FT-IR spectroscopy method, it is possible to study the molecular structure of a polymer material, as well as calculate the degree of crystallinity of a semi-crystalline polymer. The quasi-stationary method of measuring the piezoelectric modulus d allows one to study the relationship between the formation of electret and piezoelectric states in polymer films. The TSRPP method measures the change in the surface potential of a pre-polarized sample when it is heated (in linear mode). The structure of P(VDF-TFE) polymer films was studied using an FSM 1202 Fourier spectrometer using the attenuated total internal reflection (ATR) method. The spectra were obtained in the wavenumber range from 500 cm^{-1} to 1700 cm^{-1} .

The procedure for creating a polarized state in the P(VDF-TFE) copolymer using a corona discharge field was as follows: the sample was placed in the specified field at an elevated temperature (polarization temperature), kept in it for 10 min (maintaining a constant temperature), and then cooled to room temperature in the same field. This procedure for creating a piezoelectric state in PVDF and copolymers based on it is traditional and widespread. The polarization temperature of P(VDF-TFE) varied and was 50, 60, 70 and 80°C . The electric field strength required for the formation of a piezoelectric state in P(VDF-TFE) was about 1.2 MV/cm . Polarization was carried out with positive and negative polarities of the corona electrode.

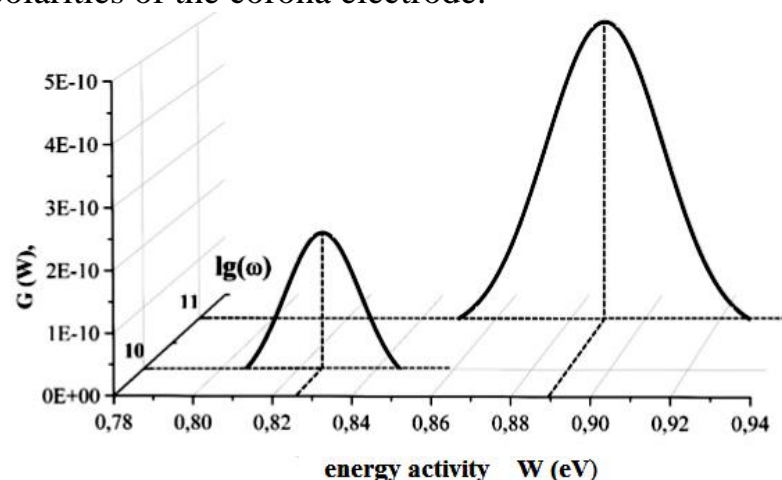


Figure 2 - depicts the two-dimensional distribution function of polar structures by activation energy $G(W)$ for two types of polar structures present in P(VDF-TFE) (taking into account the difference in the value of the frequency factor) [6-9].

To solve this problem, it was proposed to change the technique for obtaining a piezoelectric state using polarization in the internal field of a homocharge in PVDF-based polymer films. The procedure for creating a polarized state in the P(VDF-TFE) copolymer in this case was as follows: the polymer films were first polarized at room temperature in the field of a negative corona discharge for 10 minutes (the electric field strength was 1.2 MV/cm), then were heated (the sample was in an open state, without an applied external electric field) to different temperatures, and then cooled to room temperature. The heating temperature after polarization at room temperature varied and was 50, 60, 70 and 80°C. When polarized in the field of a corona discharge at room temperature, the probability of electrical breakdown becomes much less. Figure 3 shows the results of measuring the SC TSC in P(VDF-TFE) films polarized at room temperature in the field of a negative corona discharge, depending on the temperature of subsequent heating. The linear heating rate was 6°C/min[6-9].

