

УДК 537.226:678.01

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APPLICATION OF CORONA DISCHARGE FOR POLING FERROELECTRIC POLYMERS

Наведено результати досліджень сегнетоелектричних полімерів на основі полівініліденфториду. Представлено ВАХ позитивного і негативного коронного розряду та результати порівняння струмів ТСД і пірокоефіцієнтів сегнетополімерів, що містять полярну бета фазу або неполярну альфа фазу. Більш сильна поляризація і висока піроактивність спостерігається в бета зразках. Встановлено, що електризація в позитивному коронному розряді більш ефективна оскільки позитивні заряди не інжектуються так вільно в об'єм, як негативні заряди.

Приводятся результаты исследования сегнетоэлектрических полимеров на основе ПВДФ. Представлены ВАХ положительного и отрицательного коронного разряда и результаты сравнения токов ТСД и пирокоеффициентов в сегнетополимерах, содержащих полярную бета фазу, либо неполярную альфа фазу. Более сильная поляризация и высокая пиреоактивность наблюдаются в бета образцах. Установлено, что электризация в положительном коронном разряде более эффективна, поскольку положительные заряды не инжектируются свободно в объем.

The paper contains experimental results on corona charged ferroelectric polymers like PVDF. Current-voltage characteristics of positive and negative coronas are presented as well as comparison of TSD currents and pyroelectric coefficients in ferroelectric polymers containing either polar beta phase or non-polar alpha phase. It has been shown that the beta samples acquire higher polarization and show therefore higher pyroelectricity. It has been found that poling in a positive corona is more efficient, because positive charges are not so easily injected into the bulk, as do the negative ones.

Introduction. Spontaneous polarization in crystallites of a ferroelectric polymer is randomly distributed, therefore the dipoles must be oriented in one direction by application of an external electric field in order to insure high-quality characteristics of the materials. The corresponding process called poling or charging is an important step in obtaining desired properties. The most advanced is the corona charging method applied earlier in electrophotography [1], in electrets [2] and in electrostatic filters [3]. Due to its versatility, the corona method allows to optimize poling by proper selection of the poling mode, polarity and temperature.

A corona is a self-sustainable discharge occurring if a sufficiently high voltage is applied to asymmetric electrodes such as a point and a plate [4]. In the ionization area near the point, depending on corona polarity, either positive or negative ions are produced. The ions bombard the bare sample surface and no electrode is required on this side. The process takes place at atmospheric pressure, so the ions have an average thermal energy. The ions do not penetrate into the bulk, but transfer their charge and leave the surface as neutral atoms or molecules. The excess charge either resides on the surface, or injected in the bulk. The advantages of the corona charging 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 has been gradually replaced by a corona triode with a metal grid introduced between the point and the sample. Apart from charging, the corona triode was used to study dynamics of poling and charge transport phenomenon in some

polymers [5-10]. This paper gives a short review of the corona charging of ferroelectrics polymers with an accent on using constant current corona poling (CCCP).

Experimental setups. In this paper we consider only corona triode methods, because a point-to-plane technique does not provide the required quality of poling. There are four main 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 shown in Fig. 1 are not used in the mode I. One can measure the DC poling current (7), but cannot separate its components. The highest surface potential is approximately equal to the grid voltage. 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 a modified Kelvin method measuring the AC current (8). In the mode III (CCCP) additionally to the vibrating grid 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 [8-10]. In the latest version of the CCCP triode (mode IV) [12] not the corona, but the grid voltage is adjusted continuously through the feedback 9 for keeping the current constant. The sample potential can be found without using the vibrating capacitor, so elements 4 and 10 are excluded. The surface potential is found from the graduation curve obtained beforehand by substitution a real sample with a metal disk of the same area. Detailed description of the method is given in review papers [6,7].

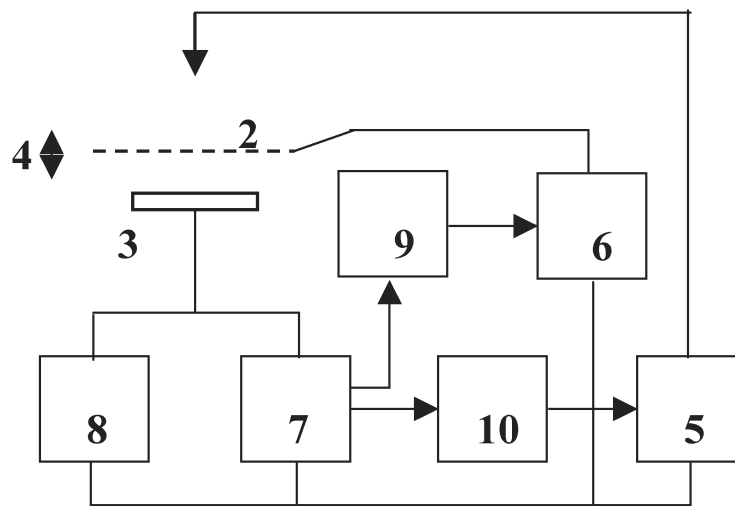


Figure 1. Block-diagram of the corona setup. 1 – the corona electrode, 2 – the grid, 3 – the sample, 4 – vibration of the grid, 5 – high voltage DC power supply for corona, 6 – power supply for the grid, 7 – DC component of the poling current, 8 – AC component of the poling current, 9 – the feedback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

To fix corona and grid voltages, point-grid and grid-sample distances we recommend to measure current-voltage characteristics at different conditions (Fig. 2). Since the corona appears at about 5 kV, the grid potential should not exceed this value, otherwise the grid itself will produce a parasitic corona. At the same time, the difference between the corona voltage and the grid voltage must not be smaller than 5 kV or it should be kept constant to ensure a stable discharge at different grid voltages. In most cases the value up to 4 kV and 12-16 kV are suitable as the grid and the corona voltages. After completion of poling a short-circuiting of the sample can be performed by grounding the grid and changing corona polarity to the opposite one. This step is desirable in many cases in order to remove the excess surface charge.

