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ХАРЧОВИХ ТЕХНОЛОГІЙ**

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РОЗДІЛ 2

ХІМІЧНІ, ФІЗИЧНІ ТА МАТЕМАТИЧНІ МЕТОДИ ДОСЛІДЖЕННЯ ПРОЦЕСІВ ТА АПАРАТІВ

and annealed films both in the heating and the cooling modes. Electrification of the samples was performed at a temperature of 20 °C and a voltage of 3 kV for 10 minutes. Preliminary, Al electrodes of 180 mm^2 area were deposited on both surfaces of the film. Annealing of the films consisted of aging for one day at 120 °C. All measurements were performed at a frequency of 1 kHz in the temperature range from 20 to 150 °C.

In the unpolarized specimens, we selected only the first and the third harmonics, while in the polarized films – the first, the second and the third harmonics. In all cases, we found real and imaginary parts of the dielectric constant of the first, the second and the third order.

Comparison of the obtained data has shown that ε'_1 was almost not affected by temperature, and ε'_1 in polarized films was smaller than in unpolarized (8-9 and 11-12). On the graphs of $P_r\gamma$ dependence on temperature one can see two relaxation processes with peaks at 50 °C and 125 °C. The first process is probably caused by the space-charge events, while the second one can be attributed to the approximation of the ferro-paraelectric transition, although the characteristic sharp increase of ε'_1 in this zone was not observed. It is possible that this transition was strongly blurred , so that the characteristic Curie temperature was close to or even above the melting temperature of the crystallites.

It was found that annealing only slightly changes the form of the $\varepsilon'_1(T)$ dependence, so that there is a weak peak at 135 °C. Upon cooling, ε'_1 of heated and annealed films remains equal to 14, regardless of temperature. Quasi-stationary state is quickly established after the electrification. After 4 hours of exposure ε'_2 decreased from $2{,}6\cdot10^{-9}$ m/V to $2{,}1\cdot10^{-9}$ m/V.

Temperature dependence of ε'_1 and ε'_3 in polarized films when heated was somewhat different from non-polarized films. The value of ε'_1 slightly but monotonically increased from 16 at 20 °C to 28 at 140 °C, while ε'_3 at 120 °C decreased dramatically changing the sign. At the same temperature, ε'_2 has also changed the sign.

Values of $P_r\gamma$ in annealed films were smaller than in non-annealed, and the temperature dependence was practically the same, except that P_r decreased to zero in the annealed films at 130 °C, and in unannealed films at 135 °C.

Upon cooling, ε'_1 and ε''_1 of the heated and annealed polarized films repeated the curves during heating, and the graph of ε'_3 noted a slight temperature hysteresis. The most strong is the difference of ε'_2 during heating and cooling. When the sample is heated, ε'_2 gradually decreases from $3\cdot10^{-9}$ m/V to zero at 130 °C and $\varepsilon'_2 = 0$ during the cooling in a wide temperature range from 110 °C to 120 °C.

It is clear from the presented results that the expected ferroelectric-paraelectric transition was not clearly seen. The most likely reason is that the characteristic transition temperature was above the melting temperature of the crystalline phase. The same feature was observed in pure PVDF homopolymer. In the copolymers with TFE relationship between the Curie point and the melting point is probably dependent on the content of TFE.

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METHOD OF NONLINEAR DIELECTRIC MEASUREMENTS IN FERROELECTRIC POLYMERS

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Dielectric properties of ferroelectric polymers depend on both crystalline and amorphous phases. Measurements of dielectric nonlinearity, i.e. the expansion coefficients of

the *D(E)* function in a power series is useful for obtaining information on the ferroelectric properties of these materials.

Phenomenological description of the ferroelectric materials is given by the Landau theory [1]. The ferroelectric contribution to the free energy *F* can be written as a polynomial of the dielectric displacement *D*

$$F = F_o + (1/2)\alpha \cdot D^2 + (1/4)\gamma \cdot D^4 + (1/6)\delta \cdot D^6 . \quad (1)$$

Landau parameters α, γ and δ are generally dependent on temperature. Direct determination of the Landau parameters is possible by measuring the dielectric nonlinearity, i.e. ε_n coefficients in the power range of the displacement field *D* on *E* expansion

$$D = P_s + \varepsilon_o \varepsilon_1 E + \varepsilon_o \varepsilon_2 E^2 + \varepsilon_o \varepsilon_3 E^3 + ... \quad (2)$$

In the paraelectric phase, i.e. when P_s = 0, the first non-linear coefficients are associated with the Landau parameters by the following relations

$$\varepsilon_o \varepsilon_1 = 1/\alpha; \qquad \varepsilon_o \varepsilon_2 = 0; \qquad \varepsilon_o \varepsilon_3 = -\gamma/\alpha^4 . \quad (3)$$

