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Additional Information

Characterization and optimization of the d_{33} constant of cellular Polypropylene films

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ABSTRACT

Piezoelectric polymer cellular films with silver electrodes are made from a PP film activated by corona discharge. This cellular polymer is characterized by its high piezoelectric d_{33} coefficients in comparison with piezoelectric ceramics and other polymers like PVDF. One of the advantages is their malleability and shape ability in different kinds of forms. Our work presents the optimization of the activation process and the results of films characterization. All the samples are made from available PP film modified by a thermal biaxial stretching. d_{33} constant was measured by a quasi-static method and laser interferometry giving similar results. Transducer coefficients of about 700 pC/N were obtained. An approximation of the surface charge density in the polymer voids was obtained with a mathematical model. Thermal stability was checked by thermally stimulated depolarization currents (TSDC) showing a relationship between TSDC and d_{33} constant. Time stability was determined with more than one year old samples. Finally, the resonance frequency was obtained from interferometry measurement.

1. Introduction

Foamed polymers have been used for than 50 years in a variety of industry sectors.Their use as piezoelectric materials is relatively recent. It was first developed by Kirjavainen in 1989 [1]. A polypropylene (PP) foam film was biaxially stretched and then charged by corona discharge on both sides (for more information about PP foams manufacturing see e.g. [2]). The corona discharge deposites a surface charge on the material thus creating a high internal electric field. This produces gas breakdown inside the voids of the foam which leave an internal surface charge on both upper and lower sides of the void with opposite polarities. The electrostatic charge creates an internal micro dipole which has the same effect as the internal dipoles of crystalline piezoelectrica materials [3]. They are also called ferro electric materials. Kirjavainen, in the sensor mode, reached a d_{33} constant of about $160 pCN^{-1}$ and a thermal stability below 50°C which is low compared to other piezoelectric materials. Another difference of these materiales is their poor piezoelectric constant d_{31} which is a limitation for applications in different areas (e.g. for thermostatic devices).

Later different authors have proposed a structural modification of the material [4][5] to improve its piezoelectric properties. Modifications have been focused on 2 mains properties of the material: on one side, the Young modulus and its contribution to the elasticity and the piezoelectric constant and, on the other hand, the cell size and shape which allows higher dipole creation. The most known process to modify the material is to produce an inflation of the thin film by applying a high gas pressure which is suddenly realesed. If the pressure inside of the cavities is higher than external pressure the film inflates increasing its thickness [6]. Samples with many hundreds of pC/N of piezoelectric constant d_{33} [7] have been obtained.

In our work, a characterization and optimization of the d_{33} constant of fisically reticulated closed cell polymer foams made from PP is presented. Materials are provided by Sekisui Company in the form of a 1mm thick film. .The original material was thermally modified through a biaxial stretching in our laboratory. The biaxial stretching reduced the porosity percentage, the density and the yound modulus.

After the thermal treatment the samples are activated by corona discharge to acquire piezoelectric properties. To assess the material's properties, different measurement were carried out: (1) d_{33} constant measurements with a quasi-static method, (2) thermally simulated depolarization currents (TSDC) and (3)v resonance frequency by laser interferometry (Doppler Effect). d_{33} constant measurements and TSDC were performed at the Institute of Electrical Technology laboratory. The resonance frequency was measured at the University of Delft Netherlands, in the department of DC Systems, Energy Conversion & Storage.

The optimization process is aimed at maximizing the internal charge (and thus the amplitude and quantity of the internal dipoles) and reducing Young modulus to obtain a higher d_{33} constant.

2. Experimental Details

2.1 Cellular PP Samples and Preparation.

All the measurements presented were carred out from the PP and PE films Sekisui Alveo company. The ratio air-polymer is approximately of 88%, the young modulus is about 2-3MPa and the density is 100kg/m³ with a thickness of 1040 μm without

treatment. This material has a high variability in size cell between 1 and 20 µm or more in the sample thickness (see figure 1).

The thermal biaxial stretching of PP is carried out in four steps with stretching ranging from 65 to 75 % in the first one, from 45% to 55 % in the second one, from 40% to 45 % in the third one and from 20% to 25 % in the last one. Thermal stretching reduced porosity down to down to the range of 60% and modified the shape of the cells making them flatter (figure 1). The density was reduced to 400kg/m³ and the young modulus was also reduced to 0.2 to 0.3MPa for a thickness of 100µm.

