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Complex dielectric permittivity of films in the infra-low frequency range as studied by relaxation maps of thermally stimulated currents

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Abstract. The paper shows the possibility of interpreting the results of thermal activation spectroscopy of PVDF polymer films obtained by thermally stimulated currents of fractional polarization using the concepts of low-frequency dielectric spectroscopy. The paper presents the results of the study of temperature-frequency dependences of the components of complex dielectric permittivity in PVDF films with different degrees of orientation, polymorphic composition and pore percentage. It also provides the parameters of electrically active defects responsible for relaxation processes in the temperature range under study.

Keywords: porous films, polyvinylidenftoride, thermactivational spectroscopy, dielectric spectroscopy, dielectric parameters

Introduction

The methods of thermal activation analysis have been actively used since the end of the 20th due to fairly simple experimental technology combined with great processing capabilities of experimental results. One of the methods of thermal activation analysis is the method of thermally stimulated currents in fractional polarization (TSC-FP). It allows to recalculate the results obtained by dielectric spectroscopy (DS) in the infralow frequencies of the order of 10^{-2}–10^{-5} Hz with significantly less time compared to the traditional method of dielectric spectroscopy.

In this paper, polyvinylidene fluoride (PVDF) films with different polymorphic composition and pore percentage were studied by the method of thermally stimulated fractional polarization currents.

The properties of PVDF, including electrophysical ones, are largely determined by various modifications of its crystal phase (α-, β-, γ- modifications) (Kochervinskii 1996). A pronounced piezoelectric effect is manifested in a PVDF film containing a large amount of the polar β- phase. The presence of pores in such materials can significantly expand the scope of their application. The formation of the polar phase and pores is possible due to orientation extraction carried out at certain tempretures.

The change in the structure also significantly affects the dielectric properties of this polymer dielectric permittivity and dielectric losses. This is explained by the change in the dipole moment of the monomer link and the relaxation time. Therefore, dielectric properties can be used as a characteristic of a rather complex polymorphic polymer structure (Kochervinskii 1996).

Materials and methods

The paper investigated porous films made from PVDF granules of the commercial brand Kynar-720 (Atofina Chemicals, USA), with a molecular weight of M_w = 190000 g·mole^{-1} and the melting point 168 °C.

The films were obtained in a four-stage process: polymer melt extrusion, isometric annealing, uniaxial stretching and thermal fixation (Elyashevich et al. 1997). The first stage of film formation is characterized by the parameter λ- multiplicity of the die drawing. This stage affects the structure of the studied samples and the degree of orientation. The paper (Gerasimov et al. 2020) shows that at low values of the multiplicity of the die extraction (λ < 20), a weakly oriented spherulite structure prevails in the crystal phase of the samples. In samples with λ > 20, an oriented lamellar structure is formed. In this paper, films with λ = 29 and λ = 15 were studied.

Annealing of the extruded films under isometric conditions was carried out at a temperature close to the melting temperature of 167 °C.

At the stage of uniaxial stretching, both the formation of pores and the structural α→β transition occur. The polymorphic composition of the crystal structure (N) and the total porosity (P) are determined by the orientation parameter *ε*—the degree of orientation extraction.

To give stability to the formed structure after stretching, the films were thermofixed for 1 hour at a temperature of T = 100 °C (Gerasimov et al. 2022).

The total proportion of pores in the polymer volume was calculated by the formula:

$$P = \left[\left(\rho - \rho_0 \right) / \rho \right] \cdot 100\%, \quad (1)$$

where ρ is the density of the extruded film, ρ_0 is the density of the porous film.

The content of the β-phase in various samples was determined by X-ray diffraction analysis. The amount of β-phase of porous films was determined by the formula:

$$N = \frac{\beta}{\alpha + \beta} \cdot 100\%. \quad (2)$$

Table 1 shows the parameters P and N for all the samples under study.

Table 1. Parameters of the studied samples

λ	ε, %	P, %	N, %
15	0	0	0
29	0	0	0
	30	13	26
	50	19	33

The samples were examined in the temperature range from 0–70°C in a helium atmosphere using TSC II by Setaram, France. The current was measured using a Keithley electrometer with a resolution of 10^{-16} A.

