Near-electrode polarization and determination of the mobility of intrinsic charge carriers in PVDF films

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Abstract. The process of near-electrode polarization in a polyvinylidene fluoride (PVDF) film was studied using reverse currents $I_{rev}(t)$. It was proven that the maxima on the $I_{rev}(t)$ curves are characteristic of near-electrode polarization. The dependences of the reversal currents on time were analyzed based on various representations. The mobilities of the intrinsic charge carriers in the film and the magnitude of the charge transferred through the dielectric layer from electrode to electrode were calculated. The conductivity of PVDF was studied and analyzed in the temperature range 90°C-130°C.

1. Introduction
If blocking contact appears between the dielectric and the electrode, then under the influence of a constant electric field the own charge carriers move to the electrodes. A bulk hetero charge is formed in the near-electrode region. This phenomenon is called near-electrode polarization. In this case, the electric field strength in the near-electrode layer increases sharply, and a charge of the opposite sign is induced on the electrode. This phenomenon is important to consider in electrical insulation, as well as in determining the dielectric constant in the low frequency region.

A transparent PVDF polymer due to its strong piezoelectric behaviour, compact size, light weight, excellent flexibility, and good dielectric properties has attracted attention of the researchers and is used in modern electronics and electric power systems [1]. In the present work, it is shown that using reverse currents determines the presence of near-electrode polarization in PVDF films. From the maxima at reverse currents, one can determine the mobility of free charge carriers.

2. Methods

2.1. Measuring charge and discharge currents
The electrical conductivity was studied under isothermal conditions (90-130)°C. The currents were measured using a picoammeter A2-1 with a two-electrode system. The diameter of the electrodes was 16 mm. The sensitivity of the picoammeter A2-1 is $10^{-15}$A. The measurement error of current is 1%. The films were coated with aluminum foil. The charging currents were measured on constant voltage ±100V, electrical field strength was $\sim 5\times 10^5$V/m. The time of current measurement was 10 minutes.

2.2. Reverse current measurement
When measuring reverse currents $I_{rev}(t)$ on the electrodes between which the film is located, a constant voltage $U$ is first applied, later the polarity was changed to the opposite ($-U$). On the $I_{rev}(t)$ curve, one or more maxima can be observed.
3. Results and Discussion

The dependences of charging current on time are presented in figure 1. As can be seen from the figure 1 the electric current decreases over time.

![Figure 1. The dependences of charging current on time: 1-130\(^{0}\)C, 2-120\(^{0}\)C, 3-110\(^{0}\)C, 4-100\(^{0}\)C A constant current value was set after 10 min of measurement. Electrical conductivity was calculated using these current values, which is shown in figure 2.](image)

The activations energies of conductivity were calculated taking into account the Arrhenius formula

\[ W = 0.75\text{eV}. \]
3.1. Study of reverse currents

Figure 3. Dependence of reversal currents on time $I_{rev}(t)$ for various temperatures: 1-130°C, 2-120°C, 3-110°C, 4-100°C, 5-90°C

It can be seen from figure 3 that the higher the temperature, the narrower the maximum, the shorter the time $t_m$ and the greater the magnitude of the current by $I_{rev}(t)$. The appearance of a current maximum at $I_{rev}(t)$ indicates near-electrode polarization [2-4]. A hetero charge accumulated in the near-electrode region redistributes the electric field of the film. The calculation of the mobility of their own charge carriers was carried out according to several models [5-6].

3.2. Estimation of the mobility of free charge carriers

The mobility of the own charge carriers can be estimated by the position of the maximum in the curve $I_{rev}(t)$ using the relation:

$$\mu = \frac{\nu}{E} = \frac{h}{E \cdot t_m} = \frac{h^2}{U \cdot t_m},$$

where $h$ is sample thickness, $U$ is electrode voltage, $t_m$ is maximal time at which the current maximum is formed in the dependence. $E$ is the electric field strength. For a more rigorous analysis of the mobility of charge carriers, $I_{rev}(t)$ was analyzed based on the model of near-polarization. In this model diffusion is not taken into account, the presence in the dielectric of charge carriers of the same type and a fixed charge $\rho_f = -\rho_0$ are assumed; initial concentration of charge carriers is $n$, total charge per unit area is $Q = n e h$, in the initial state $Q_f = -Q$. This problem boils down to solving the equations of motion of a boundary of movable charge cloud under the assumption that the sample is electrically neutral. The sample is polarized at voltage $U_p$, figure 4(a).
The sample is polarized in a constant electric field (figure 4a). After changing the magnitude and polarity of the abruptly changing voltage \( U_p = -U_p \). The sample is depolarized in figure 4 (b). When the front edge of the cloud reaches the negative electrode \( x = h \) the sample becomes neutral. Then under the action of voltage \( U \) the repolarization of the sample begins.

\[
\mu = j_m \frac{h^2}{U_p \cdot Q},
\]

where \( j_m \) is the magnitude of the electric current in the dependence \( I_{rev}(t) \), \( U_p \) is polarizing voltage, \( h \) is sample thickness, \( Q = \int_{0}^{\infty} j \, dt \) is total charge calculated by integrating the dependency \( I_{rev}(t) \).

Figure 5 shows the calculations of the mobility of charge carriers, which were calculated using models 3.1., 3.2. When comparing the two methods, we can say that the results are of the same order. The first method is more evaluative (3.1) than the second calculation method (3.2). The activation energies determined from the slope of the dependence in figure 5 are 0.8 eV and 0.5 eV.

Figure 4. Polarization (a) and depolarization (b)

A detailed description of the model is presented in [2]. Assessment of the mobility of charge carriers is carried out on a curve \( I_{rev}(t) \) by the ratio:

\[
\mu = j_m \frac{h^2}{U_p \cdot Q},
\]

Figure 5. The dependence of the mobility of free charge carriers on the reciprocal temperature, calculated by two methods: 1 - by the simplest formula; 2 - model of near-polarization.
4. Conclusions
Transient processes of electric transport and polarization in a PVDF film are investigated. On the $I_{rev}(t)$ curves, systematic reproductions of current maxima were found, which confirms the presence of near-electrode polarization in the PVDF film. Dependences $I_{rev}(t)$ were studied in the temperature range (90-130) °C at field strength $5*10^5$ V/m. Using the maxima on the curves $I_{rev}(t)$ the mobilities of the proper charge carriers in the dielectric $\mu = \left(10^{-12} + 10^{-13}\right) m^2/V \cdot s$ were calculated. The temperature dependence of mobility is described by an exponential law, and the activation energies are (0.5-0.8)eV.

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