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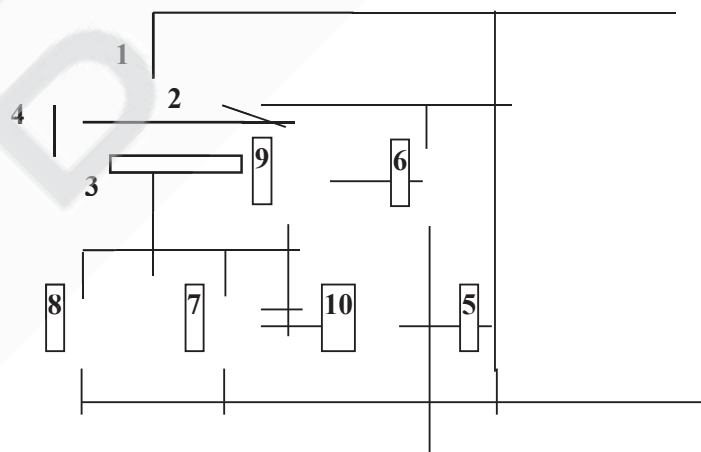
CORONA DISCHARGE POLING OF FERROELECTRIC POLYMERS

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Dipoles in ferroelectric polymers (FP) must be oriented by application of DC electric field to insure desired properties of the material. The most advanced process called corona poling was applied earlier in electrostatic filters, electrophotography and in electrets. Due to its versatility, corona method allows to optimize the process by proper selection of poling parameters.

Advantages of corona poling are: (a) poling can be performed without deposited electrodes (b) higher fields can be achieved than in case of sandwich poling, and (c) thin films can be poled in spite of defects, because breakdown is limited only to small sample area. A simple point-to-plane geometry was gradually replaced by a corona triode with a metal grid between the point and the sample. The corona triode was used to study dynamics of poling and charge transport phenomenon in polymers [1-6]. In this work we describe corona poling of ferroelectric polymers with an accent on using constant current corona poling (CCCP).

There are four modifications of the corona triode (Fig. 1). In the simplest mode I, corona and grid voltages are controlled independently by power supplies 5 and 6 and kept constant. The elements 4, 8, 9, 10 are not used in mode I. One can measure the poling current (7), but cannot separate its components. If either the sample or the grid is made vibrating (mode II, element 4 is added), one can observe the dynamics of the surface potential by the modified Kelvin method measuring the AC current (8). In the mode III the feedback 10 is introduced to control the corona voltage 6 in order to keep the poling current constant. So, all poling parameters can be measured and controlled. In the latest version of the triode (mode IV) not the corona, but the grid voltage is adjusted through the feedback 9 for keeping the current constant. There is no need for a vibrating capacitor, so elements 4 and 10 are excluded.



1 – the corona electrode, 2 – the grid, 3 – the sample, 4 – vibration of the grid, 5 – high voltage DC power supply for corona, 6 – power supply for the grid, 7 – DC component of the poling current, 8 – AC component of the poling current, 9 – the feedback circuit to control the grid power supply, 10 – the feedback circuit to control the corona power supply

Fig. 1 – Block-diagram of the corona setup

To find best poling conditions we recommend to measure current-voltage characteristics.

Since the corona appears at about 5 kV, the grid potential should not exceed this value; otherwise the grid itself will produce a parasitic discharge. At the same time, the corona voltage must be more than 5 kV higher than the grid voltage. In most cases the value up to 4 kV and 12-16 kV are suitable as the grid and the corona voltages. A short-circuiting can be performed after poling by grounding the grid and changing corona polarity to the opposite one. This step is desirable in many cases in order to remove excess surface charge.

We have studied formation of ferroelectric polarization in PVDF and P(VDF-TFE) using the constant current corona triode and found that initial poling, as well as the polarization switching consisted of 3 stages with each one corresponded to a definite part of the potential – time curve [7,8]. The fast increase in surface potential was observed at the 1st stage indicating that the capacitive component prevailed in the poling current. At the 2nd stage, there was a plateau at the voltage-time curve related to switching of the ferroelectric polarization. The surface potential again increased sharply at the third stage when switching is completed.

The plateau was not seen if poling is repeated. Polarization P in ferroelectric polymers depends nonlinearly on the field E , so the $P(E)$ function is presented by a hysteresis loop. From this curve, the remanent polarization P_r and the coercive field E_c can be found. We studied polarization and hysteresis phenomena in biaxially and uniaxially stretched PVDF films. The $P(E)$ dependence was obtained from the kinetic of the surface potential during CCCP [9]. For the biaxially stretched PVDF we found $E_c=100$ MV/m and $P_r = 64$ mC/m². We separated electronic, dipolar and ferroelectric components of the dielectric constant and obtained $\epsilon = 2$, $d = 7$, $f = 95$. In case of uniaxially stretched films we have found $f = 40$, $P_r = 42$ mC/m² and $E_c = 48$ MV/m [10], all values lower than those for biaxially stretched PVDF.