Parameters α and γ can be calculated by measuring ε_1 and ε_3. In particular, the ε_3 sign indicates the order of the phase transition. The presence of the dielectric constant of the second order ε_2 in the paraelectric phase can be explained as an effect of the biasing field E_i

$$D = P_S{}^O + \varepsilon_o \varepsilon_1^O (E + E_i) + \varepsilon_o \varepsilon_2^O (E + E_i)^2 + ... \quad (4)$$

where ε_n^O and $P_S{}^O$ are nonlinear dielectric constant and spontaneous polarization of the centro-symmetric material. Coefficients ε_n can be calculated as a function of Ei and ε_n^O. In the paraelectric phase where all the even-*n* are equal to zero, the following approximate equality is valid

$$\varepsilon_1 \approx \varepsilon_1^O; \qquad \varepsilon_2 \approx 3\varepsilon_3^O E_i; \qquad \varepsilon_3 \approx \varepsilon_3^O . \quad (5)$$

In order to find E_i, ε_2 can be measured as a function of the external applied field E_o' and then to find such a field E_o', for which $3\varepsilon_3^O (E_i + E'_o) = 0$. It is also possible to calculate E_i from the dielectric constants of the second and third order

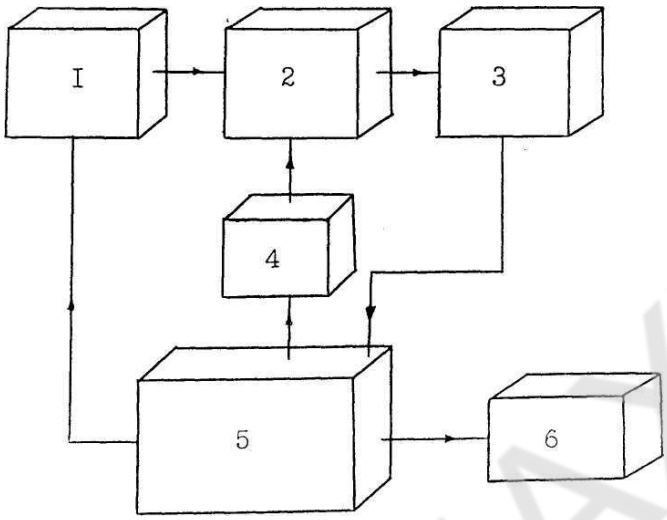
$$E_i = \varepsilon_2 / (3\varepsilon_3) . \quad (6)$$

In the ferroelectric phase, the dielectric constant of the second order is dependent on the residual polarization P_r and the spontaneous polarization P_s

$$\varepsilon_o \varepsilon_2 = -P_r (\varepsilon_o \varepsilon_1)^3 (3\gamma + 10\delta P_S^2) . \quad (7)$$

The temperature dependence of $1/\varepsilon_1$ in the ferroelectric phase provides a criterion for whether the value of $10 \cdot \delta \cdot P^2$ is a small quantity in comparison with 3γ. In this case, $\varepsilon_2/\varepsilon_1^3$ is proportional to the residual polarization

$$\varepsilon_o \varepsilon_2 / 3(\varepsilon_o \varepsilon_1)^3 \approx P_r \gamma . \quad (8)$$



1 is the sinusoidal voltage generator; 2 the thermostat with a sample; 3 the Spectrum Analyzer; 4 the automatic temperature control; 5 the Computer; 6 the printer.

Fig. 1 – Block diagram of the non-linear dielectric spectroscopy method

The measurements were carried out on the nonlinear dielectric films of P(VDF-TFE), on both sides of which the electrodes were applied of the area of 176 mm^2. The scheme of measurements is shown in Fig. 1. A generator with the high spectral frequency (V_o = 130 V, f=1000 Hz) was used as a source of sinusoidal voltage. The signal was measured at the load resistance of 100 Ω connected in series with the sample.

With the help of the spectrum analyzer, by selecting the first, the second and the third harmonics, we measured the amplitude and calculated ε_1, ε_2 and ε_3. The measurements were performed in a thermostat at temperature range from 20 to 150 °C during heating and cooling. For each cycle we found the real and imaginary parts of the permittivity. The measurements at each temperature lasted from 5 to 8 min. The results were averaged over ten spectra. The installation was completely computerized.

We conducted several series of experiments on the unpolarized and polarized, unannealed and annealed P(VDF-TFE) films during their heating and cooling. Results of experiments will be given in a separate article.

Scientific Supervisor – DSc (Physics & Mathematics), Professor A.E.Sergeeva,

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РОЗДІЛ 3 – ХОЛОДИЛЬНА ТЕХНІКА ТА ТЕХНОЛОГІЯ. ПРОЦЕСИ ТА АПАРАТИ ХАРЧОВИХ ТЕХНОЛОГІЙ

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