Study of thermally poled PET electrets using the pulsed electroacoustic and thermally stimulated depolarization current techniques

S.E. Parsa, J.C. Cañadas, J.A. Diego, M. Mudarra and J. Sellarès*
Departament de Física, Universitat Politècnica de Catalunya
Campus de Terrassa, c. Colom 1, E-08222 Terrassa, Spain.

Abstract

We have studied by pulsed electroacoustic method (PEA) and thermally stimulated depolarization current (TSDC) a set of PET electret samples. Experimental parameters such as the combined thermal and electrical history and the electrode type have been selected in order to correlate the polarization mechanisms revealed by TSDC with the charge profile measured by PEA in five different cases. Existing deconvolution procedures for PEA have been improved as a means to enhance the calibration of PEA signals in the case of thin samples. Samples where the $\alpha$ dipolar relaxation or the $\rho$ space charge relaxation is activated show a uniform polarization that manifests itself as image charge at the electrodes. In the experiments where external charge carriers are injected in the sample the same poling procedure has been tested under different electrode configurations. Charge profiles are similar in all of them but the depolarization currents show clearly different behavior. These differences are explained, on the one hand, by the different blocking behavior of vacuum-deposited aluminium electrodes with regards electrodes with a thin air gap and, on the other hand, by the distinct behavior of electrodes with air gap for both directions of the electric current. Numerical analysis of the polarization of TSDC peaks and charge per unit area of charge profiles supports this interpretation and confirms the relationship between both measurement types. All in all, PEA turns out to be a useful technique in the study of thermally poled electrets, either in the study of relaxations or of external charge.

*E-mail: jordi.sellares@upc.edu
1 Introduction

An electret is made of a dielectric material that has been poled in such a way that it creates quasi–permanent external and internal electric fields [1, 2]. Electrets can be poled by several procedures such as corona charging, electron beam irradiation or thermal poling, among other ones [2]. Thermal poling (TP) is a well-known technique to obtain electrets. It is the basis of spectroscopic techniques such as thermally stimulated depolarization current (TSDC) [3], that has been used for decades to study dipolar and space charge relaxation in solids. For this reason, the polarization that can be obtained by TP has been extensively studied from a macroscopic point of view [4]. In spite of this fact, there is still information about the microscopic mechanisms that are activated by TP that is not fully determined yet.

For example, it seems out of question that the $\alpha$ relaxation is the dielectric signature of the structural relaxation [5] and that it is due to the cooperative reorientation of molecular dipoles and that the $\rho$ relaxation is due to free charge trapped in localized states [6]. These relaxations can be detected, for example, as peaks in a TSDC spectrum. Nevertheless, it is widely accepted that additional mechanisms are needed to fully explain these phenomena. A throughout understanding of the mechanisms that give rise to a relaxation is especially useful when interpreting data from spectroscopic techniques and it can also give clues on how to obtain more stable electrets or electrets that are better suited for particular applications.

One important piece of information related to the microscopic mechanisms is the charge profile of the electret [7]. Many studies have been made about the charge profile of corona charged [8] or electron beam irradiated electrets [9, 10] but there are fewer about thermally poled electrets [11, 12]. This is because they tend to store less charge and to be less stable than electrets poled by other means. Also, polarization is more uniform which makes more difficult to detect the induced charge because of its proximity to the electrodes. As a consequence, their charge profile is more difficult to measure and results are less conclusive.

Several methods can be used to measure the charge profile of an electret sample [13] up to a certain resolution [14]. Acoustic methods can give the charge or field distribution in the sample. Additional quantities, such as surface potential, can be obtained by calculation from these ones [15]. Depending on the signal–generation process, acoustic methods can be divided into LIPP (laser-induced pressure pulse), PPS (piezoelectrically-generated pressure step) or PEA (pulsed electroacoustic) methods. In all these cases, pressure waves generated either at the sample surface or at charge layers in the bulk, propagate through the sample with the speed of sound waves. The deformations that are produced in the sample cause currents or voltages at the electrodes due to charge displacement, changes in electric permittivity or because of the piezoelectric effect at a transducer [16].

Another important information about an electret is its relaxational behavior. It is not only important to know where its charge or its polarization is located but also how these quantities relax to their equilibrium values. TSDC is a well-proven technique that can be used successfully to characterize these relaxations. One of the characteristics that
can be obtained with TSDC is the polarization attained when a relaxation is activated. This one will be interesting for our study because it can be cross-checked with the charge profile results.