We studied polarization uniformity in corona poled samples of P(VDF-TFE) copolymer containing 90 % of ferroelectric beta phase [11]. Polarization profiles were measured by the piezoelectrically induced pressure step method. It has been found that the residual polarization is distributed nonuniformly in samples poled by CCCP method independently on poling temperature. Nonuniformity of polarization was caused by nonuniform distribution of the poling field that, in its turn, was attributed to injection of negative charge during poling.

Efficiency of corona poling depends on corona polarity. We compared TSD currents and pyroelectric coefficients of PVDF samples containing preferentially either polar beta phase or non-polar alpha phase and poled in either positive or negative corona. It appeared that that beta samples were poled to the higher values and showed higher pyroelectricity than the alpha samples. Judging by values of the pyrocoefficients, poling in a positive corona is more efficient than in a negative one, probably because the positive charges are not easily injected into the bulk, as do the negative ones. In the theory of injecting current it is shown that injection usually produces a non-uniformity of the field and consequently of the residual polarization.

Thus, corona poling is a powerful method to produce residual polarization in FP. The valuable information on charge transport, storage and polarization dynamics can be obtained during poling if the advanced modifications of the corona method are used, such as, CCCP method. By using this method we were able to obtain new data on injection and drift of charge carriers, the hysteresis phenomena and polarization build-up.

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SWITCHING OF FERROELECTRIC POLARIZATION AND ITS BUILD-UP IN POLYVINYLIDENE FLUORIDE (PVDF) FILMS

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Ferroelectric polymers have an advantage over traditional ferroelectric materials due to their good mechanical properties. At the same time, the magnitude and stability of the ferroelectric polarization in ferroelectric polymers are not sufficient to ensure their wide scale practical application in sensors and actuators. Since both parameters depend on the poling conditions a deep understanding of polarization related phenomena is important for improving these material properties.

Polyvinylidene fluoride (PVDF) is a ferroelectric polymer undergoing a fast polarization reversal called also as polarization switching [1,2]. Its ferroelectricity originates from molecular dipoles associated with positively charged H atoms and negatively charged F atoms. The all-trans conformation of chain molecules and their parallel packing cause an alignment of all molecular dipoles in one direction to induce a large spontaneous polarization. Polarization reversal occurs as a result of the rotation of molecules about their chain axes.

Polarization and switching phenomena in 12 μm -thick PVDF have been studied experimentally by application of 500 to 2500 V voltage pulses from 100 ns to 100 s duration and short-circuiting with the total displacement continuously monitored. All displacement components were identified and evaluated, such as the remanent polarization, the σ -related displacement, the unstable reversible component and the conduction currents. It has been found that contrary to theoretically predicted fast switching of polarization at high fields, the ferroelectric component continued to increase even for times 5-6 orders of magnitude longer than the switching time indicating that apart from the fast component a slow one exists. A phenomenological model of polarization build-up and switching has been worked out considering nonlinear $P(E)$ dependence, effect of amorphous phase, transport and trapping of intrinsic and injected charge carriers. The following expression has been obtained for temporal development of the polarization

$$P = (E_a - E_c) \left\{ 2\varepsilon_o \varepsilon + \frac{P_s}{E_s + E_c} \left[1 - \exp\left(-\frac{t}{\tau}\right) \right] \right\} \quad (1)$$

where

$$\tau = \frac{\varepsilon_o \left(2\varepsilon + \frac{P_s}{E_s - E_c} \right)}{2e\mu n} \quad (2)$$

E_a – is the average electric field, E_c – the coercive field, ε – the dielectric constant, ε_o – the permittivity of a vacuum, P_s – the saturated ferroelectric polarization, E_s – the lowest field at which P_s is obtained, τ – the characteristic time constant, e – the elementary charge, μ – the mobility of intrinsic and injected charge carriers, n – the volume density of the charge carriers.

Considering the role of the discovered slow component of polarization it was possible to explain the previously observed experimental results and reexamine existing models.

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КОМПРОМІС ПАРЕТО МІЖ КРИТЕРІЯМИ ЕФЕКТИВНОСТІ ПРОЦЕСУ ФОРМУВАННЯ РОЗКЛАДУ НАВЧАЛЬНИХ ЗАНЯТЬ Сакалюк О.Ю., Трішин Ф.А.....	155
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