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# Electrical characterization of PEN films using TSDC and PEA measurements

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**Abstract**—Thermo-stimulated depolarization current (TSDC) measurements have been performed on poly(ethylene naphthalene 2,6-dicarboxylate) (PEN), an aromatic polyester. The aim is to develop the understanding of trapping mechanisms at play in this material, and particularly to understand the effect of temperature. Experimental results of TSDC are interpreted with the help of space charge measurements using the pulsed electroacoustic method (PEA) on PEN samples. For TSDC measurements, samples were polarized at temperatures of 130°C and 170°C. In both cases, the sub-glass transition and the glass transition relaxations are observed. However, in the case of a polarization temperature of 170°C, one more TSDC peak, so-called  $\rho$ -peak is observed at temperatures above the glass transition. From space charge results, it is shown that the  $\rho$ -peak has not a dipolar origin; it has been associated to charge detrapping in the material.

**Keywords**—PEN; TSDC; PEA; relaxation; polarization; effect of temperature; discharge current

## I. INTRODUCTION

Numerous studies have been performed on organic solid dielectrics in order to have access to information related to space charge transport and trapping. Thermo-Stimulated Depolarization Current (TSDC) measurements are likely to give information on the trapping levels for carriers. It may also contain a response from oriental polarization. Charge release and dipolar effects may both be related to molecular motions appearing in the material. [1]-[2]. Therefore, discriminating responses related from space charge relaxation from dipolar processes can be critical. Poly(ethylene naphthalene 2,6-dicarboxylate) (PEN) has been chosen for this study as it is an aromatic polar polymer, and is likely to give a significant response from dipolar mechanisms in TSDC measurements. In this study, TSDC measurements have been used with two protocols of application of the voltage and the temperature to develop the understanding of the charging and polarization mechanisms at play in this material. Space charge measurements have also been performed using the Pulsed Electroacoustic method (PEA) in order to confirm the space charge behavior in the PEN samples.

## II. SAMPLES AND MEASUREMENT PROTOCOLS

PEN films were commercial TEONEX® Q51 films provided by DuPont Teijin Films Co. The melting point of these semicrystalline materials is at 269°C and the glass transition temperature at 121°C [3]. The film thickness is 188  $\mu\text{m}$ . For all measurements, 20mm-diameter circular gold electrodes were deposited on each face.

TSDC measurements were carried out in a thermally controlled chamber following the cycle depicted in Fig. 1. Samples were first polarized with a DC voltage  $V_p$  (1 to 2 kV) at a constant temperature  $T_p$  (130 or 170°C), for a fixed time  $t_p = 15$  min. After a fast cooling under applied voltage, samples were reheated from 25 to 220°C, using a constant heating rate  $v = 3^\circ\text{C}/\text{min}$ , under short circuit conditions. The corresponding discharge current, due to charges thermally detrapped or to dipolar processes, was recorded, using a Keithley-617 electrometer. All the TSDC measurements were done under controlled helium atmosphere.

Space charge measurements were performed using the Pulsed Electroacoustic (PEA) method in order to check the charge distribution within the dielectric before (cf. step PEA-1 on Fig. 1) and after (PEA-2 on Fig. 1) the TSDC measurement.

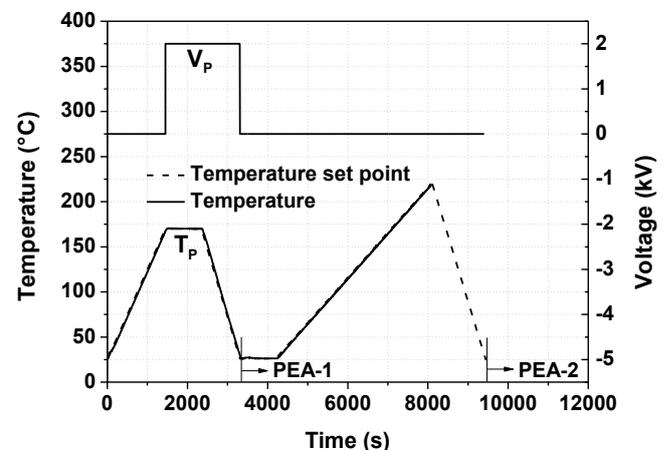


Fig. 1. Voltage and temperature protocol of TSDC measurements. Dotted and solid lines represent respectively the set point temperature and the measured temperature along the cycle.