The PEA method is based on the electrostatic force. An externally applied electric field pulse induces a perturbing force on the charges that are present in the material. This perturbation generates a sound wave which originates from the charge distribution. The acoustic signal is detected by a piezoelectric transducer placed on one of the electrodes [9]. The space-charge profile information contained in the signal is measured and calibrated through the use of digital signal processing [17]. The main difference in contrast to other methods, such as PPS or LIPP, where the pressure wave is generated externally, is that the acoustic wave is generated internally by the space charge [18]. Initially deconvolution or other data processing was essential to obtain the charge profile. Some very important improvements were made to the transducers which resulted in a more accurate signal and lessened the need for deconvolution [19]. The duration of the voltage pulse in PEA measurements is usually between 5 to 40 ns and determines the space resolution of the measurements [20].

The aim of this work is to develop new ways to improve our knowledge about thermally poled electrets. In particular, we want know if acoustic pulse methods can be used to gain a better understanding of the mechanisms that give rise to polarization in thermally poled electrets. To this end, we will measure the charge profile of samples prepared in such a way so that different mechanisms are activated and we will compare this charge profile with the TSDC relaxational spectra of the samples. We expect to find out the spatial distribution of the mechanisms that give rise to dipolar and space charge mechanisms and the role of external charge, which can depend on the electrode type. We will adapt existing deconvolution procedures for PEA so that they are better suited for thin samples. The comparison of total as charge as measured by PEA and the polarization of the sample measured by TSDC will allow us to validate our assumptions.

2 Experimental

2.1 samples and methods

Experiments have been performed on samples of amorphous (as-received) PET. PET was supplied by Autobar Packaging SA in the form of sheets with a thickness of 320 µm. Characterization by differential scanning calorimetry (DSC) has shown that the glass transition takes place at 80 °C and cold crystallization begins around 100 °C. It has also been checked by DSC that as-received material crystallinity degree is below our detection threshold and, therefore, is less than 3% [21].

Samples of 2.5 × 2.5 cm² were cut and aluminum electrodes with a diameter of 2 cm were vacuum deposited on one side or on both sides of the samples.

Prior to charge profile measurements, samples were thermally poled using a TSDC setup. An scheme of a TSDC setup is presented in Figure 1. The sample (S) is poled by the high voltage source (HVS) setting the two–way switches 1 and 2 in position A.
Table 1: Experimental parameters employed. The heating and the cooling rates are 2 °C/min in all the non-isothermal stages.

| Experiment | Al electrode side | $T_0$ (°C) | $T_p$ (°C) | $t_p$ (s) | $T_{off}$ (°C) | $T_s$ (°C) |
|------------|-------------------|------------|------------|-----------|---------------|------------|
| A          | Both              | 95         | 65         | 600       | 55            | 25         |
| B          | Both              | 140        | 95         | 0         | 80            | 25         |
| C          | Both              | 95         | 80         | 1200      | 75            | 25         |
| D          | Minus             | 95         | 80         | 1200      | 75            | 25         |
| E          | Plus              | 95         | 80         | 1200      | 75            | 25         |

Instead, switches should be in position B to depole the sample and record the depolarization current through the amperimeter. A sampleholder ensures contact of the sample with the setup electrodes. The sampleholder is located inside a forced air oven (FAO) driven by a PID controller with a thermocouple (TC) as input.

The combined thermal and electrical history in our experiments is described in Figure 2. The five sets of experimental parameters (A–E) that have been employed are summarized in Table 1.

The sample is initially heated up to 95 °C in all experiments except B, a temperature well-above the glass transition but not high enough to crystallize the sample significantly. In this way, the thermal history of the sample is erased and the experiment begins in a structural equilibrium state. In experiment B, instead, the initial temperature is 140 °C in order to crystallize the sample. This is done to suppress as much as possible the dipolar relaxation, that takes place in the amorphous phase.

After this initial heating, the sample is cooled until the poling temperature. Samples A, C, D and E have an isothermal poling stage while sample B is poled non-isothermally. In all cases, the sample is poled by applying a voltage of 5000 V. The temperature at
Figure 2: Thermal and Electrical history of the sample in the experiments that have been performed.
which the field is switched off is selected to put an upper limit on the frequency of the relaxations that are activated. After poling, the sample is cooled down to room temperature (storage temperature) at a controlled rate. Once at room temperature, polarization is relatively stable so procedures for measuring the charge profile can be performed. Finally, the sample is discharged by means of TSDC.