The method of thermally stimulated currents in the mode of a fractionally polarized dielectric was proposed by Lacabanne and Chatain. Fractional polarization is achieved by polarizing the sample for 2 minutes (τ_b) at a temperature of 40 °C (T_b). This is followed by cooling the sample to 35 °C (T_d) (usually T_d differs from T_b by only a few degrees) and follow-up depolarization at T_d for 1 minute (τ_d). During depolarization, the external field is turned off and the sample is shorted. Later, the sample is cooled to an initial temperature of 0°C (T_0), after which it is linearly heated and the thermally stimulated short-circuit current is registered. To obtain the energy spectrum of relaxers (charge traps, the described measurement procedure must be repeated many times each time increasing the temperature with a certain step T_b and T_d (other conditions of polarization and depolarization remain unchanged). Figure 1 illustrates the measurement procedure of the TSC-FP method.

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Due to partial depolarization of the sample before each subsequent heating, it is possible to narrow the interval of activation energy of relaxators (traps for charge carriers). They participate in the formation of a thermally stimulated current in the linear heating section.

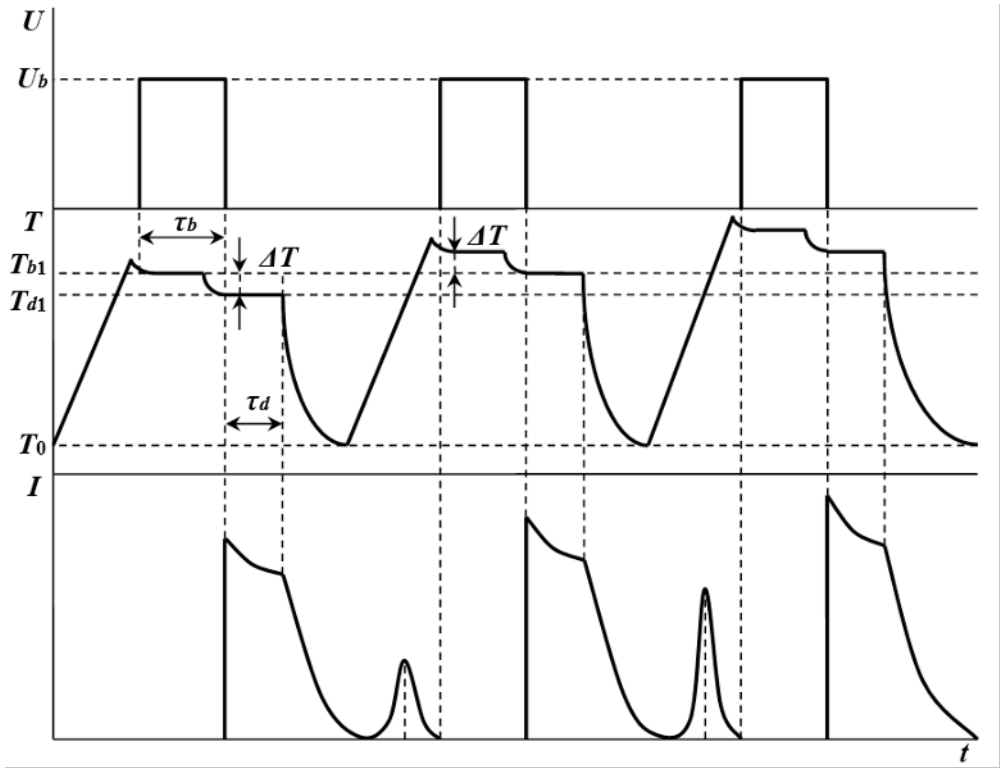

Fig. 1. Operating mode of the TSC-FP method. TSC-TS. U_b, T_b, and τ_b—voltage, temperature and relaxation time; T_d, and τ_b —temperature and time of pre–depolarization; ΔT—step of change of polarization and depolarization temperatures

The resulting current dependence is described by the expression:

$$j(T) \simeq j_0 e^{-\frac{W}{kT}}. \tag{3}$$

In (van Turnhout 1975), van Turnhout showed a quantitative relationship between experimentally obtained TSC-FP spectra and low-frequency dielectric loss spectra. The following relation illustrates the relationship between dielectric losses (ε″) and depolarization current (J(t)):

$$\varepsilon'' = \frac{J(t)}{A 2\pi\varepsilon_0 FE} \quad , \tag{4}$$

where A is the sample area, E is the polarization field strength, ε_0 is the dielectric constant and F is the effective frequency of the experiment. The effective frequency can be determined by the formula:

$$F = \frac{E_a}{2\pi s R T^2} \quad , \tag{5}$$

where s is the inverse heating rate, E_a is the activation energy.