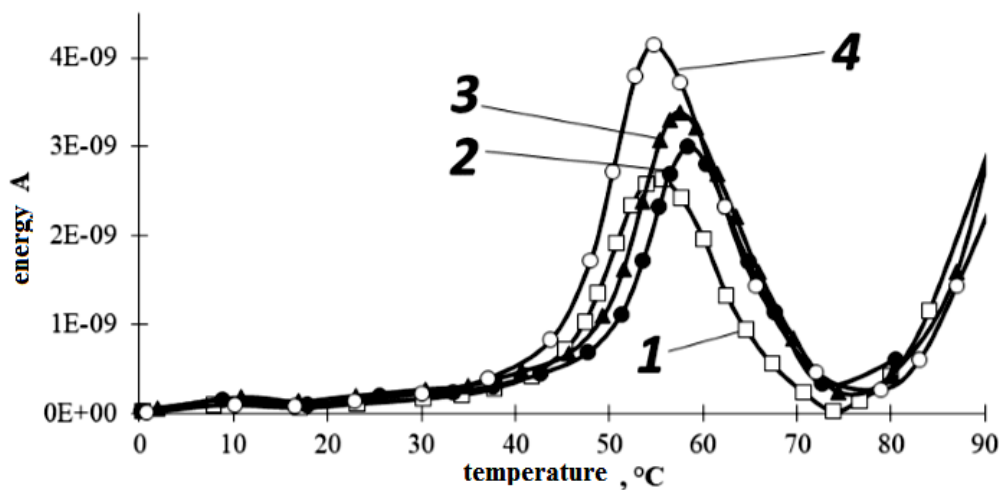


Figure 3 – in P(VDF-TFE) copolymer films polarized in the internal field of negative homocharge at a heating temperature of 50°C (curve 1), 60°C (curve 2), 70°C (curve 3), 80°C (curve 4) (linear heating rate 6°C/min) [6-9].

One peak is observed in the curves, which in its temperature position and magnitude is similar to the low-temperature peak in Figure 3, which allows us to associate it with the process of misorientation of polar structures with a lower activation energy. Using the method of varying the heating rate, the values of activation energy W and frequency factor ω were estimated. The obtained values are in good agreement with the results calculated in the case of the traditional polarization method. Since the presence and depth of near-surface traps do not depend on the polarization temperature and are determined by the structure of the material, during polarization in the field of a corona discharge at room temperature, the homocharge should also be captured by these traps. In Figure 3 this is manifested by an increase in current above 75°C. Thus, during polarization in the field of a corona discharge at room temperature, the homocharge is captured by deep surface traps, and subsequent heating in the

open state without an applied field leads to the orientation of polar structures (with a lower activation energy) in the resulting internal homocharge field.

With increasing heating temperature, the mobility of polar structures increases, therefore, more polar structures are able to orient, which leads to an increase in the magnitude and area under the peak in Figure 4. Cooling after heating to room temperature leads to “freezing” of the oriented state. The absence of a high-temperature peak in Figure 4, which is responsible for the misorientation of polar structures with a higher activation energy, may be due to the fact that the homocharge field is insufficient for the orientation of polar structures with a higher activation energy.

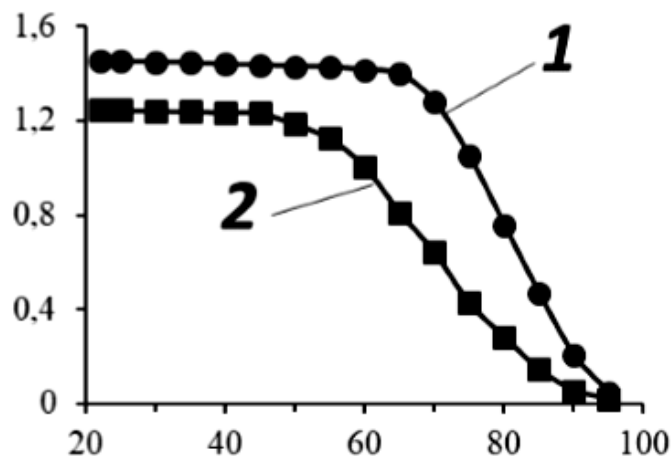


Figure 4 – P(VDF-TFE) copolymer films polarized in the internal homocharge field (heating temperature 80°C, linear heating rate 5°C/min) in the case of negative (curve 1) and positive (curve 2) polarity of the discharge electrode [6-9].

Conclusion:

The main results and conclusions of the work are as follows:

1. A model is proposed for the mechanism of polarization of polymer films of the P(VDF-TFE) copolymer in the field of a corona discharge at elevated temperatures: during polarization, a homocharge is captured by deep near-surface traps, in the internal electric field of which orientation and maintaining the oriented state of polar structures. In this case, 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 given charge.

2. It has been determined that the depth and number of traps for positive and negative charge carriers are different. The activation energy (trap depth) is $W=1.90\pm 0.09$ eV for negative charge carriers and $W=1.20\pm 0.06$ eV for positive charge carriers.

3. It has been established that P(VDF-TFE) contains two types of polar structures that differ in their characteristics (activation energy and frequency factor). Increasing the polarization temperature increases the contribution of polar structures with higher activation energies.

4. Using the integrated application of traditional and numerical methods for processing CG TSC peaks, the parameters of polar structures of both types were calculated: for low-energy polar structures, the activation energy is $W = 0.83 \pm 0.03$ eV, the frequency factor is 10^{10}c^{-1} (with an accuracy of half decades); for high-energy polar structures, the activation energy is $W=0.89 \pm 0.04$ eV, the frequency factor is 10^{11}c^{-1} (with an accuracy of half a decade).

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