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Thus, for obtaining high values of the  $d_{33}$  piezoelectric coefficient, the intrinsic Young modulus  $Y_p$  of the porous layer, as well as the geometric factor  $\alpha$  should be as small as possible. The real modulus  $Y_p=0.3$  MPa was calculated using experimental results of  $d_{33}=550$  pC/N for samples with  $d_F=12.5$   $\mu\text{m}$ ,  $d_P=63$   $\mu\text{m}$  ( $\alpha=0.4$ ),  $\varepsilon_F=2.1$ ,  $\varepsilon_P=1.1$ , and  $E_p=22.3$  MV/m.

From the first glance, a rather simple formula (1) could easily show how to obtain high values of the  $d_{33}$  piezoelectric coefficient. However, experimental results have shown that the situation is not so simple. It was found that the experimental data correspond to the theoretical model only in the range of  $\alpha$  from 1 to 8, while different behavior of  $d_{33}$  was observed at  $\alpha < 1$ . Instead of decreasing with  $\alpha$ , as predicted by (1),  $d_{33}$  increased in contradiction with (1).

The reason is that  $d_P$  affects  $E_B$  and the  $d_{33}$  coefficient. It appeared that the breakdown field for the various ePTFE layers in the sandwich structure exceeded the Paschen values by a factor of  $\sim 1.8$ . Substituting the experimentally measured function  $E_B(d_P)$  in (1), we obtained dependence of  $d_{33}$  from  $\alpha$  in good agreement with experimental points. Thus, considering the thickness dependence of the breakdown field, the conclusion concerning inverse proportionality between  $d_{33}$  and  $\alpha$  should be corrected. At a constant thickness of the porous layer  $d_P$ ,  $d_{33}$  increases with decrease of  $\alpha$ , i.e. at the smaller thicknesses of the solid layers. However, if the decrease of  $\alpha$  is the result of increasing the porous layer thickness with the same blocking layers, the  $d_{33}$  coefficient is smaller in the case of the thicker porous layers.

The final conclusion that we made is as follows: the thinner a porous layer of the sandwich, the higher  $d_{33}$ , if the solid layer is not too thick. For example, at  $d_P=25$   $\mu\text{m}$  and  $d_F=5$   $\mu\text{m}$  one can obtain the  $d_{33}$  value of about 1000 pC/N. Considering low elasticity of ePTFE and creep at low frequencies, one effective way for increasing  $d_{33}$  could be the substitution of the porous material by closed air gaps guaranteeing the lowest possible Young's modulus.

## **BUILD-UP AND SWITCHING OF FERROELECTRIC POLARIZATION IN POLYVINYLIDENE FLUORIDE**

**Prof. S. N. Fedosov and Prof. A. E. Sergeeva**  
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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  $\mu\text{m}$ -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  $\varepsilon$ -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,  $\varepsilon$  the dielectric constant,  $\varepsilon_o$  the permittivity of a vacuum,  $P_s$  the saturated ferroelectric polarization,  $E_s$  the lowest field at which  $P_s$  is obtained,  $\tau$  the characteristic time constant,  $e$  the elementary charge,  $\mu$  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.

### References

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## POLING OF FERROELECTRIC POLYMERS IN CORONA DISCHARGE

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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 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.

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