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д-ра техн. наук, професора Б.В. Єгорова

Укладач Т.Л. Дьяченко

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

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

where

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

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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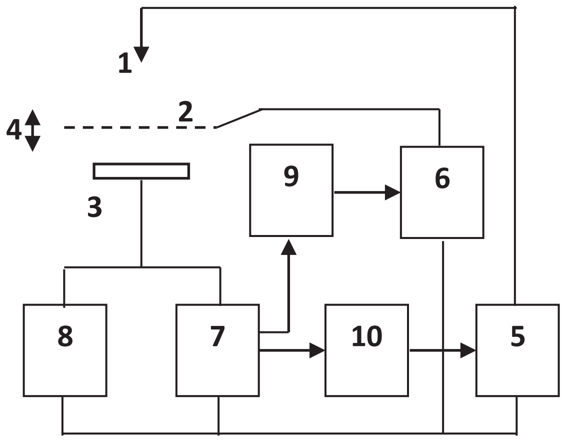
POLING OF FERROELECTRIC POLYMERS IN CORONA DISCHARGE

Prof. A.E. Sergeeva, Prof. S.N. Fedosov
Odessa National Academy of Food Technologies

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 ferroelectrics 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.

Figure 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/m^2. We separated electronic, dipolar and ferroelectric components of the dielectric constant and obtained $\varepsilon_e = 2$, $\varepsilon_d = 7$, $\varepsilon_f = 95$. In case of uniaxially stretched films we have found $\varepsilon_f = 40$, P_r = 42 mC/m^2 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 that 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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RELAXATION PROCESSES IN FERROELECTRIC AND NON-LINEAR OPTICAL POLYMERS STUDIED BY DIELECTRIC SPECTROSCOPY AND TSDC METHODS

Prof. A.E. Sergeeva, Prof. S.N. Fedosov
Odessa National Academy of Food Technologies

Non linear optical polymers with huge chromophore molecules incorporated in a polymer matrix have prospects of wide application in modern optical devices for the second harmonic generation (SHG), the optical parametric amplification (OPA), the optical rectification (OR), etc., therefore their stability and relaxation behavior are of the great practical and theoretical interest.

It is known that the relaxation behavior of dye molecules in guest-host polymer systems is related to the molecular motion in the polymer. From another side, addition of a foreign substance to a polymer modifies its relaxation behavior. These processes in nonlinear optical (NLO) polymers are interrelated and both affect stability of the poled order. Therefore, investigation of the relaxation processes can give information on the chromophore dynamics and stability of the poled order.

In this work we study a system obtained by doping atactic polystyrene (PS) with disperse red 1 (DR1) dye molecules. Main transitions in PS are well established. The α-process is the glass-rubber transition observed near T_g temperature. The β-transition is seen at sub-T_g temperatures from –10 to +60 ºC, while γ and δ are cryogenic transitions at –120 and –230 ºC correspondingly. The objective of this study was to find how doping affects the relaxation processes in PS.

Dielectric properties of PVDF, P(VDF-TFE) and polystyrene doped with DR1 dye molecules have been studied by the dielectric spectroscopy from –60 to +120 ºC at frequencies from 1 Hz to 5 MHz and by the TSDC method from –160 to +140 ºC. Relaxation peaks were also calculated from isothermal absorption currents using Hamon's approximation.

Three relaxation processes were identified in ferroelectric polymers, namely α-relaxation in amorphous phase, β-relaxation in a glassy state and interfacial or space charge relaxation at 60-

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