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Fractional Corona Poling and Electrical Relaxation in Electret Films

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A new method has been proposed for analyzing experimentally obtained response (electret potential) of a polar dielectric film on application of rectangular current pulses of infra-low frequency. The current is supplied by a corona discharge; and the whole poling process is divided in a number of fractions, each one consisting of a potential growth stage under a constant charging current and a stage of the potential decay in the gap between two adjacent current pulses. Corresponding expressions are obtained for kinetics of the dielectric constant and the apparent conductivity during the poling process. The method has been applied for studying corona poling and electrical relaxation in PVDF films, while it is applicable in principle for any dielectric with a appreciable apparent conductivity.

Key words: electrets, corona poling, PVDF, polar dielectrics, electret potential.

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Introduction

The electret state of a dielectric is usually studied by measuring the surface potential kinetics [1,2] in order to calculate the time constant of the electret potential decay and predict its further behavior. The method is simple, though the obtained information is rather limited. During the last years, a new method of corona poling was successfully applied for studying space charge and polarization processes in different dielectrics and electrets [3-11]. A modification of corona poling with a constant charging current [3-7] is especially promising in electret studies. An attempt to combine advantages of these two methods resulted in developing a new experimental method described below.

Rectangular current pulses are applied to a dielectric placed in a corona triode. Alternative periods of charging and pause are repeated until the electret potential continuously measured by Kelvin's method becomes equal to the grid potential. Relaxation parameters are obtained by comparing experimental and calculated kinetics of the electret potential.

I. Description of the method

One surface of a thin dielectric sample is metallized in a vacuum to form an electrode with a typical thickness of about 0.1 μm . It is essential that another surface of the sample is left free, because the apparent electret potential has to be measured continuously during the experiment.

The sample is placed in a corona triode with the pre-set grid potential equal to the highest electret potential expected in the given sample. The voltage at the corona electrode is automatically controlled by a feedback circuit in order to maintain the charging current at a constant level during the charging periods. The control grid is made vibrating for giving a possibility to measure the electret potential by Kelvin's method directly during both poling and discharging stages.

The experiment starts with switching the constant charging current on and applying the current to the sample for a definite period of time T . This stage can be considered as a pulse of the constant current. Then the high voltage at the corona electrode is switched off, while the sample is left to relax in open-circuit conditions for the same period of time T . One charging and one discharging stages form a complete cycle that is repeated several times until the electret potential becomes equal to the grid voltage.

Thus, each cycle consists of two stages, namely, the stage of the potential growth under the constant charging current and the stage of the potential decay in the time interval between the two adjacent current pulses. The apparent frequency of the cyclic charging, as well as the charging current density are settled on experimentally in order to obtain at least 10-20 cycles in one experiment. During each cycle, a definite portion of the charge Q is transferred to the sample.

For example, in the case of PVDF we used the following values of the parameters: the current density $i = 80 \mu\text{A}/\text{m}^2$, the charging-discharging time $T = 300 \text{ s}$, the apparent frequency $f = 1,7 \text{ mHz}$, the charge absorbed during one cycle $Q = 24 \text{ mC}/\text{m}^2$. The 25 μm thick

samples were charged to a potential of 3 kV by application of 10-15 pulses. Typical $V(t)$ curves of the electret potential kinetics obtained under these conditions

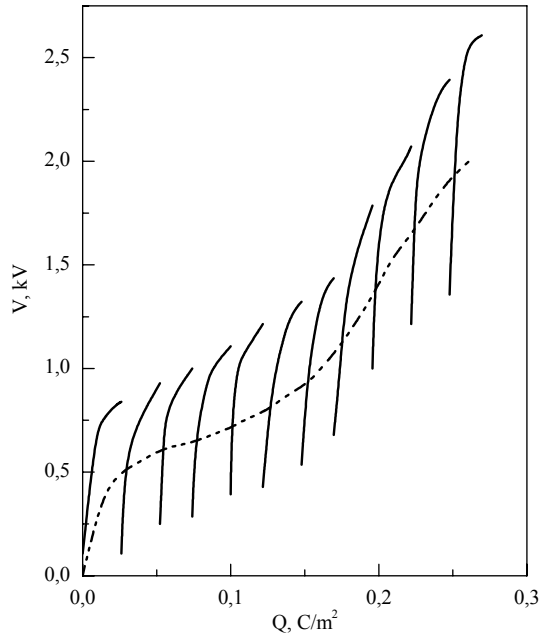


Fig. 1. Kinetics of the electret potential of PVDF films during the charging fractions as a function of the charge density supplied to the sample by corona ions. The dash line shows the average value of the electret potential.

