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Additional Information

Relationship between surface potential and d_{33} Constant in Cellular Piezoelectric Polymers.

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Abstract. The development of cellular piezoelectric polymers has shown very promising results thanks to their high d_{33} piezoelectric constants which make them candidates for many applications. Cellular piezoelectric polymers, known as ferroelectrets, are obtained by means of an activation process which consists in generating an internal dipole with electrostatic charges produced by internal electric discharges. The most common system for this activation process is the application of a corona discharge on the surface of the sample in order to produce a high internal electric field. The theoretical electrostatic model of the process which is widely used is the Sessler model which relates the internal surface charge density, the air and polymer layers thickness, the dielectric permittivity of the polymer and the Young's Modulus of the cellular material to the d_{33} piezoelectric constant. In our work, we relate the internal charges of the material with the d_{33} piezoelectric constant by means of a surface potential scanning of cellular polypropylene biaxially stretched samples. Samples were charged by a corona discharge controlled with a triode electrode. Surface potentials were high enough to generate internal discharges and obtain measurable d_{33} piezoelectric constants but low enough to be measured with spatial resolution by means of a 3kV electrostatic probe. Surface potential profiles showed some deviations from the expected bell-shape profile due to the internal electric field generated by the internal static charge. These deviations can be numerically related to the measured d_{33} piezoelectric constant with the electrostatic Sessler model.

1. Introduction.

Since 1960, corona discharge has been intensively used to charge polymer films during the manufacturing process of electrets. It has been an important tool for the improvement of the charge stability in electrets. More recently, corona discharge is used to activate polymer foams and provide them piezoelectric properties [1][2]. The development of piezoelectric polymer foams has been extensively improved in the last years [3-8]. As a general procedure, a corona discharge created by a tip connected to a high voltage generator is applied to the surface of a sample which is placed on a ground plane. Thus the corona ions reach the sample surface and create a surface charge distribution with an expected bell shape. This is true if the sample shows no irregularities like conductive particles, bubbles or impurities or no phenomena like charge injection or internal discharges occur. If the sample is highly insulating, then the electric field in the sample and its surface potential increase until the corona discharge extinguishes.

With this corona system it is, however, not possible to achieve a good control of the charge deposition on the surface [1]. An improved system to control the charge deposition on the sample surface is the triode system. In this arrangement, a potential control grid is placed between the sample and the tip. When controlling the grid voltage it is also possible to control the potential on the sample surface below the grid. The surface potential of the sample increases until it reaches approximately the grid potential [1-2]. Then the ion flux from the grid to the sample is stopped. In this work, the triode system is used to investigate the relationship between the surface potential of charged polymer foams and their resulting d_{33} constant [3]. All measurements were carried out with commercial polypropylene (PP) foam films which were thermally biaxially stretched in our laboratory [4] and then charged by a triode controlled corona discharge. The piezoelectric coefficient d_{33} was measured by means of the quasi static method [8].

2. Experimental Measurements.

2.1. Samples preparation.

The material has been selected from different types of foam PP film from the Sekisui Alveo Company. The original material thickness is 1040 µm. The ratio air-polymer is approximately of 88% air and 12% polymer. The Young's modulus is about 2-3MPa and the density is 100 kg/m³. The polymer film was thermally modified through biaxial stretching in two steps producing a 90% decreased in its thickness (see figure 1). This biaxial stretching increases the piezoelectric properties of the material compared to non-stretched samples: the d_{33} constant of non-stretched samples was about 10pC/N compared to 600pC/N for stretched samples [9]. Another effect of biaxial stretching was a reduction of porosity down to 60%, and in increase of density up to 400kg/m³. The Young's modulus was also reduced to 0,2 to 0,3 MPa for a thickness of 100 µm or less.
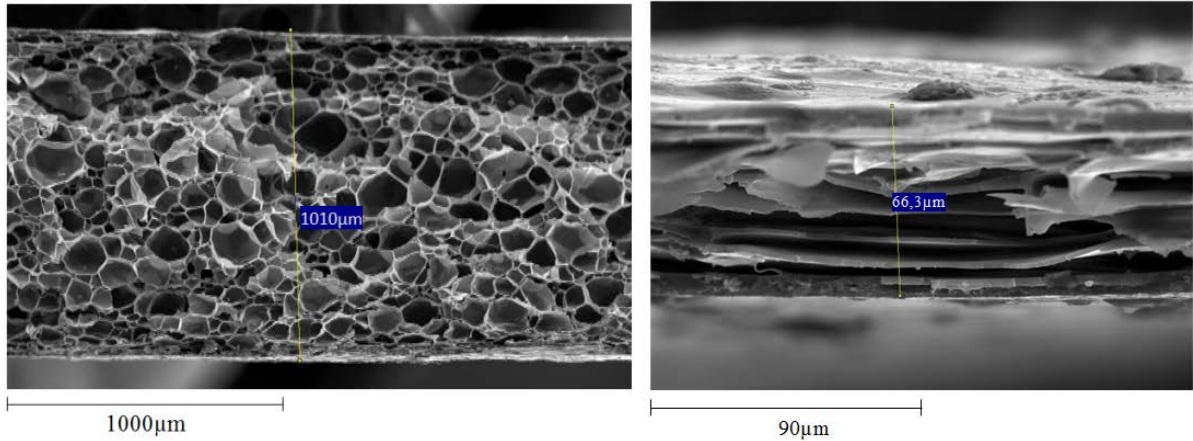