In that goal, PEN samples were submitted to the voltage and temperature protocols in the TSDC chamber, as the PEA set-up does not withstand temperatures higher than 90°C. Samples were removed from the TSDC set-up at PEA-1 and PEA-2 (Fig. 1), and space charge measurements were carried out at room temperature under short circuit conditions.

### III. TSDC RESULTS

PEN samples were polarized at two temperatures  $T_P$ : 130°C and 170°C for different voltages  $V_P$ . Fig. 2 presents the TSDC profiles obtained for PEN samples polarized at 130°C. Two relaxation peaks were observed. The first one, called  $\beta^*$  is located at 65°C. It has been ascribed to the relative motion of the two naphthalene rings present in the polymer chain [4]-[5]. The mechanisms associated with this relaxation process are complex and depend upon the measurement frequency [6].

The second peak, called  $\alpha$ , is located at 140°C. It has been related to the glass transition of this material, involving long-range cooperative segments motion [1]. It has a characteristic dielectric loss peak, which is broad, asymmetrical in the Cole-Davidson representation [7]. The magnitude of the  $\beta^*$  and  $\alpha$  peak vary almost linearly with the applied voltage. The area under the  $\alpha$  peak increases also linearly with the voltage, although it is more difficult to observe as the two peaks overlap. The TSDC profiles of PEN samples polarized at  $T_P = 170^\circ\text{C}$  are presented in Fig. 3. As for a polarization temperature of 130°C, a  $\beta^*$  and a  $\alpha$  relaxation peak can be observed, at 65 and 140°C respectively. A third peak is observed for  $T_P = 170^\circ\text{C}$ , called  $\rho$ , and located at 180°C. This relaxation peak has already been observed by Canadas et al [8] and appear related to charge detrapping within the material. Several TSDC measurements were carried out at  $T_P = 170^\circ\text{C}$  for different applied voltages.. As for  $T_P = 130^\circ\text{C}$ , an increase in the applied field implies a linear increase in the  $\beta^*$  and  $\alpha$  peak area. This is however not the case for the  $\rho$  peak area, which clearly shows a non-linear increase. This non-linearity goes in the direction of a non-polar phenomenon at the origin of the  $\rho$  peak.

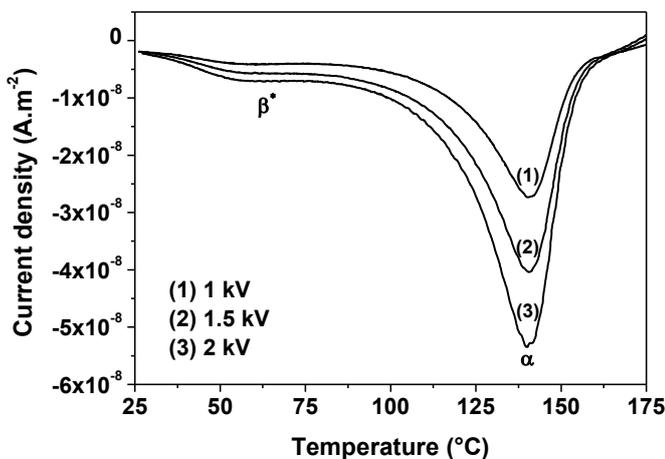


Fig. 2. TSDC profiles of PEN polarized at  $T_P = 130^\circ\text{C}$ : evolution of the  $\beta^*$  and  $\alpha$  peaks with the applied voltage  $V_P$ .