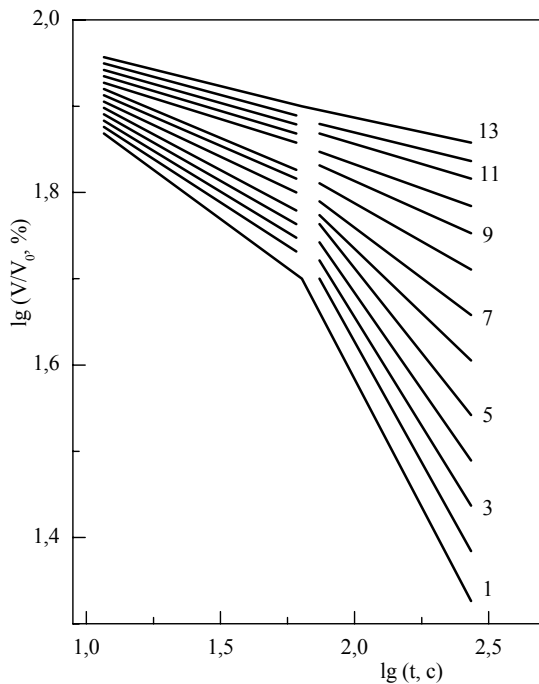


Fig. 2. Time dependence of the normalized electret potential during the intervals between the pulses of the constant charging current. The numbers indicate the total quantity of the pulses applied to the sample.

are shown in Fig. 1 and Fig. 2.

It has been revealed by special measurements that immediately after switching the current on, the diffusive capacitance was formed by the space charge floating over the surface of the sample. The charge disappeared almost instantly at the moment of the switching off the current. The phenomena result in appearance of pulses at the experimental $V(t)$ curve, so the corresponding correction must be made by subtracting these pulses.

Expression for the total current under assumption of the field uniformity in the sample, as well as permanency of the apparent conductivity g and the dielectric constant ε during one charging cycle, can be written as

$$i(t) = \frac{\varepsilon_0 \varepsilon}{x_0} \frac{dV}{dt} + \frac{g}{x_0} V(t), \quad (1)$$

where $i(t) = I = const$ at $t < T$ and $i(t) = 0$ at $t > T$, x_0 is the thickness of the sample; ε_0 is the permittivity of a vacuum. The above mentioned assumptions imply that values of ε and g are averaged over the period of one cycle ($2T$), therefore Eq. (1) must be applied as many times, as the number of cycles with ε and g considered as constants during any particular cycle, but having different values in different cycles.

Solving Eq. (1) under the initial condition of $V(0) = U$, where U is the residual electret potential at the end of the preceding cycle, one gets

$$V(t) = \frac{Ix_0}{g} + \left(U - \frac{Ix_0}{g} \right) \exp\left(-\frac{t}{t_0} \right), \quad t < T, \quad (2)$$

$$V(t) = \left[\frac{Ix_0}{g} + \left(U - \frac{Ix_0}{g} \right) \exp\left(-\frac{T}{t_0} \right) \right] \exp\left(-\frac{t-T}{t_0} \right); \quad t > T, \quad (3)$$

where $t_0 = \varepsilon_0 \varepsilon / g$ is Maxwell's relaxation time (time constant). The values of t_0 , g and ε are found by the curve fitting technique using the experimental $V(t)$ curve and Eq. (2) and (3). Thus, it is possible to separate contributions of g and ε to the value of the time constant t_0 .

If the dielectric has a negligible conductivity ($g \rightarrow 0$), the dielectric constant can be calculated as

$$\varepsilon = \frac{Qx_0}{\Delta V \varepsilon_0 S}, \quad (4)$$

where ΔV is the increment of the potential corresponded to the charge Q ; S is the area of the sample surface. It is obvious that the decay of the potential should not be observed in such a case.

II. Experimental results and discussion

The proposed method has been applied for studying corona poling and electrical relaxation processes in PVDF, although it is applicable in principle for any dielectric. The study was performed on the 25 μm thick uniaxially stretched PVDF films supplied by Plastpolymer Co. and composed of amorphous and crystalline (Form 1) phases in nearly equal parts.

As one can see from Fig. 1, the overall appearance of

the electret potential curve is similar to that obtained under constant current poling [3-6]. The curve contains an initial stage of the steep rise of the potential followed by a slightly sloping plateau that finally transforms in the second steep rise of the potential.