Samples are then charged by a corona discharge treatment with a positive electric field. The voltage at the needle is 12 kV, and the surface potential was controlled by a triode corona arrangement. Samples were metalized in one side before corona discharge (the ground side) and after metalized on the other side. Both electrodes were made with silver by sputtering.
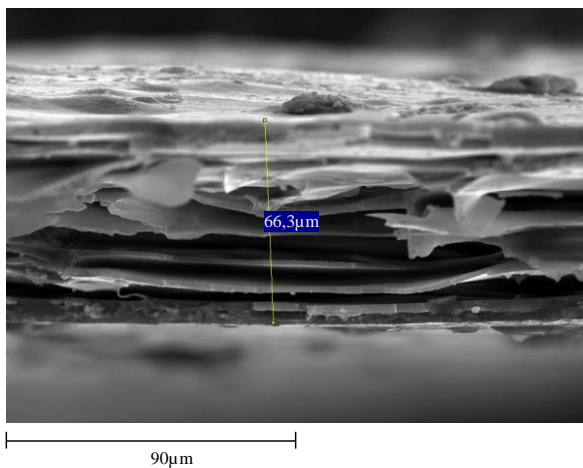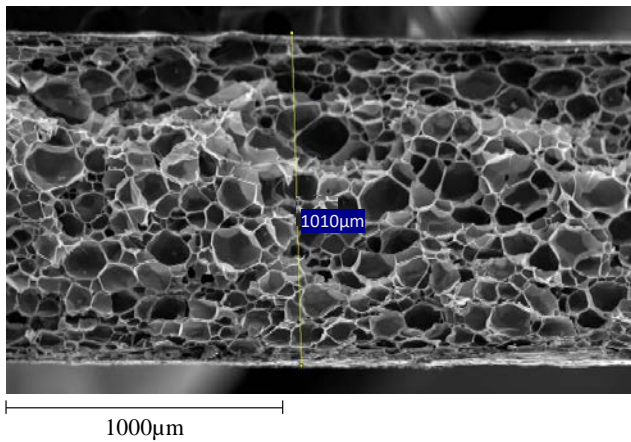

Figure 1. PP sample before and after thermal biaxial stretching.

2.2. Piezoelectric d33 Constant measurement.

The quasi-static d_{33} piezoelectric coefficient was measured by an own design setup (figure 2). An actuator pressed the sample with controlled increasing mechanical pulses. The control signal was generated by a function generator (Trektronics model AFG 3251)

and amplified in a control box. A pressure sensor in series with the sample gives the applied mechanical force.The current in the sample is registered and integrated. Both signals are measured by means of a Yokogawa DL9040 oscilloscope.
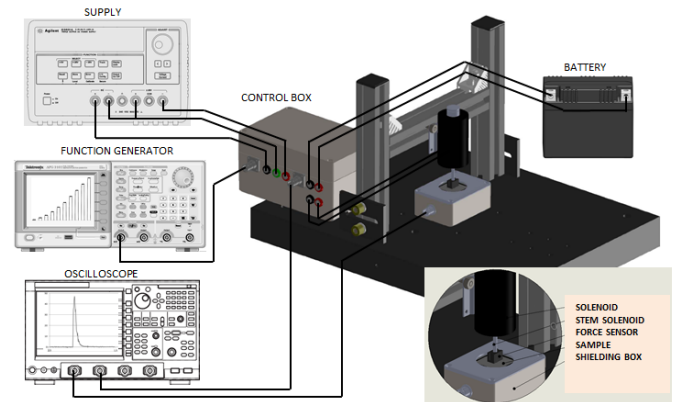

Figure 2 Experimental setup to measure d_{33} piezoelectric coefficient by the quasi-static method.

2.3. TSDC Measuring.

TSDC measurements were performed with a heating system (a natural convection over Pselecta model Conterm 36L). The heating slope was fixed and the value was 4°C/min. To have an homogeneus temperature, an smooth temperature curve and an electromagnetic field shielding, samples was placed in an aluminium conductive box (figure 3). The temperature was measured by type J thermocouple (Fe/CuNi) located on the bottom electrode. All cables were shielded. Samples have an area of 272.25mm² (2.72cm²)
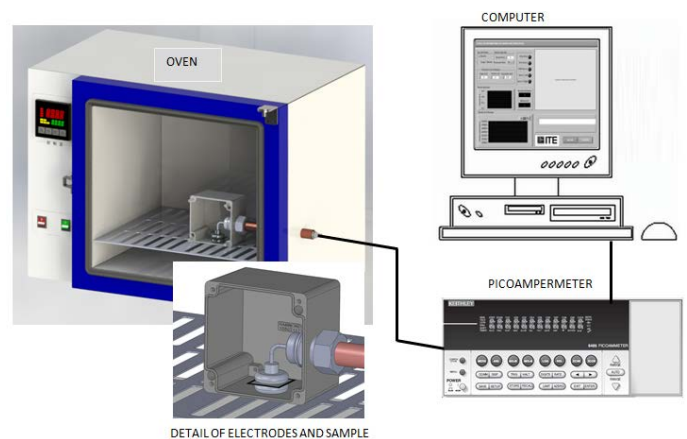

Figure 3.Experimental setup with equipment to measure TSDC.