The charge profile has been measured by the PEA method. A commercial setup provided by TechImp (Italy) was employed. A typical PEA setup is presented in Figure 3. Within this method, an electrical pulse (in our setup with a width of 20 ns and an amplitude of 400 V) is applied to the sample. This electrical pulse produces a back-and-forth movement in the charges of the system that produces an acoustic signal given by

$$p(t) = Cv \int_0^t \rho(\nu \tau) e(t - t_0 - \tau) \, d\tau$$  \hspace{1cm} (1)

where $v$ is the speed of sound in the material, $e(t)$ is the electric field of the electrical pulse, $t_0$ is a time offset due to the electrode thickness, $\rho$ is the charge density profile and $C$ is an adimensional constant that depends on the acoustic properties of the material and can be expected to be 0.5 for homogeneous materials in a unidimensional waveguide [19]. $\rho$ will correspond to the charge profile across the whole setup, not only at the sample but also at the electrodes, if transmission of the sound waves across the interfaces between the sample and the electrodes is complete. To increase transmission as much as possible air is substituted at the interfaces by silicon oil.
This acoustic signal $p(t)$ is registered by a piezoelectric sensor, amplified and captured by an oscilloscope. For sharp electrical pulses $p(t)$ is approximately proportional to $\rho(vt)$.

During measurements, a direct current high voltage can be applied to the sample to pole it in–place but we have used this possibility only in calibration measurements. In all the other charge profile measurements the sample is poled previously in the TSDC setup.

### 2.2 PEA calibration

The time duration of the electrical pulse in our setup is short enough so that an acceptable resolution can be obtained without deconvolution. Nevertheless, the deconvolution process not only accounts for the shape of the electrical pulse but also serves as a calibration that allows us to convert the voltage measured by the oscilloscope to proper charge density units and to deal with the characteristic response of the sensor. We have adapted a digital signal processing method from reference 22 because the commercial software supplied by TechImp gave poor results on thin samples.

From the discretization of Equation 1 it follows that the signal captured by the oscilloscope and sampled as a vector $V$ can be expressed as the product of a convolution matrix $H_{\text{PEA}}$ and a vector that represents the charge profile $\rho$.

$$V = H_{\text{PEA}}\rho$$

Moreover, since $H_{\text{PEA}}$ represents a convolution it is a Toeplitz matrix and the product is commutative.

$$V = \Gamma h_{\text{PEA}}.$$  

The Toeplitz matrices $H_{\text{PEA}}$ and $\Gamma$ can be easily determined from vectors $h_{\text{PEA}}$ and $\rho$, respectively using publicly available routines for circulant matrices 23.

To calibrate a given PEA experiment a particular signal $V_{\text{cal}}$ has to be obtained in a calibration experiment where the corresponding $\rho_{\text{cal}}$ can be calculated theoretically. We measure a discharged sample with the same characteristics and thermal history as the one employed in the experiment. An electric field of $E_{\text{pol}} = 5$ kV/mm is applied in order to avoid charge injection and measure $V_{\text{cal}}$ in a situation that can be considered as an ideal capacitor. For this reason the charge profile will only consist of the two image charges at the electrodes

$$\rho_{\text{cal}}(x) = \epsilon_0 E_{\text{pol}} \left\{ \delta(x - l) - \delta(x) \right\}$$

where $x = 0$ is the position of the ground electrode and $l$ is the thickness of the sample. Deliberately, we omit the additional image charge that would result from taking into account the relative permittivity $\epsilon_r \approx 3.3$ 24 of the sample because it is cancelled by the induced charge that appears at the internal face of the electrodes. Therefore, Equation 4 assumes a complete transmission of sound waves at the sample-electrode interfaces.

The key point of the method is that for the discrete version of $\rho_{\text{cal}}$ we will use gaussian functions instead of deltas of Dirac

$$\rho_{\text{cal}} = \epsilon_0 \sqrt{\frac{\pi}{2}} E_{\text{pol}} \left\{ \exp\left(-\frac{2(x - l)^2}{d^2}\right) - \exp\left(-\frac{2x^2}{d^2}\right) \right\}$$
with no change on the total charge at the electrodes. Now $x$ is a discretized representation of the position variable. To represent it so that it matches $V_{\text{cal}}$ we need to know the speed of sound $v$ in the sample, the sampling rate of $V_{\text{cal}}$ and the index of the element of $V_{\text{cal}}$ that corresponds to the electrode at $x = 0$. This information is obtained from the sampling rate of the oscilloscope and an analysis of the maxima and minima of $V_{\text{cal}}$.