Figure 1. Photography of the polymer foam without treatment (left) and after biaxial thermal stretching (right).

Figure 1 shows the PP foam sample before and after the thermal treatment. In this case the thickness of the sample was less than 100µm. It can be observed how the shape of air voids is dramatically modified. Samples were cut in squares of 61x61mm from which 9 squared samples (20mm×20mm) could be cut. All the samples were metallized by sputtering with silver on the ground side before corona charging. A grounded edge around the sample was used as a sample holder. Its influence was discarded in the measurements (see §3.1).

2.2. Experimental Measurements.

To achieve a better control on surface potential distribution the triode system was used to charge the samples. An x-y scanning system was built with two servo motors SMC model E-Y2 and LJ1H20. It allowed the scanning of the surface with the triode charging system in order to charge a large area. After sample charging, the surface potential was scanned with an electrostatic probe Trek model 370 up to 3kV. The voltage resolution of the probe is 1V, the distance from the probe to the surface was 2mm as recommended by the manufacturer, The area "seen by the probe" was not calculated but it was experimentally estimated as a 5 mm radius circle. The electrostatic probe scans the surface of the sample moving at a speed of without contact and without modifying surface charge distribution. The proved moved over the surface during the scanning at a speed of 1cm/s. The surface potential scanning was done 5 minutes after charging of the sample.

The output of the probe was registered by means of an oscilloscope Yokogawa model DL9402. A high voltage amplifier Trek model 30/20 was the voltage generator for the tip electrode. A Spellman SL150 generator was used for the grid voltage control. All the measurements were performed under constant conditions of temperature and humidity (25ºC±3ºC, 50% humidity) inside a climatic chamber. The testing setup is represented in figure 2.

It was then possible to optimize the scanning parameters of the triode, i.e., acceleration, velocity and spatial resolution of the steps for better surface charge deposition. The exposition time of the sample to the corona discharge can be controlled with the scanning parameters which were set as follows: an acceleration of 4.9 m/s^2, a scanning speed of 100mm/s and spacing between scanning lines of 2mm. These parameters lead to an average exposure time of about 1.5s. In the triode electrode, the distance of the grid to the sample was 15mm and the distance between the tip electrode and the sample was also 15mm.