All depolarization currents have been measured through pico amperemeter (Keithley model 6485) connected to a PC by the RS232 communication device port. The measured currents were in the range of pA.

2.4. Laser Interferometry Measurements.

In figure 4, it is shown an outline of the setup for laser interferometry measurements. The assembly was made with a controller OFV-5000 model, VD-decoder 02 and decoder DD-100 model displacement speed Polytec system. The head (sensor) of the laser Vibrometer has a cutting distance measured from the laser lens head of 204mm + (n · l) mm where the values of n = 0,1,2 .... and it has a cavity length of l = 204 ± 1mm. A focal length of 295mm was used for these measurements. The resolution of the displacement decoder was 80nm. A control signal generated by a function generator (Trektronics, AFG 3251 model) is amplified by piezoelectric driver (Trek model PZD700A) and applied A Yokogawa DL9040 registers all the measurements.
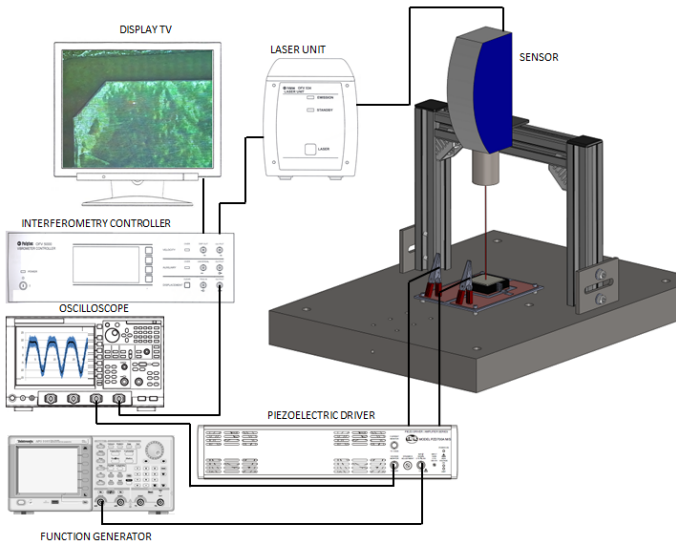

Figure 4. Outline of the setup to measure frequency resonance by laser interferometry.

Additionally, to increase sensitivity, a second interformeter setup was used to characterize and accurately measure the resonant frequency of the samples. A resolution of 2-3 nm can be achieved allowing to observe displacements. , it was used to perform measurements with another laser interferometer that uses the same technique but has a higher resolution, with. This measurement was taken at.

The equipment is composed of a laser interferometer (Polytec MMA-400 model). To measure has an (OFV-5000) controller where the (VD-09) decoders speed cards are accommodated with a maximum speed of 20 m / s and a maximum frequency of 2.5 MHz and has a decoder card displacement (DD-900) with a resolution of 0.015 nm and a maximum frequency of 2.5 MHz. The equipment has a microscope up to 100x, a system including a signal generator and an amplifier with an output of up to 10 Vp 50 mA. To inject higher voltages an external piezoelectric amplifier, which can inject a voltage up to 1000 V with a maximum current of 8 mA was used.

The measurement was performed by tracing a grid (figure 5) consists of 25 points over an area of 12.4mm² with 20x magnification. The measuring equipment fixed intervals determined at each point measured velocity and displacement;

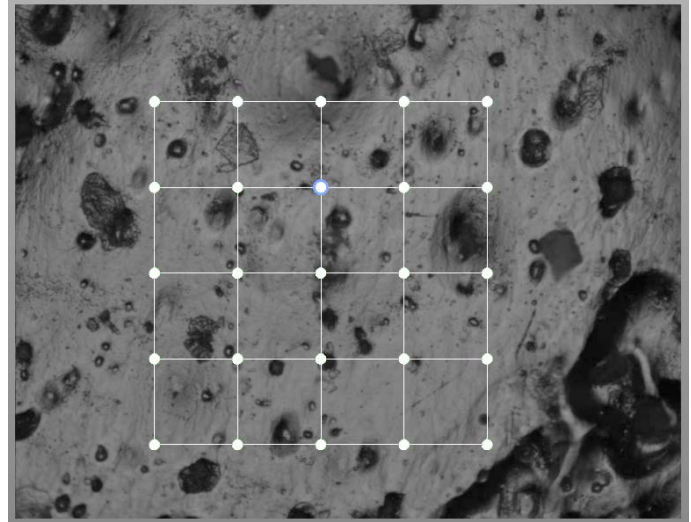performing the same procedure for a predetermined frequency range.