Each TSC scan represents a convoluted spectrum of the dielectrically active relaxations excited between T_b and T_0. It has been shown that the integrated peak area of a given transition is related to the strength of the transition defined by the dielectric increment (van Turnhout 1975)

$$\Delta\varepsilon = \frac{1}{E\varepsilon_0}\int_{t_0}^{\infty}\frac{J}{A}dt \quad , \tag{6}$$

where t_o to infinity is the time-span which covers the entire transition measured upon reheating at a constant rate, and the dielectric increment is defined as:

$$\Delta\varepsilon = \varepsilon'_{\infty} - \varepsilon'_{0} \quad , \tag{7}$$

where ε' is the dielectric constant at high frequency (or low temperature), and ε" is the dielectric constant at low frequency (or high temperature). Since the TSC experiment is obtained at a constant heating rate, temperature was converted to time in eq. (6).

Results

Figures 2 and 3 show the results of the dependence of dielectric losses in the infra-low frequency region on temperature for samples λ = 29 and λ = 15.

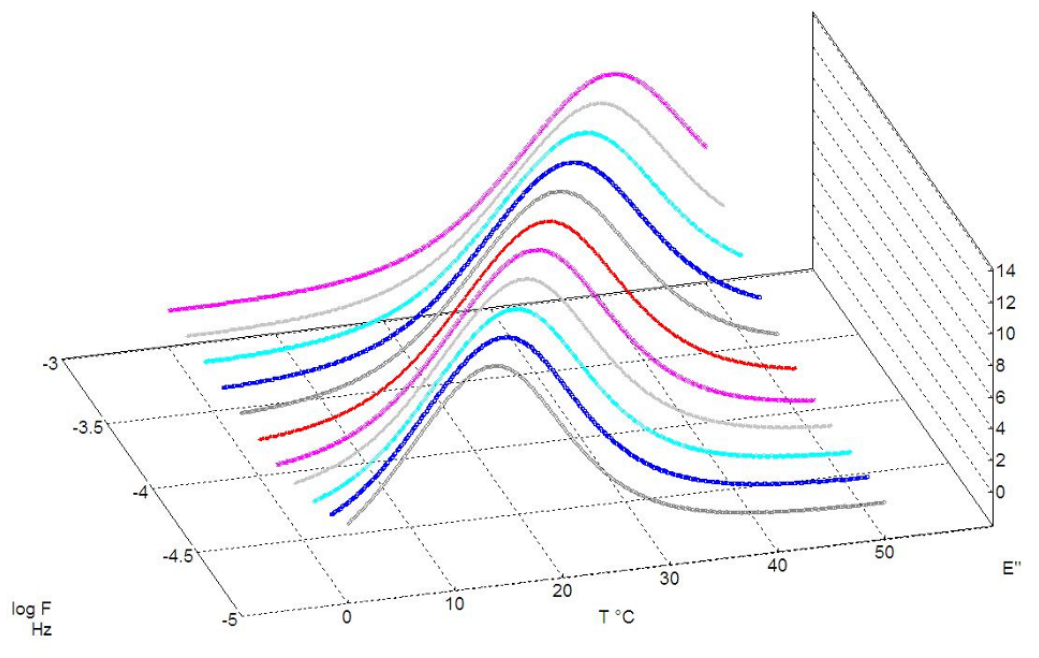

Fig. 2. Temperature-frequency dependence of dielectric losses for λ = 15

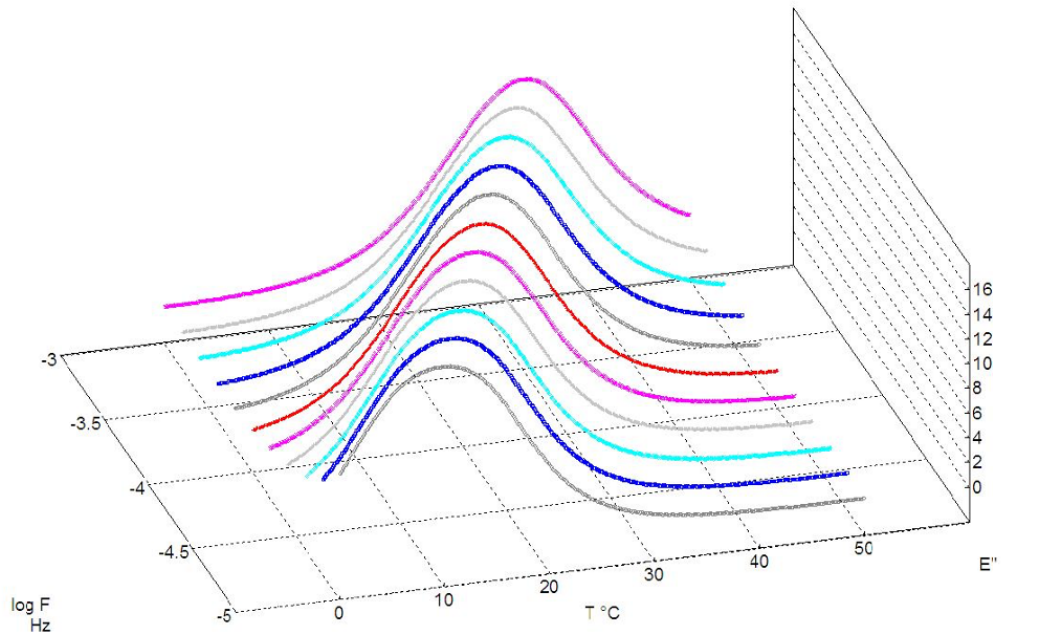

Fig. 3. Temperature-frequency dependence of dielectric losses for λ = 29