Different electric potential values of grid and tip electrodes were applied. The grid voltage was 0,5kV, 1kV, 2kV and 3kV and the tip voltage ranged among the following values: 4kV, 6kV, 8kV, 10kV and 12kV. The more homogeneous and bell-shaped distributions were obtained for the values of 10kV and 12kV at the tip electrode. At lower tip voltages, some irregularities appeared on the surface not linked to internal discharge but related to poor performance of the corona discharge. The grid voltage was limited to 3kV due to the surface potential probe limit. Of course, higher d_{33} constants could be obtained with higher grid voltages [9] but then it was not possible for our equipment to measure the surface potential.
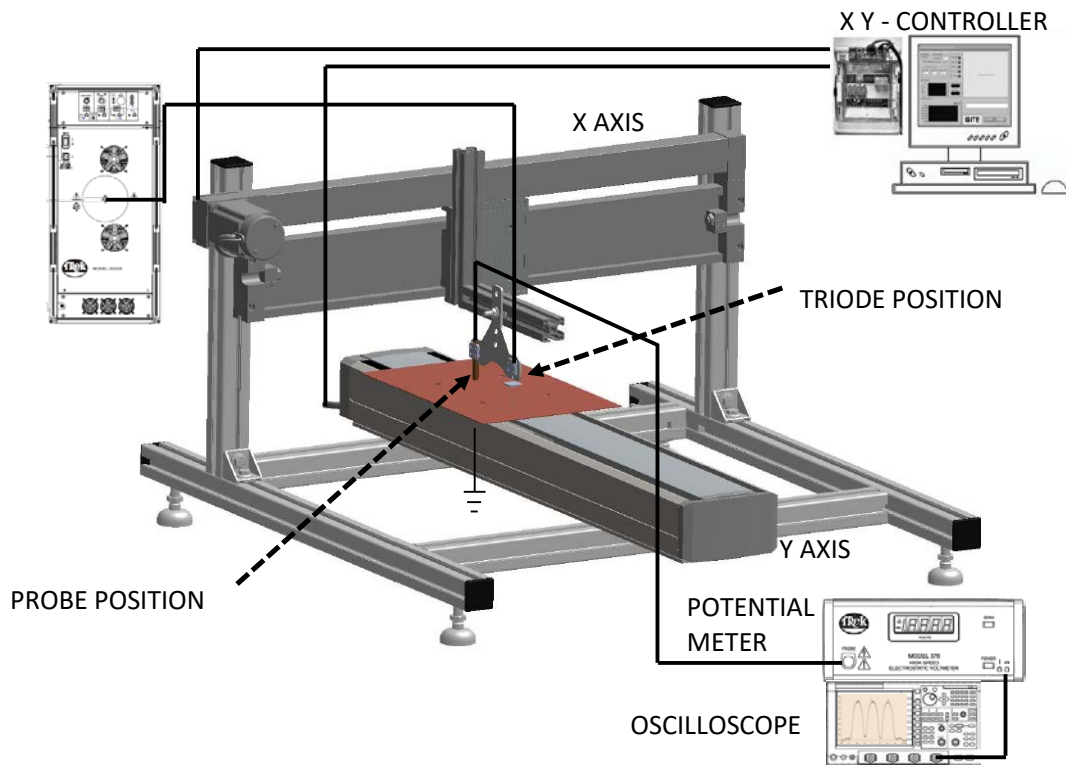

Figure 2. Automatized charging and measuring system.

The d_{33} piezoelectric constant was measured with an own design setup (figure 3) made of a force actuator, a force sensor, a power controller system that converts the signal from signal generator to the force actuator and the equipment to register the data. The control signal was generated by a function generator (Tektronics model AFG 3251) and amplified by a control box. A pressure sensor in series with the sample measured the applied mechanical force. Current in the sample was registered and integrated. Both signals were measured by means of a Yokogawa DL9040 oscilloscope. A series of 10 mechanical force pulses linearly increased from 1N to 15N with time enough for material relaxation were applied to check the linearity of the material.
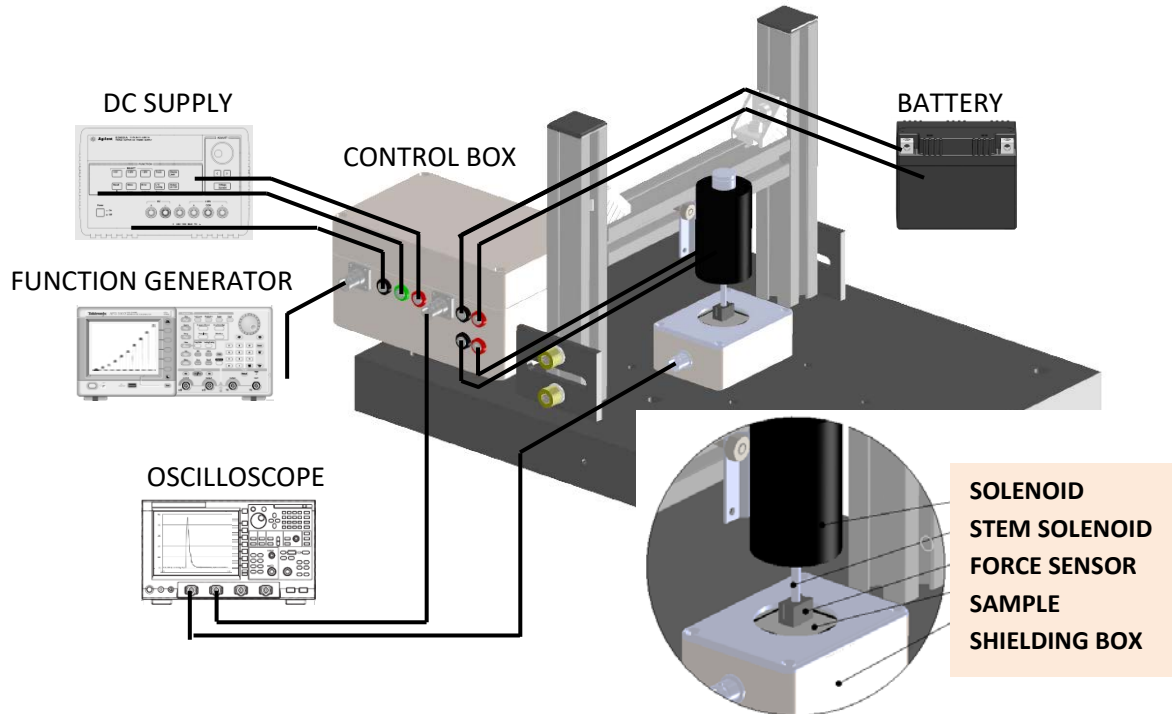
DC SUPPLY