Figure 5. Photo of the sample through microscope equipment of Polytec interferometry.

3. Results.

3.1. Piezoelectric d_{33} constant measurements results and corona charging method.

The d_{33} constant can be improved by means of increasing the intensity of the internal dipoles and/or reducing the Young Modulus. The biaxial stretching reduces the Young modulus but the stretching degree reached is closed to mechanical breakdown. It was not possible to further increase it. Thus the optimization process was focused on increasing the internal charge of the dipoles in biaxially stretched samples. This section describes the charging process of the samples to optimize the d_{33} constant.

Initial measurement of piezoelectric constant as a function of the voltage applied to the tip electrode of a simple corona setup can be seen in figure 6. The needle was placed 15mm over the sample and an X-Y system swept the needle over the sample in a 6cm×6cm surface at a maximum speed of 10cm.s^{-1}.There was no noticeable piezoelectric constant up to 2kV. The constant increases from 2kV to 12kV and the reaches a saturation. This applied voltage is limited by the geometry of the mounting arrangement and the electric breakdown of the sample. In fact, for high voltages there were localized discharges producing superficial defects like holes, without electrical breakdown or an increase of the current. Some samples presented broken cavities after the corona treatment. Higher voltages lead to total breakdown of the samples. Shorter needle to sample distances produced earlier breakdown and larger distances required high voltages levels too high to produce the same result. Thus 12kV was set as the optimum charging voltage for a 15mm distance from needle to sample. The sweeping speed of the system was also fixed at 10cm.s^{-1} . Higher speed lead to less d_{33} constants and slower speeds produced space charge accumulation in the air generating shocks in random areas.
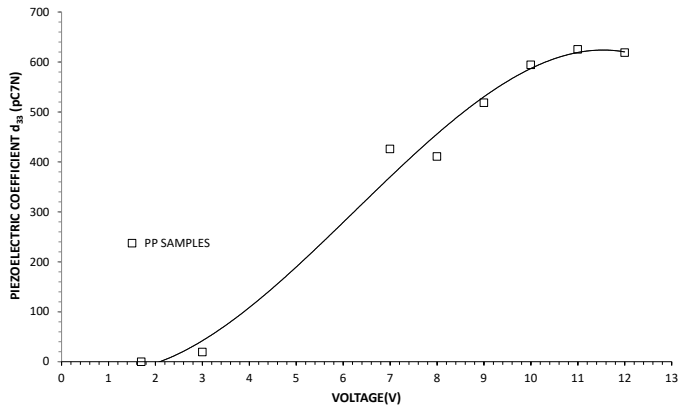
Figure 6. d_{33} values in a PP sample as a function of the applied voltage at the corona tip of the charging system.

Electrically charging through a triode configuration proved to be more efficient and homogeneous. Dielectric strength measurements were also made to check the distances between the grid and the surface of the sample and between the grid and the point charge. The grid to sample distance was chosen at 15mm and the needle to grid distance was also kept a 15mm. Those values gave good results and reasonable high voltage values. The charging voltages were 12 kV for the grid voltage of 22 kV for the point voltage.
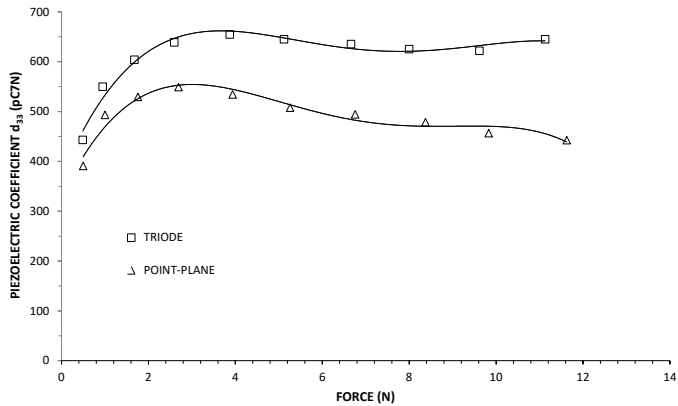

Figure 7. Curves of d_{33} coefficients in (□) triode charged samples and (□) point plane charged samples.

