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РОЗДІЛ 2

**ХІМІЧНІ, ФІЗИЧНІ ТА МАТЕМАТИЧНІ МЕТОДИ
ДОСЛІДЖЕННЯ ПРОЦЕСІВ ТА АПАРАТІВ**

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TWO COMPONENTS OF POLARIZATION IN FERROELECTRIC POLYMERS

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Ferroelectric polymers differ considerably from conventional polar electrets, because they possess spontaneous switchable polarization in β phase crystallites [1]. But still almost half of the volume is occupied by the polar amorphous phase. It means that ferroelectric properties of FPs may interfere with their electret properties. The purpose of this paper is an attempt to separate the ferroelectric component of polarization from the electret component.

It is known that polarization in electrets is usually thermally frozen and unstable thermodynamically, while ferroelectric polarization is stable, provided the depolarizing field is neutralized anyhow [2]. We have shown that injected and trapped charges play an important role in the buildup of polarization in FPs. It was proved that ferroelectric polarization and trapped charge form a self-consistent system with its stability governed by that of the space charge [3]. In this paper, the important role of the space charge is confirmed. Moreover, we obtained evidence that the space charge stabilizes not only the ferroelectric component of polarization, but also the electret one.

We studied thermally stimulated depolarization (TSD) currents in short circuit (SC) and open circuit (OC) modes in differently poled polyvinylidene fluoride (PVDF) and copolymers of PVDF with trifluoroethylene P(VDF-TrFE) and tetrafluoroethylene P(VDF-TFE). A new phenomenon was observed, namely a double inversion of the TSD current in the OC mode and appearance of two well structured peaks in the SC mode in poled samples stored more than one year, indicating that two different kinds of polarization exist in ferroelectric polymers, both accompanied by deeply trapped charges. The difference between the two currents is quite essential, because two pairs of peaks were seen instead of one. Independence of the phenomenon on the material and poling conditions indicated that it was rather fundamental. The more stable component of polarization had presumably a ferroelectric nature, while the less stable one was attributed to polarization in amorphous phase.

It follows from our results that very slow redistribution of charges and polarization takes place in ferroelectric polymers after completion of poling until the electret and ferroelectric components of polarization are finally separated, both accompanied by the trapped charges. For the first time, existence of these four relaxation processes in ferroelectric polymers has been clearly shown.

In order to obtain high and stable polarization in ferroelectric polymers, it is necessary to remove the unstable electret component of polarization. For example, in case of P(VDF-TFE) films poled at 85 °C through a glass, it is sufficient to heat poled sample to 60 °C. The procedure may not be the same for other ferroelectric polymers.

Scientific Advisor – Prof. S. N. Fedosov, DSc (Physics & Mathematics)

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RECONSTRUCTION OF THE HYSTERESIS LOOP IN FERROELECTRIC POLYMERS

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Polarization (P) in ferroelectric polymers depends non-linearly on the field strength (E), so that the $P(E)$ function is presented by a hysteresis loop typical for all ferroelectrics [1]. Determination of the coercive field (E_c) and the residual polarization (P_r) from this dependence is important not only for selection of poling parameters, but also for estimation of piezoelectric and pyroelectric properties of poled films.

In order to obtain the $P(E)$ function correctly, one should consider some important features. The commonly used Sawyer-Tower's method is not applicable in the case of ferroelectric polymers, because Maxwell's relaxation time is in the range of hundreds seconds [2]. Therefore, measurements must be performed at infra-low frequencies. Besides, it is necessary to extract the polarization component of the total poling current and to separate it from other two components corresponded to capacitive and conductive currents. Moreover, in calculations of the $P(E)$ function, one must consider a finite apparent resistivity and cannot take the value of the dielectric constant (ϵ) from reference books, because of its strong frequency dependence, while the listed values correspond usually to the frequency of 1 kHz. All these features have not been consistently accounted so far, although attempts were made repeatedly to obtain $P(E)$ hysteresis loops in ferroelectric polymers.

It is worthwhile to mention that almost all data on the $P(E)$ hysteresis in ferroelectric polymers were obtained by direct application of voltage to electroded samples, while it is general practice now to use corona for their poling [3]. We developed a new method to obtain the $P(E)$ dependence from experimental kinetics of the electret potential during the initial constant current corona poling, as well as during repeated poling and switching of polarization in the corona of the opposite polarity, but under the same value of the poling current. We use a true value of the dielectric constant in our calculations and do not neglect the apparent conductivity, obtaining the both parameters during the same poling experiments. As an example, the $P(E)$ dependence for polyvinyl fluoride (PVDF), a typical ferroelectric polymer, was obtained and values of the coercive field and the residual polarization were found.

We used extruded and uniaxially stretched PVDF films of 25 μm thickness electroded on one side by evaporation of Al in vacuum and subjected to a constant current poling in a corona triode with a constant potential of -3 kV applied to the vibrating grid. By processing experimental curves we found that $P_r=42 \text{ mC/m}^2$ and $E_c=48 \text{ MV/m}$. Switching of polarization took about 1800 s meaning that one hysteresis loop was completed in one hour, i.e. the equivalent frequency of the measurement was $2.8 \cdot 10^{-4} \text{ Hz}$.

Scientific Advisor – Prof. A. E. Sergeeva, DSc (Physics & Mathematics)

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Наукове видання

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