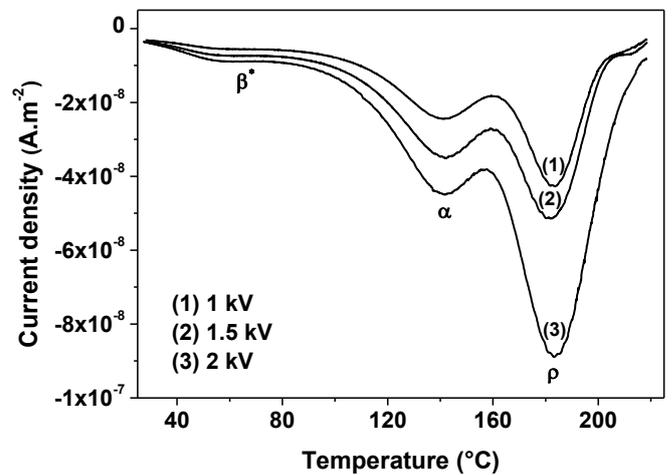


Fig. 3. TSDC profiles of PEN polarized at  $T_P = 170^\circ\text{C}$ : evolution of the  $\beta^*$ ,  $\alpha$  and  $\rho$  peaks with the applied voltage  $V_P$ .

### IV. PEA MEASUREMENTS

In order to confirm the mechanism responsible of the observed  $\rho$  peak, space charge measurements were performed on PEN samples which were already polarized with a DC voltage (2kV) at temperatures of 130°C or 170°C.. Fig. 4 shows the space charge profiles obtained under short-circuit conditions (a) after polarizing at 130°C and freezing the polarization to room temperature (PEA-1) and (b) after subsequent TSDC measurement (PEA-2), meaning after temperature increase to 220°C in depolarization followed by cooling to room temperature. No charges are detected within the bulk at the end of the TSDC polarization protocol (Fig. 4a), even after 15 min under short-circuit. However, influence charges are observed at each electrode, which do not change with time. These charges could be due to heterocharges within the dielectric in the narrow region close to the electrodes, hence not detected by the set-up. These image charges could also be linked to polarization phenomena of the PEN sample. A rough calculation of the area under the influence charge peak of Fig. 4a gives a surface charge of  $2.1 \cdot 10^{-5} \text{ C/m}^2$ . When calculating the area under the  $\alpha$  current peak of Fig. 2, for 2kV and a heating rate of 3°C/min, and taking into account the fact the  $\beta^*$  and a  $\alpha$  current peaks overlap, the surface charge obtained is  $2.5 \cdot 10^{-5} \text{ C/m}^2$ . The two values are consistent, meaning that dipolar processes dominate the influence charge peaks observed in the PEA measurements. At the end of the TSDC scan (PEA-2), no charges are detected within the PEN sample (Fig. 4b). It is to note that the image charge on the anode seems to be an artifact, as no more charge are observed on the cathode, and the integrated charge over the sample should be void. This could be due to a bad matching impedance between the PEN sample and the semiconductor at the top electrode of the PEA set-up. As long as this is true, no more polarization exists within the sample at the end of the TSDC protocol.

Fig. 5 shows the space charge profiles obtained under short-circuit conditions (a) before (PEA-1) and (b) after (PEA-2) the TSDC scan, for a polarization temperature of 170°C. At