Figure 7 shows the d_{33} values as a function of the applied force for samples obtained with a point-plane corona charging system and samples obtained with the triode arrangement. The upper curve (squares) represents measurements of samples charged by a triode with a grid voltage of 12kV and the lower curve (triangles) represents samples charged by a simple pont-plane corona arrangement at 12kV. Both curves represent the average of 9 samples. The standard deviation for triode charge samples is of 11.2 % and 16.1% for point plane charged samples.

Triode charged samples showed a higher average piezoelectric constant (up to 650pC/N) with more homogenous results. Moreover, the d_{33} constant was more stable in triode charged samples up to 14N, which makes the material response more linear

than point-plane charged samples probably due to a better efficiency in creating internal micro dipoles.

In fact, the internal polarization (σ) of the material can be estimated by means of Sessler equation [9].

$$d_{33} = \frac{\varepsilon \cdot S}{Y} \cdot \frac{S_1 . \sum_j S_{2j} \cdot \sigma_j}{S_2 (S_1 + S_2 \cdot \varepsilon)^2} \qquad (1)$$

Where Y is the Young modulus of the material, ε the dielectric constant of the polymer, S the total thickness of the sample, S_1 the polymer layers total thickness, S_{2j} the individual air layer thickness and σ_j the surface charge at each air layer.

From equation (1) if a constant charge density is assumed in all the layesr then σ_j is also the charge at the electrodes and it can be calculated as:

$$\sigma_j = \frac{d_{33} \cdot Y}{\varepsilon \cdot S} \cdot \frac{(S_1 + S_2 \cdot \varepsilon)^2}{S_1 . S_2} \qquad (2)$$

The Young modulus experimentally measured was 0.3 MPa. For a thermally stretched sample (figure 1) with an average thickness of 100 microns and a porosity of 60% of air, the polymer thickness will be S_1 = 40 μm and the thickness of air S_2 = 60 μm. The relative permittivity of the sample was taken as ε = 2 from dielectric spectroscopy measurements. Considering piezoelectric constant values of d_{33} = 650 pC/N it can be obtained σ_j = 630 μC/m^2 which is consistent with literature materials with similar characteristics [10][11].

3.2. TSDC measuring Results.

TSDC measurements where performend from room temperature to 140 °C. These values were taken according to the measurements of differential scanning calorimetry (DSC), where the melting point was detected at 100 °C of this material, and its glass transition temperature T_G in the order of 45 °C. Figure 8 shows thermally stretched samples with an average thickness of 100 microns. Depolarization currents reach a maximum of up to 70pA at 85°C. In the same figure, the relation between the depolarization current and the d_{33} values can be observed. Results also support DSC measurements (it can be clearly observed the T_G and melting temperature).

As thought, direct relationship exists between the depolarization curve and the piezoelectric response of the material but high accuracy between both cannot be achieved.
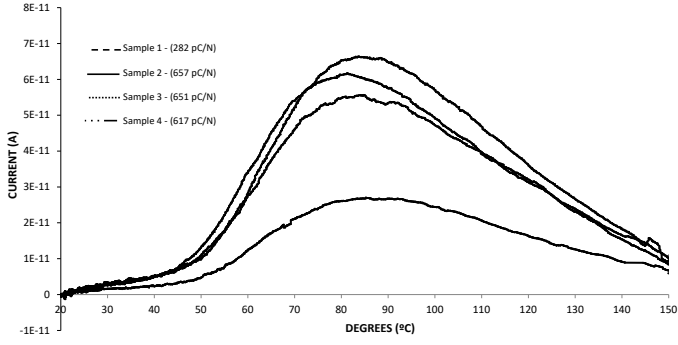
Figure 8. Measures of TSDC with samples of the thermal stretching PP.

From curves of figure 8, the electric internal polarization of material for each sample can be calculated through integration of the current density as a function of the temperature, according to:

$$P(t) = \int_T^{T\infty} \frac{J(t)}{\beta} \cdot dT \qquad (3)$$

Where P(t) is the polarization of the sample, β the temperature rise ratio and J(t) the current density.

This method was used for computing the polarization, the activation energy E_a and finally the natural relaxation time τ_0 0. Those variables have a behavior describe by Arrhenius. Table 1 shows the obtained results:

d_{33} (pC/N)	Polarization P_o (µC/m²)	Activation Energy E_a (eV)	Relaxation Time $\tau(T)$ (s)	Polarization P_o (µC/m²) Model Sessler
282	197.3	0.35	2.54×10^{+04}	134.0
657	323.2	0.38	2.28×10^{+04}	230.7
651	303.2	0.42	2.14×10^{+04}	202.1
617	277.2	0.34	6.66×10^{+03}	236.9

Table 1.Measuring of samples by TSDC technique and calculations of polarization, activation Energy and relaxation time for PP streteched samples.