The $d$ parameter has dimensions of length and plays a role similar to the Wiener and Gaussian filter parameters in the original deconvolution scheme [9]. It should be small compared to the thickness of the sample but large enough to obtain artifact-free results. In most cases $d = 30 \, \mu m$ is an appropriate choice for our signals. An example of an experimental $V_{\text{cal}}$ calibration signal and its calculated $\rho_{\text{cal}}$ charge profile is presented in Figure 4.

We can obtain $h_{\text{PEA}}$ by inversion of Equation 3 and applying it to the calibration case

$$h_{\text{PEA}} = \Gamma_{\text{cal}}^{-1} V_{\text{cal}}$$

and finally we obtain the deconvoluted charge profile $\rho$ from $V$ by inversion of Equation 2

$$\rho = H_{\text{PEA}}^{-1} V$$

where $H_{\text{PEA}}$ can be specified in terms of $h_{\text{PEA}}$.

A comparison between a charge profile obtained using this method and the original signal recorded by the oscilloscope is presented in Figure 5. To ease the comparison between the two curves, the original curve has been scaled in such a way that there is
maximum likelihood in the image charge at the anode (positive electrode). Aside from the calibration, changes in the shape of the curve are rather limited, which is logical when using short pulses, but are significant at the cathode (negative electrode) where a much sharper image charge is obtained.

The difference of the extreme values of the peaks located at the electrodes in the experimental signal indicates that our assumption of complete transmission at the interfaces is not exact even though we expect it to be good enough to obtain meaningful results.

3 Results

Experiments A, B and C are performed on samples that have vacuum-deposited aluminium electrodes on both sides of the sample and differences in the results will be due to different thermal and electrical histories. In experiment A the thermal history has been chosen to activate the $\alpha$ relaxation and the sample remains in amorphous state throughout the experiment.

Instead, sample $B$ is brought to a semi–crystalline state at the beginning of the experiment. This is done to suppress as much as possible the $\alpha$ relaxation that takes place in the amorphous phase. The non–isothermal poling stage and the range of temperatures at which the electric field is activated is meant to activate the $\rho_c$ relaxation, which is physically similar to the $\rho$ relaxation but taking place in the crystalline phase.
Finally, the experimental parameters of experiment C try to activate a mixed set of mechanisms through a long isothermal poling stage at a temperature close to $T_g$.

The relaxations that are activated in each experiment can be analyzed by TSDC. The resulting depolarization currents are plotted in Figure 6. In this case, no PEA measurements were carried on the sample before depolarization so as to register the activated relaxations with as much precision as possible.

The spectrum recorded in the A experiment is dominated by the $\alpha$ relaxation, which has its maximum at 86 °C. In the insert of Figure 6 there is a hint of the $\rho$ peak as a shoulder visible at 97 °C. In experiment B only one relaxation, $\rho_c$, can be observed, with a maximum at 105 °C, because the sample is in semi-crystalline state during the poling stage. Finally, in experiment C, the $\rho$ peak is located approximately at the same temperature as in experiment A.

The charge profile of these samples as measured by PEA is presented in Figure 7.

In the A experiment the image charge at the electrodes is clearly visible. This charge shields the polarization of the $\alpha$ relaxation, that appears to be uniform since no variation along the bulk of the sample can be observed.

The charge profile of experiment B corresponds to a sample where $\rho_c$ is activated. As in the previous case it also consists of image charge but with lower density. This can be attributed to a lower polarization of the sample, as it can be deduced from Figure 6. Since polarization appears to be uniform and no accumulation of charge can be observed anywhere in the bulk we relate the $\rho_c$ relaxation to microscopic displacement of charge carriers (electrons or vacancies) and their subsequent trapping in localized states (charge traps).
Because of the long isothermal poling stage at close-to-$T_g$ temperature, there is charge injection in experiment $C$. It can be inferred that during the poling stage the aluminium electrodes are non–blocking since they allow charge carriers, either electrons or vacancies, to be injected into the sample. The charge profile is conditioned by homocharge (charge of the same sign as the closest electrode) due to the external charge of either sign that can be observed close to both electrodes. Between the external charge there is a heteropolar macroscopic dipole but with lower density than injected charge. In spite of this fact, the depolarization current consists only in heterocurrent.