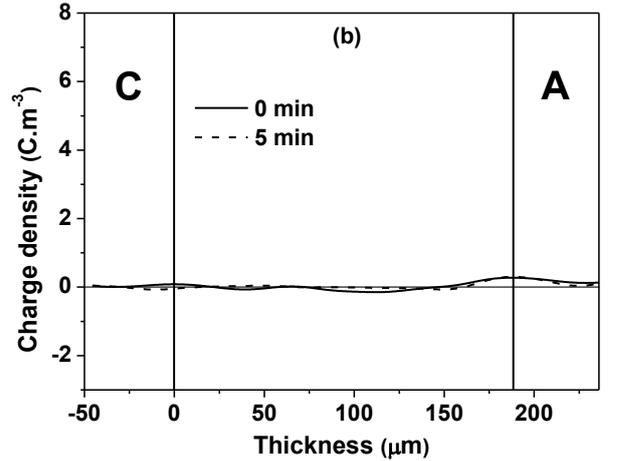
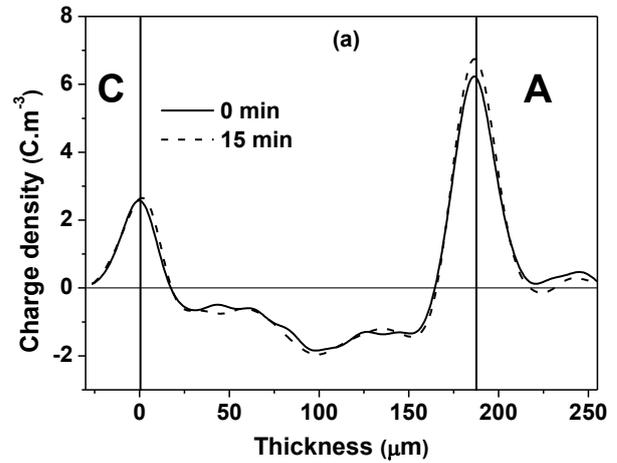
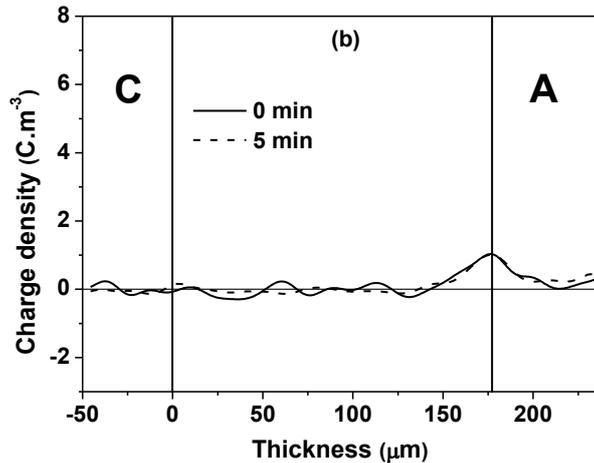
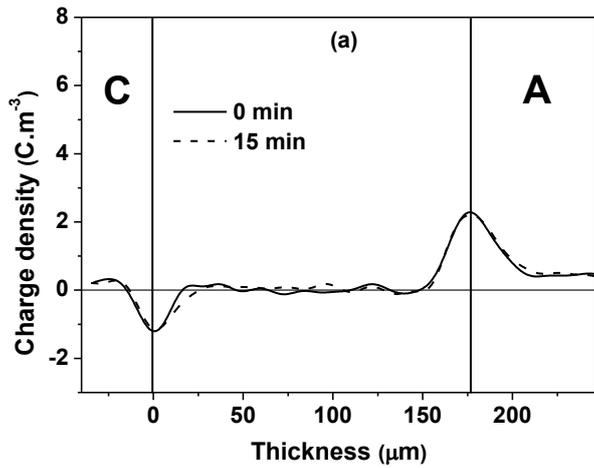


Fig. 4. Space charge profiles by PEA in Volt off for PEN previously polarized at 130°C: (a) Before reheating (PEA-1) of TSDC protocol; (b) After reheating (PEA-2) of TSDC protocol; C: Cathode, A: Anode during pre-polarization..

Fig. 5. Space charge profiles by PEA in Volt off for PEN previously polarized at 170°C: (a) Before reheating (PEA-1) of TSDC protocol; (b) After reheating (PEA-2) of TSDC protocol; C (Cathode), A (Anode).

the end of the TSDC polarization (PEA-1), negative charges are observed in the bulk of the sample. This is a remarkable behavior given the relatively low field (10kV/mm) applied in these measurements. These negative charges do not move after 15 min of short-circuit at room temperature. At the end of the TSDC scan (PEA-2), a negligible amount of charges are detected within the PEN sample (Fig. 5b), and no surface charges are observed. Negative charges have been evacuated during the ramp-up, and polarization mechanisms have also been released. The charge profiles for a polarization temperature of 130°C and 170°C are then really different, and the presence of charges at PEA-1 for  $T_P = 170^\circ\text{C}$  explains the difference in the TSDC profiles. Hence, the  $\rho$  peak is certainly due to negative charges present within the dielectric, and released during the reheating rate. It is to note that the negative charges within the bulk alone cannot explain the magnitude of the influence charges at each electrode. As for  $T_P = 130^\circ\text{C}$  (Fig. 4), there should also be a contribution of a polar phenomenon in the influence charges.