Polarization values present a similar trend as d_{33} constant measurements and are in good agreement with the values predicted by the theoretical model. The activation energy was calculated based on [13] and the Bucci method [12] in figure 9 Bucci graph is represented showing current as a function of the inverse of the temperature 1/T and the curve of relaxation time as a function of 1/T also. The slope of the straight line is Ea/k and the independent term is ln(τ_0). It has to be taken into account that there is an error due to the fact that current measurements do not reach the zero level before the sample fusion. Thus the parameters of the Arrhenius equation can be obtained according to equation (4).

$$ln\big(\tau(T)\big) = ln(\tau_0) + \frac{E_a}{kT} \qquad (4)$$

The internal polarization can be calculated by means of (5):

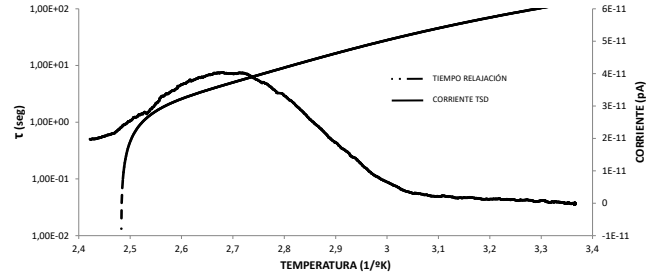$$P_0 = \frac{\sigma_i \cdot s_2}{s} \qquad (5)$$

Figure 9. Bucci representation of current I and relaxation time τ as a function of Temperature T.

Polarization values can be checkec with the charge density values obtained with the Sessler model in (table 1). There is a positive relation between both values.

3.3. Temporal Stability Results.

An essential property of the piezoelectric polymer foams for industrial applications is the life of the piezoelectric properties. Thermal depolarization gives information about thermal stability but with that technique it cannot be exactly determined how long the material can hold the charge. Long time measurements were performed to obtain more information about this property. Measurements of temporal stability of samples kept under constant environmental conditions are represented ranging from some hours to some years old samples.

It is observed that the piezoelectric constant values always decrease with time. In figure 10, it can be seen the response as a function of the applied force during 75 days. Reduction of the d_{33} constant can be as high as 75%. Reduction is faster at the earlier stages. After 46 days the d_{33} constant tends to be stabilized. There is no apparent relation between the initial value of the d_{33} constant and the long terme value. All the samples reach roughly the same final value. This behavior is similar to the surface potential decay observed in corona charged polymer films.
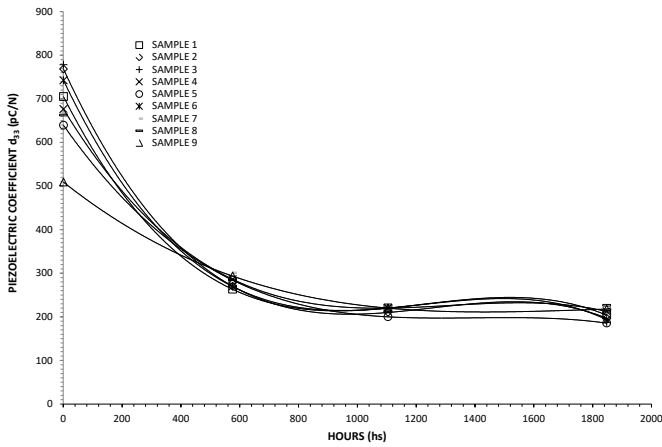
Figure 10. Measures of piezoelectric coefficient d_{33} of PP sample with thermal stretching treatment in 46 days spacing.