CONTROL BOX

BATTERY

FUNCTION GENERATOR

SOLENOID
STEM SOLENOID
FORCE SENSOR
SAMPLE
SHIELDING BOX

OSCILLOSCOPE

Figure 3 Experimental setup to measure d_{33} piezoelectric coefficient by the quasi-static method.

3. Results and discussion.

3.1. Surface potential measurements.

The effect of the grounded frame of the sample holder was checked. In *Figure 4* samples charged with triode system with grid voltages of 3kV and 1,5kV. It can be seen that for low potentials (1,5kV) the surface potential profile is regular and shows a well-defined bell shape. For the case of 3kV, there was a deviation between the measured surface potential and the expected bell-shape. As it is shown in figure 4, surface potential is reduced in some places, indicating that the internal distribution of the electric field may have changed due to internal discharges and the appearance of an internal dipole. These internal dipoles induce an internal electrical field in opposition to the applied electric field and this finally reduces the surface potential. This was further investigated with d_{33} constant measurements.
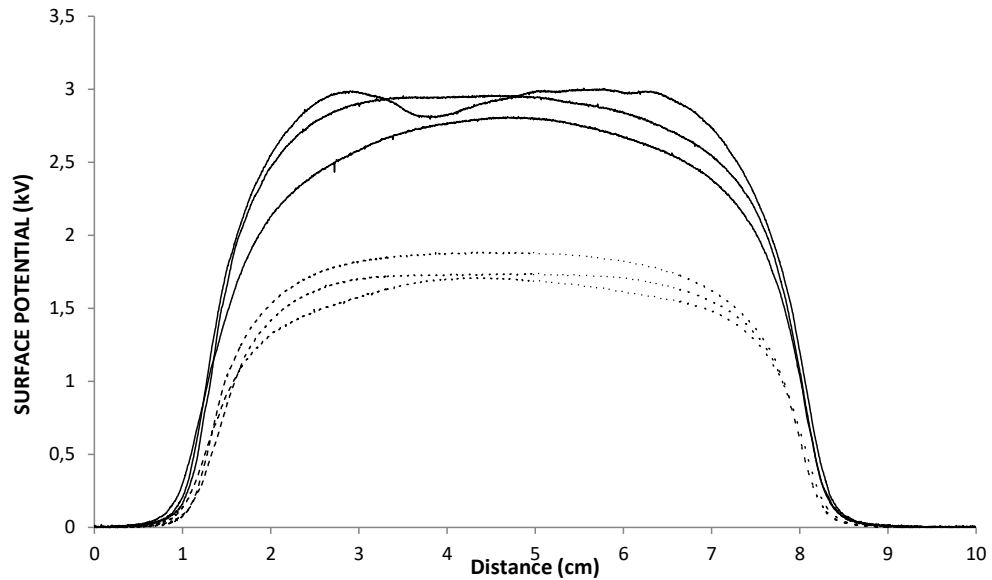
Figure 4: Surface potential for samples charged with a triode system
(——3kV charged samples, ---- 1,5kV charged samples)