It is also interesting to consider the role of the electrodes in this injection process comparing samples with the same thermal and electrical history and different electrode configuration. This is done through the comparison of experiments $C$, $D$ and $E$. Experiments $D$ and $E$ are performed with samples with only one vacuum-deposited aluminium electrode. This leaves a very thin air gap between the setup electrode and the sample on the other side. During the poling stage, the air gap is on the positive electrode in experiment $D$ and on the negative electrode in experiment $E$.

The relaxations that are activated can be obtained from the depolarization currents plotted in Figure 8. What stands out most is that the relaxational spectra of samples with an air gap is more complex. In experiment $D$ we can see the same heterocurrent $\rho$ peak as in experiment $C$, at approximately the same temperature of 97 °C but also a homocurrent peak, labelled as $\rho^*$, with a maximum at 107 °C. A huge homocurrent $\rho^*$ peak with a maximum at 101 °C conditions experiment $E$. There is also an heterocurrent peak at 85 °C, labelled as $\alpha$ because it is probably due to indirect dipolar polarization caused by the homopolar charge. As in previous experiments, the $\rho$ peak corresponds
to the relaxation space charge trapped after microscopic displacement. Instead, we attribute the $\rho^*$ peak to recombination of homocharge in the bulk after macroscopic displacement and therefore we assume that it is more related to the mobility of external charge carriers.

A numerical study of the polarization that has been attained can be done integrating the depolarization current corresponding to a given relaxation on the time variable. The data obtained is presented in Table 2.

These data can be compared with the charge per unit area of the charge distributions in the profiles that are presented in Figures 7 and 9. Also, these profiles indicate if the mechanisms registered by TSDC are distributed uniformly across the thickness of the sample or are located in particular regions.

It can be observed in experiment D that the air gap facilitates the penetration of external charge from the positive electrode into the bulk of the sample. This is probably
due to a corona charging current made of positive ions in the air gap while poling the sample. Once on the surface of the sample, the positive ions attract electrons leaving vacancies in the bulk. Instead, corona charging does not seem to increase negative injection significantly in experiment $E$. Therefore negative injection is similar in the three cases. This is a sign that when a strong electric field is applied neither the vacuum-deposited electrodes nor electrodes with an air gap are able to block injection of charge carriers in the sample. Moreover, the fact that the ratio between vacancies and electrons is higher in experiment $D$ than in $E$ may affect the overall mobility and trajectory of the external charge during discharge. Therefore this may be responsible of the 6 °C degree difference between the temperature of the maxima of the $\rho^*$ peaks in experiments $D$ and $E$ visible in Figure 8.

The charge per unit area corresponding to each distribution of the charge profile is obtained integrating its charge profile along the depth axis. The data obtained is presented in Table 3. In this last table only charge densities on the side of the sample closer to the piezoelectric sensor have been measured since we expect them to be more accurate [12].

4 Discussion

According to our initial premises, uniform polarization, as obtained in experiments $A$ and $B$, should be difficult to be detected. In these cases, induced charge takes the form

Figure 9: Charge profiles for experiments with the same history and different electrode configuration obtained with PEA
Table 3: Charge per unit area measured in PEA experiments.

| Experiment | img. charge (C/m²) | ext. charge (C/m²) | macr. dipole (C/m²) |
|------------|--------------------|--------------------|----------------------|
| A          | $1.74 \times 10^{-4}$ |                    |                      |
| B          | $4.03 \times 10^{-5}$ |                    |                      |
| C          | $-3.45 \times 10^{-5}$ | $5.30 \times 10^{-5}$ | $-1.77 \times 10^{-5}$ |
| D          | $-5.55 \times 10^{-5}$ | $8.97 \times 10^{-5}$ |                      |
| E          | $-3.52 \times 10^{-5}$ | $4.06 \times 10^{-5}$ |                      |

of a surface charge distribution at the internal face of the electrodes that has the same magnitude and opposite sign as the image charge in the electrodes when the sample is shortcircuited. In a first analysis, the signal from induced charge and image charge should cancel because they would have the same magnitude, opposite sign and their origins would be placed very close. Instead, image charge is very clearly seen in both electrodes of the A and B charge profiles of Figure 7. This situation has been observed previously on similar polymers in equivalent experiments [12].

With our current equipment we can not discern the cause why the image charge on the electrodes gives a more visible response than the induced charge in the sample but we can make a plausible hypothesis to be tested with further means. Equation 1 does not distinguish between the response of real charge in the electrodes (which is made of free carriers in a conductive medium) and the response of induced charge of an activated mechanism (which consists of bound charge in a dielectric medium). Maybe there is a larger response time in the first case that gives a broader sound signal. This signal would be easier to be detected by the piezoelectric sensor and its associated amplifier circuit.