For longer times, the d_{33} constant value seems also to be stable. In figure 11 for samples manufactered the 10th april 2014 and measured the 17th april 2014 and 2nd june 2015, it can be observed the reduction of the d_{33} constant to a stable value as shown in figure 10 The shape of both curves is the same which indicates a general neutralization of the internal charge in all the voids.
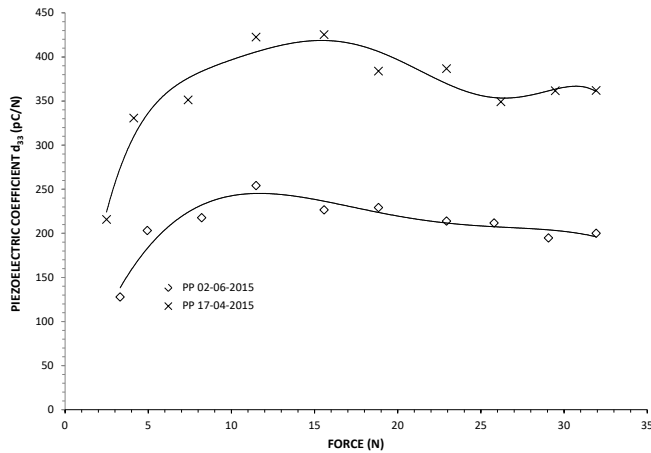

Figure 11. Measures of piezoelectric coefficient d_{33} of the PP samples with thermal stretching treatment.

As conclusions we can say that the discharge behavior is similar in all the samples and tends to stabilize around a value of 200pc/N some months after manufacturing. Of course, the decay continues but the constant time are longer. Probably this value should be consireded, for practical reasons, the actual value of the d_{33} constant of the material.

3.4. Laser Interferometry Results.

For laser interferometry measurements, thermally stretched PP samples 100 μm thick, with a constant d_{33} average 500 to 600 pC/N at the time of manufacture, were taken. The d_{33} constant

estimated by the discharge curve at the time of the measurements were about 300 400 pC/N.

It the first interferometer setup, 340V are applied to the sample (close to electric breakdown) and a displacement 132 nm was measured. According to:

$$d_{33} = \frac{Vibrometer\ Range\ \left(\mu \frac{m}{V}\right) \cdot Measure\ Voltage\ (V)}{Applied\ Voltage\ (V)} \quad (6)$$

a piezoelectric constant of 375pC/N is obtained which is coherent with previous results.

The second interferometer setup allows a better resolution and a frequency scan. Results are shown in figure 12. A scan was performed from 10 kHz to 200 kHz with a 10V voltage. The maximum displacement is measured at a frequency of 97.25 kHz which corresponds to the resonance frequency of the charged material. The following equation provides the resonance frequency as a function of the Young's modulus values measured experimentally [14]:

$$F_r = \sqrt{\left(\frac{1}{4 \cdot S}\right) \cdot \left(\frac{Y}{\rho}\right)} \quad (7)$$

Where S is the total thickness of the sample, ρ is the density of the film in kg/m³ and Y Young's modulus measured in kg/m. By replacing values in equation (6) a resonant frequency of approximately 90kHz is obtained.

As a particular feature of the frequency scan, it can also be observed a periodical number of peaks along the curve. One of the possible causes of this behavior is due to the heterogeneous structure of this material. Another possibility is that the material moves in waves provoking this effect at specific frequencies. Further research is needed for this phenomenon.
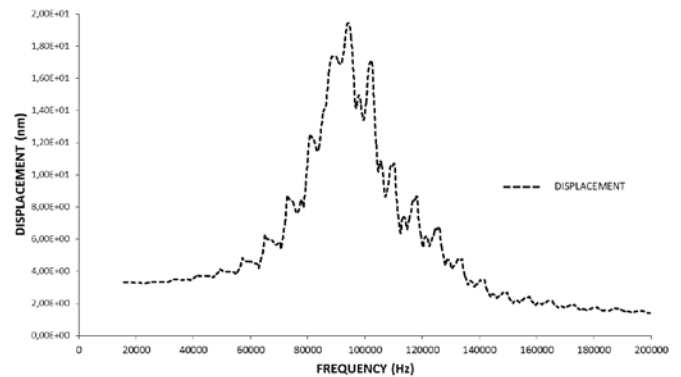

Figure 12. Measurement of the displacement and resonance frequency on laser interferometry system.

To calculate the piezoelectric constant d_{33} displacement is directly provided by the acquisition system, thus:

$$d_{33} = \frac{Measured\ displacement\ (nm)}{Applied\ voltage\ (V)} \quad (8)$$

For the displacement value of the resonance constant (32nm for an applied voltage of 10V) the d_{33} value reaches 3200pC/N. To compare with the quasi-static measurement method, if the displacement value is getting out of resonance measured below 20kHz, the value of the d_{33} constant is 390 pC/N. The resonance factor is of 8.2.