3.2. Measurements of d_{33} piezoelectric constant.

The change in shape of superficial electric measure field indicates the presence of internal discharges inside the sample and the modification of the internal electric field. If this is true, there has to be a relationship with the d_{33} constant values. The initial sample of 61x61mm was divided into 9 square smaller samples numbered from (1) to (9). d_{33} constants were measured for each new sample and then the values were overlapped with surface potential curves. It has to be pointed out that for measuring d_{33} constants, the upper side of the sample is also metalized and the initial surface potential distribution of *Figure 4* is lost.

Figure 5 shows three initial profiles of surface potential for one sample and their d_{33} piezoelectric constant in each section. The shadowed areas represent the difference between the bell-shape expected surface potential and the measured one. The bell-shape expected curves are obtained by scaling one of the 1,5kV curves where no internal discharges are appreciated.

The values of areas and d_{33} constant can be found in table 1. For clarity, figure 6 shows graphically the data of table 1. The relation between the d_{33} constant and the area is apparent for the central profile (samples (4), (5) and (6)). It clearly shows the effect of the internal charge on the surface potential and the d_{33} constant. This relation is less evident for the other samples due to the accuracy of the method. Thus the central sample (5) will be used for further estimation of internal surface charge density.

Sample	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Unit Area (a.u.)	5	60	30	34	213	12	5	60	31
d_{33} (pC/N)	5,4	19,5	2	22,2	67,6	20,8	6,5	26,2	6,2