We can compare the polarization of the peaks as presented in Table 2 with the charge per unit area presented in Table 3. The polarization of the current peak in the A experiment is larger but of the same order of magnitude than the image charge per unit area measured by PEA while in experiment B the polarization is still in the same order of magnitude than the image charge per unit area but smaller.

These comparisons indicate, in first place, that the experimental workflow is consistent and gives acceptable results. The values obtained for the image charge per unit area can be lower than the polarization of the current peak if part of the response of the image charge is suppressed by the induced charge. This happens in experiment A but not in experiment B, probably because space charge relaxations behave in a less predictable way and TSDC and PEA measurements have been performed on separate samples.

The profiles obtained from C, D and E do not present this problem since they are dominated by external charge at some depth in the bulk. Their broad profile and distance from the electrodes allows an easy detection with the PEA technique.

The most striking feature of our results is that the qualitatively similar charge profiles C, D and E from Figure 9 correspond to depolarization currents that have a very different structure in terms of heterocurrents and homocurrents, as represented in Figure 8.
Depolarization current $C$ is heteropolar, $D$ has comparable heteropolar and homopolar parts while $E$ is predominantly homopolar.

This paradox can be explained in terms of the blocking behavior of the electrodes. The lack of homocurrent in experiment $C$ is related to the fact that both vacuum-deposited electrodes are equally non-blocking during discharge while the preponderance of homocurrent in experiment $E$ compared with experiment $D$ happens because the electrode with an air gap, which can be assumed to be more blocking than the vacuum-deposited one, is even more blocking in experiment $E$ than in experiment $D$.

If during the discharge both electrodes are equally non-blocking then depolarization of external charge takes place predominantly through recombination with its image charge at the electrodes. If this process takes place simultaneously at both electrodes there will be no homocurrent flowing through the shortcircuit. A heterocurrent can be present due to recombination of the macroscopic dipole in the bulk of the sample and/or to the depolarization of a uniform polarization that, as seen previously, can only be observed indirectly.

In a similar way, asymmetry in the blocking behavior of the electrodes yields homocurrent. This happens because recombination takes place faster at the least blocking electrode leading to a change in the symmetry of the charge profile and a redistribution of image charges.

A graphical representation of these ideas is presented in Figure 10. As seen in the representation, when one electrode is completely blocking there will be no recombination at this electrode. The exact path of the charge may be difficult to predict but when the discharge process is completed all the image charge at the blocking electrode will have flowed through the circuit as homocurrent and, therefore, this situation would give the greatest possible area under the homocurrent curve. Finally, when one electrode is partially blocking the behavior will be something intermediate between these two cases since only part of the image charge at the partially blocking electrode will make its way to the other electrode through the electrometer, depending on how much blocking is the electrode.

Numerical analysis of the data in Tables 2 and 3 is consistent with this hypothesis. In experiment $C$ the polarization of the $\rho$ peak is one order of magnitude smaller than the image charge per unit area and, moreover, has opposite sign. This peak can not be related to external homocharge and has to be attributed to relaxation of uniform polarization, not registered by PEA. The external homocharge is mainly recombined at the electrodes without giving rise to homocurrent.

In experiment $E$ the polarization of the homocurrent peak is one order of magnitude greater than in experiment $D$ and very close to the value of the image charge per unit area. This is compatible with a highly blocking behavior of the air gap electrode in experiment $E$. In the case of experiment $D$ image charge per unit area values are comparable with $E$ but the polarization of the homocurrent peak $\rho^*$ is much lower, compatible with a less blocking behavior of the air gap electrode in this case.

Even if numerical data obtained with TSDC and PEA support this interpretation, there remains the question of whether the observed behavior of the electrodes is aligned with current knowledge about this matter.
Figure 10: Interpretation of influence of blocking behavior on depolarization currents.
It has been reported previously that vacuum-deposited electrodes present no initial potential barrier for electron injection or extraction because the Fermi level of the metal and its equivalent in the dielectric tend to level at the junction between both materials [25]. So, it is reasonable to assume that vacuum-deposited electrodes are mostly non-blocking even in short-circuit conditions.

While it is clear that electrodes with an air gap also do not impede charge injection when a strong electric field is applied, it is reasonable to think that they are going to be more blocking than vacuum-deposited electrodes under short-circuit. This would explain why homocurrent appears in experiments $D$ and $E$ but, unfortunately, not why the electrode with an air gap is more blocking in the $E$ than in the $D$ experiment, so we have to push further our analysis.