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The analysis of the obtained curves shows the presence of one maximum in the temperature range from 0 ˚C to 50 ˚C. The construction of the dependence of dielectric losses on temperature at one frequency shows that a change in the supramolecular structure shifts the peak of dielectric losses to the region of lower temperatures (Fig. 4).

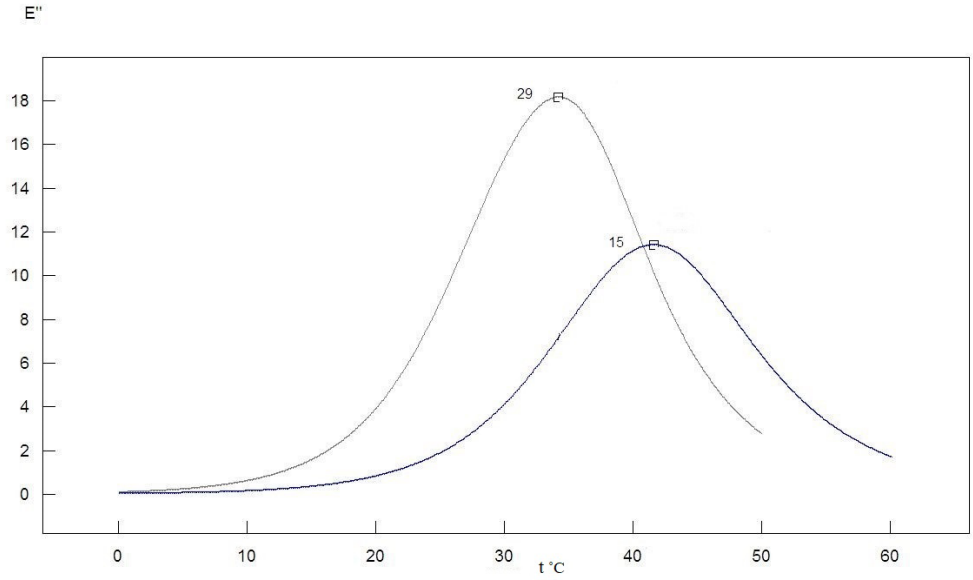

Fig. 4. Dependence of dielectric losses on temperature at one frequency of 10^{-3} Hz for samples λ = 15 and λ = 29

The paper also analyzes the dependences of dielectric losses on temperature in samples with different polymorphic composition (different percentages of β-phase) and different percentages of pores (Fig. 5). The activation energy in the samples with ε = 30% in its values approximately coincides with the original films —0.94 eV. In the samples with a large amount of β-phase (ε = 50%), there is a noticeable decrease in the activation energy to 0.83 eV (Gerasimov et al. 2022), which leads to a noticeable shift of the peak of dielectric losses to the low-temperature region.

It can be seen from the diagrams (Fig. 6) that with an increase in the degree of orientation drawing, the angle formed by the abscissa axis and the line connecting the center of the circle increases, which indicates a change in the distribution of relaxation times in the studied films (Gusev 2008).