Corona poling of ferroelectric polymers. Due to high piezo- and pyroelectricity, ferroelectric polymers may replace conventional inorganic materials in sensors and transducers. Therefore, such materials as PVDF have attracted attention recently. To induce orientation of dipoles, the polymers are usually poled in a corona [6-12], because high electric fields in this case can be achieved without breakdown. Using a constant current corona triode we have found that the initial poling and switching pass three stages, each one corresponded to a definite part of the potential - time curve [7,8,11-15]. A fast increase in surface potential was observed at the first stage indicating that the capacitive component prevailed in the poling current. At the second stage there was a plateau at the voltage-time curve related, most probably, to switching of the ferroelectric component of 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 [8]. 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 $\epsilon_e = 2$, $\epsilon_d = 7$, $\epsilon_f = 95$. In case of uniaxially stretched films we have found $\epsilon_f = 40$, $P_r = 42$ mC/m² and $E_c = 48$ MV/m [14,15], all values lower than those for biaxially stretched PVDF.

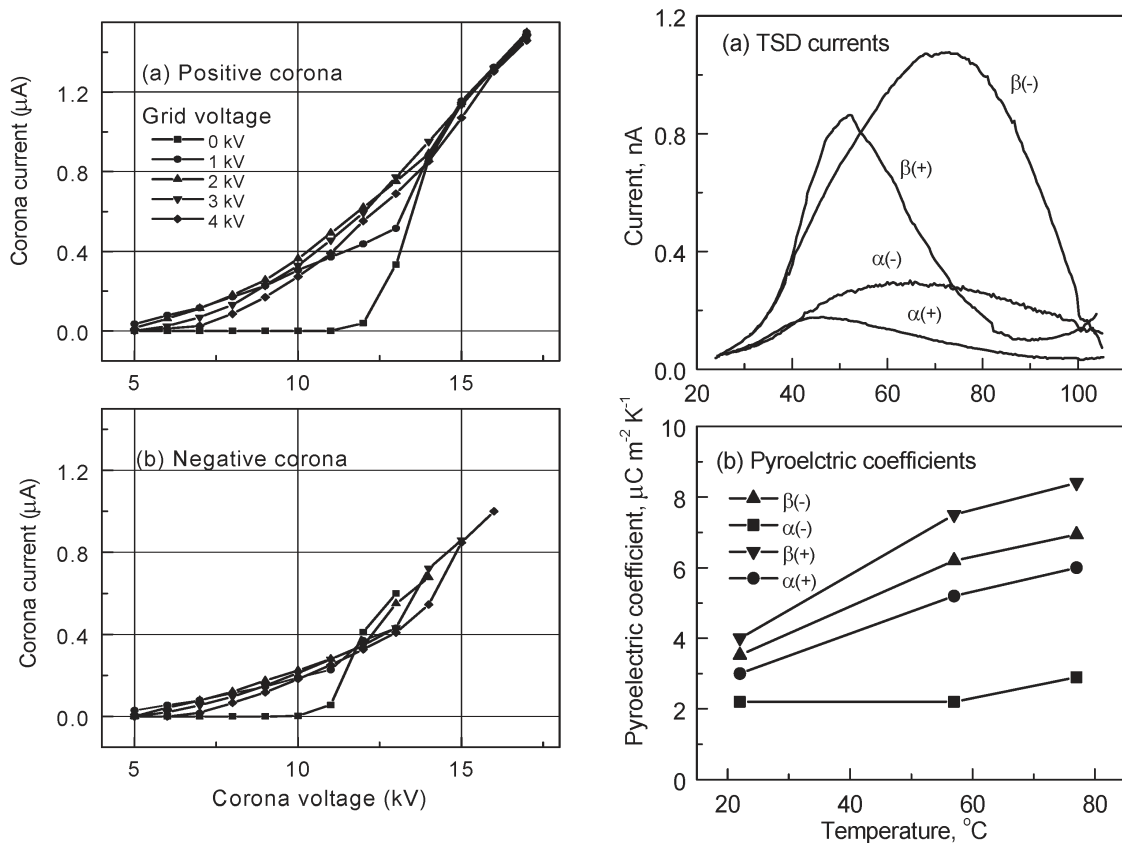


Figure 2. Current-voltage characteristics of positive (a) and negative (b) coronas

Figure 3. TSD currents (a) of negatively and positively corona charged α - and β -PVDF and corresponding pyroelectric coefficients measured by the dynamic method (b)

We studied polarization uniformity in corona poled samples of P(VDF-TFE) 95:5 copolymer (Plastpolymer, Russia) containing 90% of ferroelectric β phase [15]. Polarization profiles were measured by the piezoelectrically induced pressure step (PPS) 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. Corresponding results are presented in Fig. 3. It is seen that beta samples are poled to the higher values and show 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.

Final remarks. Corona poling is a powerful method to produce residual polarization in ferroelectric polymers. The advantages of corona charging are that samples can be poled without deposited electrodes, higher fields can be achieved in corona than in case of sandwich contact poling, thin films can be poled in spite of defects. Moreover, the valuable information about charge transport, storage and polarization can be obtained during poling in a corona triode. The constant current method facilitates analysis of experimental results and gives additional information on injection and drift of carriers, the hysteresis phenomena and polarization buildup.

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