It has been found that the value of the potential reduction in the intervals between the current pulses was always smaller than the preceding increment of the potential during the first stage of the same cycle. The difference progressively increased from cycle to cycle, indicating that the electret potential became more and more stable (see Fig. 2). Such a phenomenon is not normally observed in the case of conventional electrets. It follows from Fig. 2 that the $V(t)$ function shows a power dependence characteristic for the dispersive

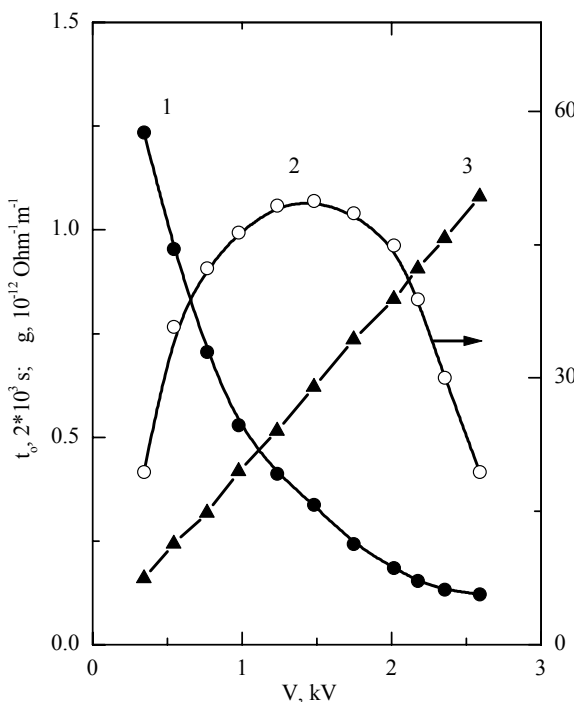


Fig. 3. Dependences of the specific conductivity (1), the relative dielectric permittivity (2) and the time constant of the electret potential decay (3) on the average electret potential during the fractional charging of PVDF films obtained by processing the experimental $V(t)$ curves shown in Fig. 1 and Fig. 2.

transport of injected charge carriers [12]. The elbows observed at about $t = 90$ s might correspond to the time of flight of the carriers through the whole thickness of the sample. Independence of this time on the field shows that the apparent mobility of the charge carriers decreases with field. This fact correlates with the assumption of the constant Schubweg used in the model

of the polarization buildup in PVDF [13].

Increase of the dielectric constant in the second stage of the charging (Fig. 3) is typical for ferroelectric polymers [3-6] and probably caused by formation of the ferroelectric polarization in Form 1 crystallites. As for the apparent conductivity, it is affected by intrinsic carriers and injected ones. It is easy to show that an abrupt decrease of the conductivity observed in Fig. 3 is not caused by the limited injection, because the $I-V$ dependence is super-linear, if the injected carriers are not trapped [14]. It is known that the large-scale fluctuations of the potential energy at the ferroelectric crystallite boundaries during the polarization buildup act as deep traps for the charge carriers [6,9]. Thus, the density of the trapped charges increases, while the conductivity, resulted from delocalized carriers, decreases. That is why the electret potential becomes more stable and the time constant increases with growth of the ferroelectric polarization, as it is seen in Fig. 2 and Fig. 3.

Conclusion

A number of complex phenomena are involved, if a dielectric is subjected to corona poling including injection of charge carriers, their transport and trapping, formation of polarization, its interaction with the space charge, etc. In such a case, the dielectric constant and the specific conductivity are not the material constants, but rather the apparent parameters dependant on the electric state of the sample. The proposed method allows to follow their evolution during the charging and obtain valuable information on the physical nature of space charge and polarization processes.

The proposed method might have some limitations in the case of very stable homo-electrets, since the stages of the electret potential decay would not be observed. However, the method is reliable and convenient, if applied to polar dielectrics usually having the relatively high conductivity. It can also be successfully applied to study dynamics of the corona charging, the conduction phenomena and the electric relaxation in ferroelectric polymers.

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Фракційна поляризація в коронному розряді та електрична релаксація в електретних плівках

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Запропоновано новий метод обробки отриманого експериментально відгуку (електретного потенціалу) полярних діелектричних плівок на прикладення прямокутних імпульсів струму інфранизької частоти. Джерелом струмів є коронний розряд, так що увесь процес поляризації розбивається на окремі фракції, кожна з яких складається із стадії зростання потенціалу при сталому зарядному струмі і стадії зменшення потенціалу в інтервалах між двома сусідніми імпульсами струму. Отримані відповідні вирази для кінетики діелектричної сталості та ефективної провідності під час процесу поляризації. Вказаний метод було застосовано для вивчення поляризації в коронному розряді і електричної релаксації в плівках ПВДФ, в той час як він в принципі може бути застосований до будь-якого діелектрику із помітною ефективною провідністю.

Ключові слова: електрети, поляризація в коронному розряді, ПВДФ, полярні діелектрики, електретний потенціал.