Table 1. Relation between shadowed area of the center profile of figure 5 and the d_{33} constant.
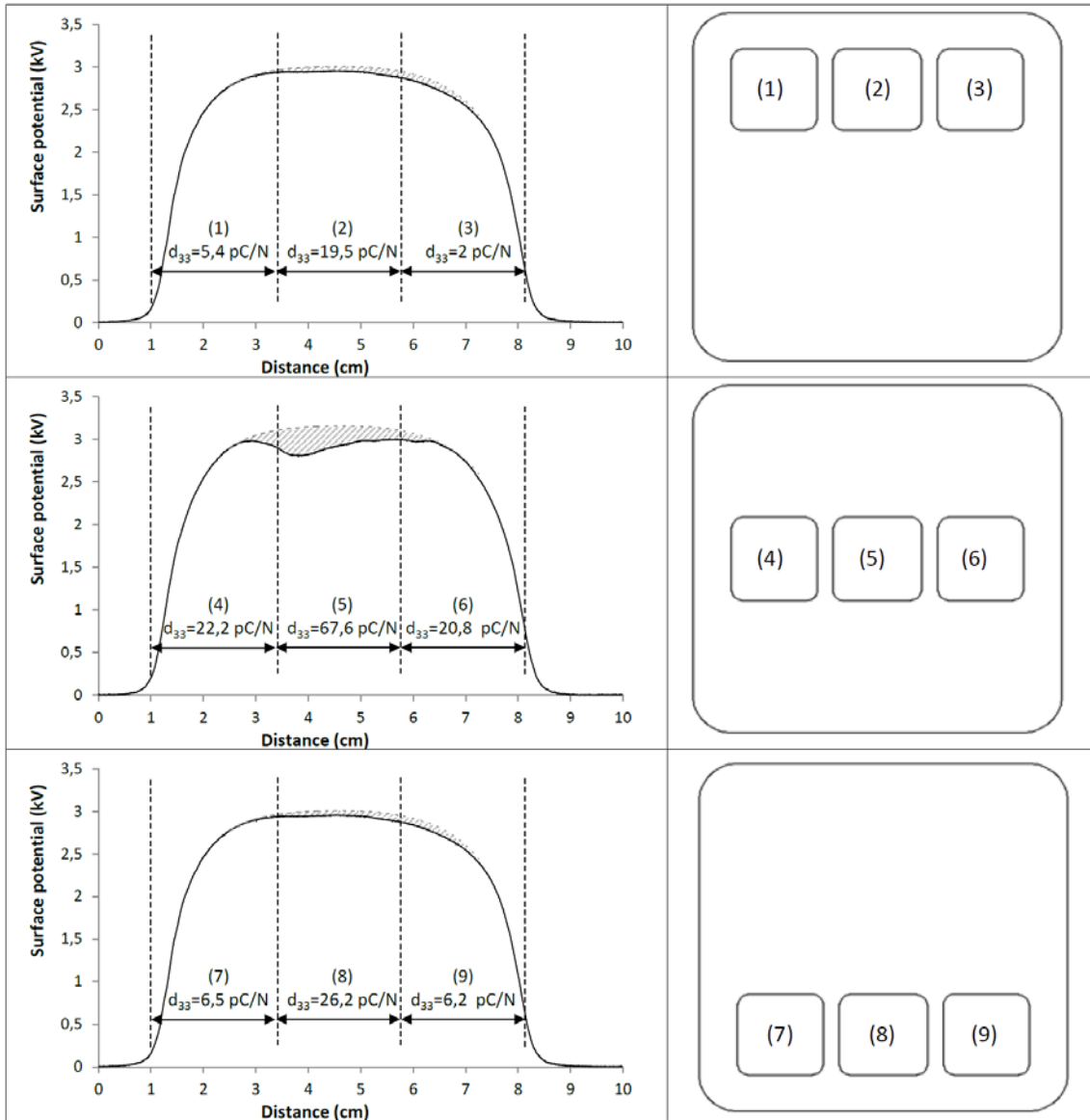
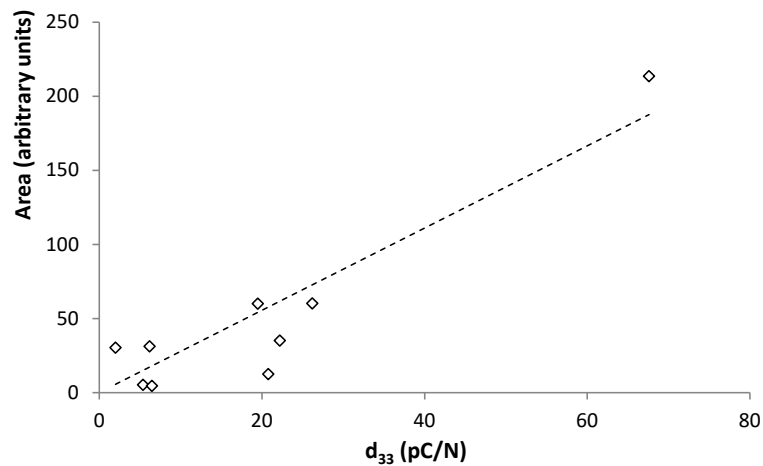*Figure 5: Surface potential and d_{33} measurement for samples of PP charged up to 3kV with the triode electrode.*

Figure 6: Relation between the shadowed area and the d_{33} constant.

3.3. Internal surface charge estimation.

According to the thickness of the sample and considering a simplified 1 dimension 2 layer model (figure 7), the internal surface charge can be estimated. As shown in [10], a 2 layer model gives a good accuracy for modelling cellular piezoelectric polymers. Polarization of PP is neglected and only the surface charge deposited by the corona discharge and the internal discharges are considered. It has to be taken into account that, when measuring with the electrostatic probe, the electric field in the air between the sample and the probe is zero [11]. The distribution of the internal electric field is represented in figure 8.

If σ_0 is the deposited charged density, σ_i is the internal surface charge density due to the internal discharges, ε_0 is the dielectric permittivity of air and ε_r the relative dielectric permittivity of PP, then the electric field in the air in the cells inside the sample is given by:

$$E_{air} = \frac{(\sigma_0 - \sigma_i)}{\epsilon_0} \tag{1}$$

And the electric field in the polymer is:

$$E_{PP} = \frac{(\sigma_0 - \sigma_i + \sigma_i)}{\epsilon_r \epsilon_0} = \frac{\sigma_0}{\epsilon_r \epsilon_0} \tag{2}$$

Thus the surface potential can be calculated as:

$$V = \int_0^d E dx = \frac{(\sigma_0 - \sigma_i)}{\epsilon_0} d_{air} + \frac{\sigma_0}{\epsilon_r \epsilon_0}(d - d_{air}) \tag{3}$$