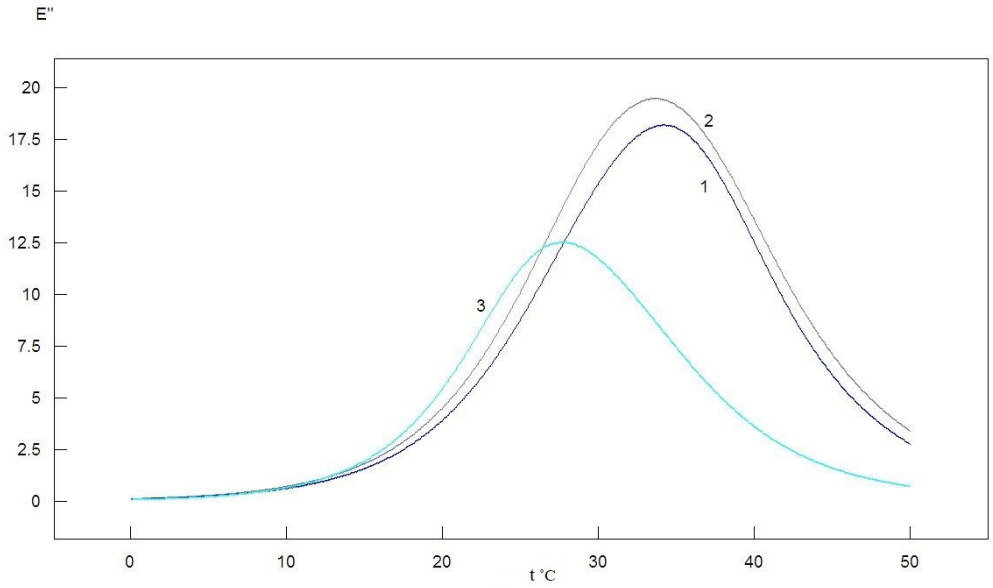

Fig. 5. Dependence of dielectric losses on temperature at one frequency of 10^{-3} Hz for samples λ = 29, 1—ε = 0, 2—ε = 30%, 3—ε = 50%

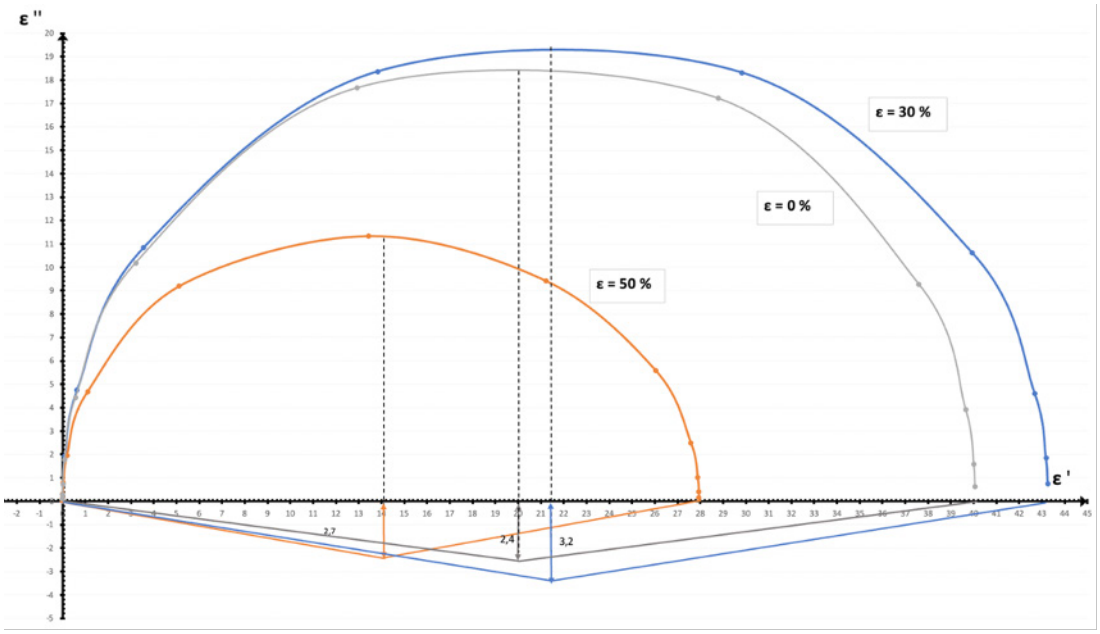

Fig. 6. Dependence of ε' on ε'' for samples with different polymorphic composition and different percentages of pores

Conclusions

The dielectric properties of PVDF polymer films with different structures, polymorphic composition and percentage of pores have been studied. The expediency and relevance of presenting the results of thermal activation spectroscopy in the framework of dielectric spectroscopy at infra-low frequencies is shown. It is revealed that a change in the supramolecular structure entails a shift of the peak of dielectric losses to the low-temperature region.

The peak of dielectric losses for films with different degrees of orientation extraction is shifted to the low temperature region. This is consistent with the results of E_a (Gerasimov et al. 2022), which decrease with an increase in the amount of β-phase.

Interpretation of the results within the framework of the Cole-Cole diagrams indicates a change in the distribution of relaxation times.

Conflict of Interest

The author declares that there is no conflict of interest, either existing or potential.

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