4. Conclusions.

A cellular polymer PP film thermally biaxial stretched with approximately 100 μm thickness characterization has been activated by corona discharge. The piezoelectric properties of the material have been characterized. A high piezoelectric constant in the range of 600-700pC/N can be obtained inmediatly after sample preparation. The long term constant (more than 1 year) is stabilized around 200pC/N at room temperature. The films exhibitis high flexibility and low Young Modulus (from 0.2 to 0.3 MPa). A mathermatical model allows the estimation of the internal surface charge in the range of 500 μC/m² from the d_{33} constant measurements and TSDC measurements. Finally, a resonance analysis gives a resonance frequency of 97kHz and a resonance factor of 8.2.

References

[1] K. Kirjavainen, "Electromechanical film and procedure manufacturing same", US Patent Nº4.654.546. 1989. http://www.google.es/patents/US4654546

[2] J.I. Raukola, "A New Technology To Manufacture Polypropylene Foam Sheet and Biaxially Oriented Foam Film", VTT Publications 361, Technical Research Center of Finland (1998).http://www.vtt.fi/inf/pdf/publications/1998/P361.pdf

[3] J. A. Giacometti, S. Fedosov, and M. M. Costa, "Corona charging of polymers: recent advances on constant current charging," Brazilian Journal of Physics, vol. 29, no. 2, pp. 269–279, 1999. http://dx.doi.org/10.1590/s0103-97331999000200009

[4] Wegener, W. Wirges, R. Gerhard-Multhaupt, M. Dansachmüller, R. Schwödiauer, S. Bauer-Gogonea, S. Bauer, M. Paajanen, H. Minkkinen, and J. Raukola, "Controlled inflation of voids in cellular polymer ferroelectrets: Optimizing electromechanical transducer properties," Appl. Phys. Lett., vol. 84, no. 3, p. 392, 2004. http://dx.doi.org/10.1063/1.1641171

[5] J. Hillenbrand and G. M. Sessler, "High-sensitivity piezoelectric microphones based on stacked cellular polymer films (L)," The Journal of the Acoustical Society of America, vol. 116, no. 6, p. 3267, 2004. http://dx.doi.org/10.1121/1.1810272

[6] S. Bauer, R. Gerhard-Multhaupt, and G. M. Sessler, "Ferroelectrets: Soft electroactive foams for transducers," Phys. Today, vol. 57, no. 2, pp. 37–43, Feb. 2004. http://dx.doi.org/10.1063/1.1688068

[7] X. Zhang, J. Hillenbrand, and G. M. Sessler, "Piezoelectric d[sub 33] coefficient of cellular polypropylene subjected to expansion by pressure treatment," Applied Physics Letters, vol. 85, no. 7, p. 1226, 2004. http://dx.doi.org/10.1063/1.1781388

[8] M. Lindner, H. Hoislbauer, R. Schwodiauer, S. Bauer-Gogonea, and S. Bauer, "Charged cellular polymers with 'ferroelectric' behavior," IEEE Transactions on Dielectrics and Electrical Insulation, vol. 11, no. 2, pp. 255–263, Apr. 2004. http://dx.doi.org/10.1109/tdei.2004.1285895

[9] G. M. Sessler and J. Hillenbrand, "Electromechanical response of cellular electret films," Appl. Phys. Lett., vol. 75, no. 21, p. 3405, 1999. http://dx.doi.org/10.1063/1.125308

[10] D. M. Taylor and O. Fernandez, "Thermal instability of electromechanical films of cellular polypropylene," IEEE Transactions on Dielectrics and Electrical Insulation, vol. 12, no. 4, pp. 768–778, Aug. 2005. http://dx.doi.org/10.1109/tdei.2005.1511102

[11] J. Peltonen, M. Paajanen, and J. Lekkala, "Determination of the actuator sensitivity of electromechanical polypropylene films by atomic force microscopy," Journal of Applied Physics, vol. 88, no. 8, p. 4789, 2000. http://dx.doi.org/10.1063/1.1290448 .

[12] C. Bucci, R. Fieschi, and G. Guidi, "Ionic Thermocurrents in Dielectrics," Physical Review, vol. 148, no. 2, pp. 816–823, Aug. 1966. http://dx.doi.org/10.1103/physrev.148.816

[13] J. van Turnhout, "Thermally Stimulated Discharge of Polymer Electrets," Polym J, vol. 2, no. 2, pp. 173-191, Mar. 1971. http://dx.doi.org/10.1295/polymj.2.173

[14] X. Zhang, J. Hillenbrand, and G. M. Sessler, "Piezoelectric d[sub 33] coefficient of cellular polypropylene subjected to expansion by pressure treatment," Appl. Phys. Lett., vol. 85, no. 7, p. 1226, 2004. http://dx.doi.org/10.1063/1.1781388