During depolarization in the $D$ experiment electrons from the setup electrode have to cross the surface of the sample to enter the bulk and recombine with the vacancies while in the $E$ experiment it is the other way round, the electrons have to escape from the bulk exiting through the setup electrodes. From our interpretation it follows that, under short-circuit, the aluminium-air-PET interface favors the jump of electrons from a metal into the bulk rather than the opposite, making a difference in the blocking behavior in experiments $D$ and $E$ during discharge and, in particular, making the electrode with air gap less blocking in experiment $D$ than in $E$.

A possible explanation could arise from an acceptor-like character of the aluminium-PET interface. It has been argued that the silver-PET interface is acceptor-like because of the interplay between the Fermi energy of silver and the charge neutrality level of PET [26]. Since aluminium has a lower work function than silver [23] it would be reasonable to expect an even more accentuated acceptor-like character of the aluminium-PET interface. A thin air gap would difficult the levelling between the Fermi levels of the metal and the dielectric. This would partially block bidirectional charge circulation under short-circuit but, arguably, would not impede a one-way transfer of electrons from the metal to the acceptor-like levels of the dielectric.

5 Conclusions

We have improved a simple but useful calibration scheme for PEA measurements on thin samples. It is exact while $C$ in Equation 1 is not too different across the setup and sound wave transmission is complete across the interfaces. Since these conditions are not exactly met in usual cases there is room for further improvements, even at the expense of more complication in the calculations and the procedures.

One of the limitations of the calibration process is that the deconvolution matrix is obtained from a calibration case where there is only free charge. For this reason it can be expected to work better for image charges than for charges in the bulk of the sample.

Uniform polarization such as the one of $\alpha$ and $\rho$ relaxations can only be detected indirectly because induced and image charge are too close. Only image charge is visible, probably in a partial way. The reason why image charge on the electrodes is more visible than induced charge on the sample is unclear but may be related to different responses.
of both kinds of charge to the electric pulse combined with the frequency response of the piezoelectric sensor. The classical interpretation of these relaxations is reinforced because none of them appears to involve macroscopic displacement of charge.

Vacuum-deposited aluminium electrodes do not avoid charge injection under a strong electric field but under short-circuit they suppress homocurrent because they favour that recombination takes place at the electrodes without homocurrent flow. This, is, nonetheless, useful in TSDC relaxational studies where often the interest is the intrinsic mechanisms of the material rather than the behavior of external charge.

In fact, electrodes are more determinant in the discharge of the sample than in its charge. None of the electrodes that have been used blocks charge carriers when a strong electric field is applied but differences appear when the sample is short-circuited, probably due to the role of the surface states of the sample. Differences in the blocking behavior of the electrodes during the discharge trigger the appearance of homocurrent in TSDC experiments.

In electrodes with an air gap this blocking behavior depends on the sign of the charge carriers, changing the amount of homocurrent depending on which electrode has the air gap. We can infer that electrons move more easily in the aluminium-air-PET direction than in the other way.

Numerical analysis of TSDC and PEA data support these conclusions with a reasonable concordance between the polarization obtained by time integration of the depolarization currents and the charge per unit area obtained by integration along the depth axis of the charge profile.

PEA can always supply information about thermally poled electrets. External injected charge results are easier to interpret but mechanisms that give rise to a more uniform polarization can also be studied. In combination with techniques such as TSDC, PEA can be usefully employed in relaxational studies of dielectric materials.

References

[1] Mototarō Eguchi. On the permanent electret. The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 49(289):178–192, 1925.

[2] R. Gerhard-Multhaupt. Electrets: Dielectrics with quasi-permanent charge or polarization. Electrical Insulation, IEEE Transactions on, EI-22(5):531–554, Oct 1987.

[3] R. Chen and Y. Kirsh. Analysis of Thermally Stimulated Processes, chapter 3, pages 60–81. Pergamon, Oxford, 1st edition, 1981.

[4] J. van Turnhout. Electrets, volume 1, chapter 3, pages 81–215. Laplacian, Morgan Hill, CA, 3rd edition, 1999.

[5] J. Belana, P. Colomer, S. Montserrat, and M. Pujal. Glass transition temperature of amorphous poly(ethylene terephthalate) by thermally stimulated currents. Macromol. Sci. Phys. B, 23(4-6):467–481, 1984–1985.
[6] M Mudarra and J Belana. Study of poly (methyl methacrylate) space charge relaxation by TSDC. *Polymer*, 38(23):5815–5821, 1997.