If there were no internal surface charge, then the surface potential V_{est} (which is the estimated surface potential in figure 5), would be:

$$V_{est} = \frac{\sigma_0}{\epsilon_0} d_{air} + \frac{\sigma_0}{\epsilon_r \epsilon_0}(d - d_{air}) \tag{4}$$

Thus:

$$V_{est} - V = \frac{\sigma_i}{\epsilon_0} d_{air} \tag{5}$$

Finally:

$$\sigma_i = \frac{\epsilon_0 (V_{est} - V)}{d_{air}} \tag{6}$$

With the experimental average value of $V_{est} - V \approx 3130 - 2930 = 200V$ for the central sample number (5) of figure 5 and an air thickness of d_{air}=60µm, an internal surface charge of $\sigma_i = 44,27\ \mu C/m^2$ can be estimated.

According to Sessler equation [8] for a 1 dimension 2 layer model of the sample, it can be written that:

$$d_{33} = \frac{\varepsilon_r d}{Y} \cdot \frac{d_{PP}\sigma_i}{(d_{PP} + d_{air}\varepsilon_r)^2} \tag{7}$$

Where ε_r is the relative permittivity of PP (a value of 2,2 was measured by dielectric spectroscopy [9]) and Y the Young's modulus of the material (the experimental average value is 0,25MPa [9]). With the previous values, one obtains d_{33}= 55,3 pC/N which is in reasonable agreement with the measured value.
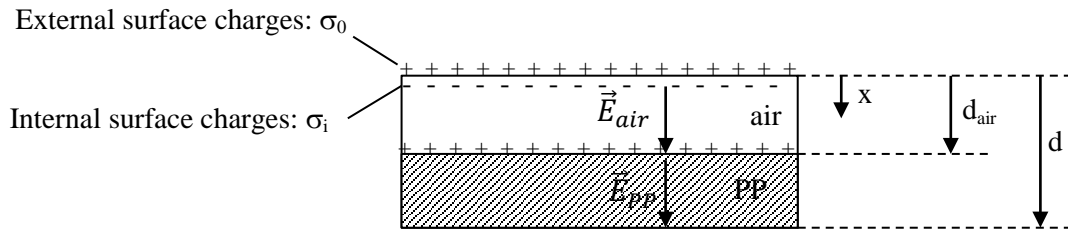

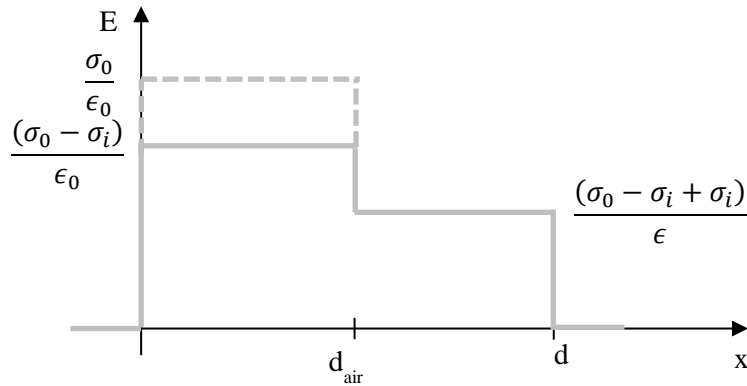*Figure 7: Simplified 1 dimension 2 layer model of the sample and internal electric field.*

Figure 8: Internal Electric field distribution on the x-axis
----- Electric field distribution without internal charges
—— Electric field distribution with internal charges

4. Conclusions.

In this work we present measurements of surface potential of biaxially stretched cellular PP films and their relation with the d_{33} piezoelectric constant after corona charging with a triode system. Results show the relation between the value of the surface potential and the piezoelectric constant d_{33}: in the areas where the surface potential decreases, the d_{33} constant is higher. In a 100 µm thick sample, it was found the highest d_{33} measurement of 67pC/N correlated with a clear decrease of surface potential in the central area. The reduction of the surface potential is due to the internal discharges and the resulting internal surface charge density which in turn creates an internal dipole in an opposite direction to the applied field. An internal surface charge of about 44 µC/m^2 can be estimated which is in relative good agreement with the experimental d_{33} measured constant in a 1 dimension 2 layer model of the material.

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