

## Piezoelectric Properties in Porous Fluoropolymer Having Isolated Voids

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Recently, the porous fluoropolymer films have been known as the promising materials which have excellent piezoelectric properties comparable to piezoelectric ceramics. However, because they usually have spatially-opened non-isolated voids, there exist some demerits, such as the degradation under high-humidity environments, the poor reproducibility of the piezoelectricity, and so on. We obtained newly-developed foamed fluorinated ethylene propylene copolymer films (FFEP), which have spatially-closed isolated-voids, and studied the fundamental piezoelectric properties, namely, the relationship between the measurement or the poling conditions and the piezoelectricity. The effects of the pretreatments for FFEP before the poling on the piezoelectricity were also studied.

The FFEP films were provided by Junkosha Inc.. By the cross-section observation with an optical microscope, FFEP films were confirmed to have the spherical isolated-voids with the average diameter of 0.05 mm.

The poling by utilizing corona discharge is required for developing the piezoelectricity in PPEF without giving heavy damages in the void walls. For the generation of the corona discharge, DC voltage higher than 10 kV is applied to tungsten wires with 0.05 mm diameter arranged parallel to FFEP sheets on an grounded electrode plate. In order to estimate the quantitative piezoelectricity, the piezoelectric constant in thickness direction,  $d_{33}$ , was measured using  $d_{33}$  meter (IACAS ZJ-6B) with the accuracy of  $\pm 3\%$ .

The maximum  $d_{33}$  larger than 300 pC/N was obtained in the samples poled at 16 kV for 1 minute as shown in Fig. 1. Because of the breakdown in the void walls,  $d_{33}$  decreased when the applied voltage was higher than 16 kV, or the poling period was longer than one minute.

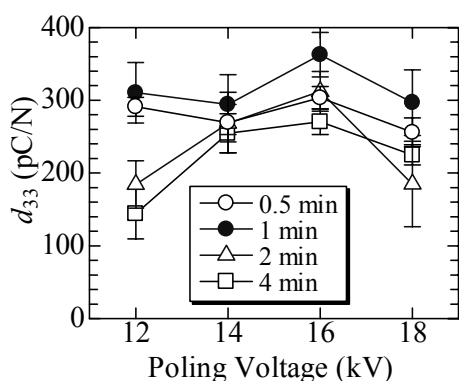


Fig. 1. Effects of poling voltage and poling period on piezoelectric constant

The piezoelectricity of FFEP was found to be stable at high temperature. Although  $d_{33}$  slightly decreased with increase in the poling temperature at the region higher than 120 °C, the  $d_{33}$  values observed in the samples kept at 170 °C for several hours after the poling were maintained larger than 80 % of the value in the samples poled and measured at room temperature.

The strongly negative correlation between  $d_{33}$  and the static stress applied to the samples during the measurement was observed. The  $d_{33}$  values measured in the samples under the static stress larger than 30 kPa became as small as those of homogeneous piezoelectric polymers without any voids. This seems to be caused by the cramping the void displacement due to the piezoelectricity. On the other hands, the  $d_{33}$  shows a positive correlation with the dynamic stress applied during the measurements.

The firing potential for inducing partial discharge is known to be relatively higher in the voids having a spherical shape in dielectric materials. This means that the effective poling of FFEP by corona discharge is difficult compared with the conventional porous fluoropolymer, which has lenticular or plate-like voids. In order to increase the effects of the poling by mean of reducing the firing potential, the following pre-treatments, a uniaxial compression to distort the void shape flatly, a helium-gas displacement in the voids, and an RF oxygen plasma radiation were performed before the poling.

Figure 2 shows the effect of the uniaxial treatment. The piezoelectricity increased with the increase of the compression stress. When FFEP was compressed at 5 GPa, the  $d_{33}$  was over 1000 pC/N, which is larger than a twice of  $d_{33}$  observed in non-treated FFEP. The helium-gas displacement and RF oxygen plasma radiation also increased  $d_{33}$  by 60 % and 150 %, respectively. These results are considered to be due to the effective reduction of the firing potential which enhances the generation of the partial discharge in the voids during the poling.

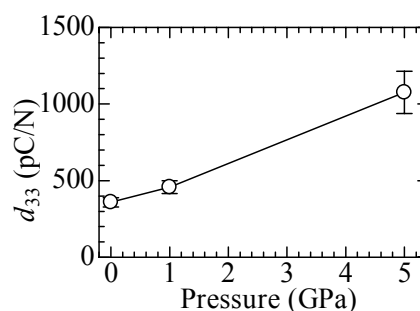


Fig. 2. Effect of pre-treatment of uniaxial compression