[7] G.C. Montanari and P.H.F. Morshuis. Space charge phenomenology in polymeric insulating materials. *Dielectrics and Electrical Insulation, IEEE Transactions on*, 12(4):754–767, Aug 2005.

[8] Ryo Ono, Masaaki Nakazawa, and Tetsuji Oda. Charge storage in corona-charged polypropylene films analyzed by lipp and tsc methods. *IEEE Transactions on Industry Applications*, 40(6):1482–1488, 2004.

[9] T. Maeno, T. Futami, H. Kushibe, and T. Takada. Measurement of spatial charge distribution in thick dielectrics using the pulsed electroacoustic method. *IEEE Transactions on Dielectrics and Electrical Insulation*, 23(3):433–439, 1988.

[10] ME Banda, V Griseri, Gilbert Teyssedre, and Séverine Le Roy. Polarization of electron-beam irradiated LDPE films: contribution to charge generation and transport. *Journal of Physics D: Applied Physics*, 51(15):155303, 2018.

[11] P. G. Kazansky, A. R. Smith, P. St. J. Russell, G. M. Yang, and G. M. Sessler. Thermally poled silica glass: Laser induced pressure pulse probe of charge distribution. *Applied Physics Letters*, 68(2):269–271, 1996.

[12] M-Q Hoang, L Boudou, S Le Roy, and G Teyssedre. Dissociating space charge processes from orientation polarization in poly(ethylene naphthalate) films. *Journal of Physics D: Applied Physics*, 47(45):455306, 2014.

[13] Jacques Lewiner, S. Hole, and Thierry Ditchi. Pressure wave propagation methods: a rich history and a bright future. *Dielectrics and Electrical Insulation, IEEE Transactions on*, 12(1):114–126, Feb 2005.

[14] S. Hole. Resolution of direct space charge distribution measurement methods. *Dielectrics and Electrical Insulation, IEEE Transactions on*, 15(3):861–871, June 2008.

[15] G Chen, Z Xu, and L W Zhang. Measurement of the surface potential decay of corona-charged polymer films using the pulsed electroacoustic method. *Measurement Science and Technology*, 18(5):1453, 2007.

[16] G. M. Sessler. Charge distribution and transport in polymers. *IEEE Transactions on Dielectrics and Electrical Insulation*, 4(5):614–628, 1997.

[17] G Chen, Y L Chong, and M Fu. Calibration of the pulsed electroacoustic technique in the presence of trapped charge. *Measurement Science and Technology*, 17(7):1974–1980, 2006.
[18] N. H. Ahmed and N. N. Srinivas. Review of space charge measurements in dielectrics. *IEEE Transactions on Dielectrics and Electrical Insulation*, 4(5):644–656, 1997.

[19] Ying Li, Masata ka Yasuda, and Tatsuo Takada. Pulsed electroacoustic method measurement of charge for accumulation in solid dielectrics. *IEEE Transactions on Dielectrics and Electrical Insulation*, 1(2):188–195, 1994.

[20] R. J. Fleming. Space charge profile measurement techniques: Recent advances and future directions. *IEEE Transactions on Dielectrics and Electrical Insulation*, 12(5):967–978, 2005.

[21] J Sellarès, JA Diego, and J Belana. A study of the glass transition in the amorphous interlamellar phase of highly crystallized poly (ethylene terephthalate). *Journal of Physics D: Applied Physics*, 43(36):365402, 2010.

[22] Mohamad Arnaout, Khaled Chahine, Fulbert Baudoin, Laurent Berquez, and Denis Payan. Iterative deconvolution of pea measurements for enhancing the spatial resolution of charge profile in space polymers. *Journal of Polymers*, 2016:4684796(11), 2016.

[23] Eric Jones, Travis Oliphant, Pearu Peterson, et al. SciPy: Open source scientific tools for Python, 2001–.

[24] David R Lide. *CRC handbook of chemistry and physics*, volume 84, chapter 13. CRC press, 2003.

[25] Eugen R Neagu. A method to measure the electric charge injected/extracted at the metal-dielectric interface. *Applied Physics Letters*, 92(18):182904, 2008.

[26] Eugen R. Neagu and C. Dias. Charge injection/extraction at a metal-dielectric interface: Experimental validation. *Electrical Insulation Magazine, IEEE*, 25(1):15–22, January 2009.