## V. TSDC WITH PARTIAL HEATING

To further investigate the behavior of the the  $\rho$ -peak, TSDC measurements were conducted according to a partial heating method [9] following the protocol described in Fig. 6a. After the polarization period at  $T_P = 170^\circ\text{C}$  and  $V_P$  (2 kV in this case) followed by a rapid cooling, sample is heated a first time, from 25°C to 150°C. The upper temperature was selected according to Fig. 3 and corresponds to the temperature between the  $\alpha$  and the  $\rho$  peak. The sample was then cooled to 25°C and reheated up to 220°C with the same heating rate  $\nu = 3^\circ\text{C}/\text{min}$ . TSDC profiles are presented in Fig. 6b. The current recorded during the first partial heating, up to 150°C, is consistent with what has been already presented in Fig. 3 for an applied voltage of 2 kV. The  $\beta^*$  and  $\alpha$  relaxations can be observed, at 65 and 140°C respectively. During the second heating, these peaks are not present anymore, and only the  $\rho$  peak is measured, with a current maximum at around 180°C. We suppose that during the first partial heating rate, only the polar groups responsible of  $\beta^*$  and  $\alpha$  peaks relaxed. Thus, trapped charges still present are released at a temperature higher than 150°C during the second heating.

However, care has to be taken, as the  $\rho$ -peak could be due to a combination of space charge and orientation polarization phenomena (due to charge or other). Hence, space charge measurements after the first partial heating at 150°C need to be performed, in order to verify if trapped charge are still present within the bulk.

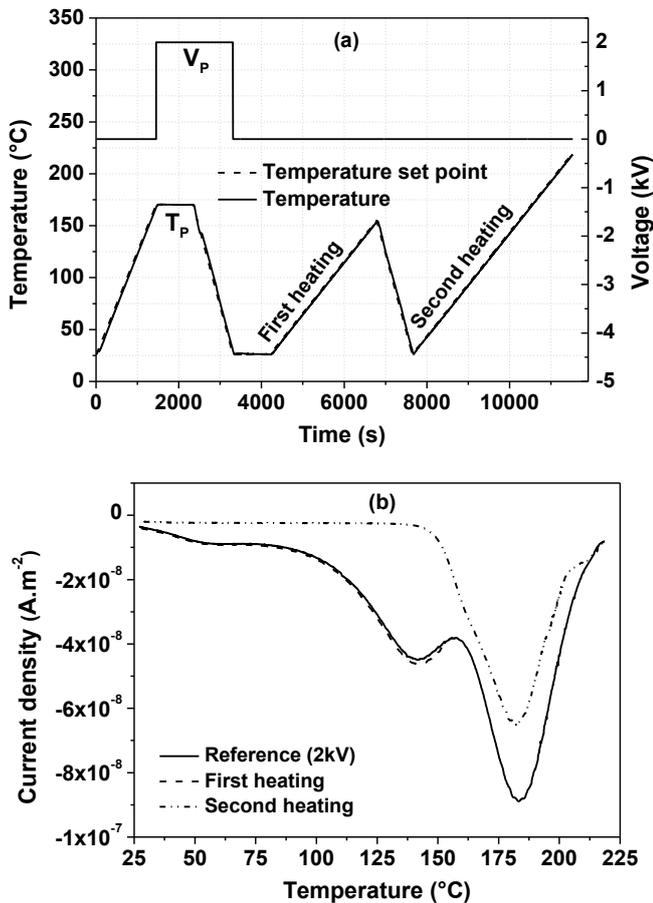


Fig. 6. (a) Voltage and temperature protocol for partial heating method; (b) TSDC responses without partial heating (solid line), after the first partial heating to 150°C (dashed line) and after the second heating rate (dash-dotted line).

## VI. CONCLUSION

TSDC and PEA methods at various temperatures reveal that the voltage and especially the temperature play an important role in the electrical properties of PEN films. An increase in the polarization temperature gives rise to different TSDC results, as only polarization peaks are observed for a

polarization temperature of 130°C, while a third peak at 180°C is detected when the polarization temperature is higher. This peak has been attributed to space charge present within the bulk of the PEN samples. Space charge measurements, performed at different points on the TSDC protocol, have confirmed the presence of negative space charges in the bulk of PEN when the sample is polarized at 170°C, while no charges are detected for a lower temperature. It has also been possible to observe a polarization phenomenon with the PEA method. However, more work needs to be done in order to check if the  $\rho$  peak in TSDC can be attributed only to space charge, or if polar phenomenon also contribute to this current peak.

## ACKNOWLEDGMENT

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