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Mai Quyen Hoang, Laurent Boudou, Séverine Le Roy, Gilbert Teyssedre. Electrical characterization of LDPE films using Thermo-Stimulated Depolarization Currents method: measurement and simulation based on a transport model. 8ème conférence de la Société Française d'Electrostatique, Cherbourg-Octeville, France, Jul 2012, Cherbourg-Octeville, France. 5 p. hal-03942787

HAL Id: hal-03942787

<https://hal.science/hal-03942787>

Submitted on 18 Jan 2023

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Electrical characterization of LDPE films using Thermo-Stimulated Depolarization Currents method: measurement and simulation based on a transport model.

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Abstract: Thermo-stimulated depolarization current (TSDC) measurements have been performed on low density polyethylene (LDPE), a non polar polymer material. The aim is to develop the understanding of the conduction mechanisms at play in this material, and particularly to understand the effect of temperature and antioxidant presence.

Variations of the TSDC experimental protocol (charging voltage, pre-heating temperature before quenching) are investigated. Furthermore, original measurements are also performed, aiming at driving the carriers outside the dielectric during the reheating rate. To do so, a relatively small voltage, positive or negative, is applied during the temperature ramp. Experimental results obtained with LDPE samples are interpreted with the help of a bipolar transport model.

1. INTRODUCTION

LDPE is a low polar polymer which has been widely used as electrical insulating material due to its properties such as low permittivity and losses [1]. It is a semicrystalline polymer composed of lamellar crystals, which are typically arranged as spherulites when cooled from the melt. The polymer crystal formation and the spherulitic structure in bulk polymers have been extensively described in the literature [2]-[5], and this microstructure widely influences the final electrical properties of the dielectric. 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. In this communication, TSDC measurements have been used with two original protocols of application of the voltage and temperature to develop the understanding of the charging mechanisms at play in this material.

2. SAMPLES AND TSDC PROTOCOLS

Test samples were films of LDPE with Santonox-type antioxidant. It was obtained from pellets in 100 μ m film form by hot pressing. 32mm-diameter circular electrodes were gold coated on each face.

TSDC experiments were carried out in a thermally controlled chamber following the cycle depicted in Fig. 1. Samples were polarized with a DC voltage V_p at a fixed temperature T_p , for a fixed time $t_p = 30$ min. Then they were rapidly cooled to a temperature close to the boiling point of nitrogen. The voltage was then removed, and the depolarization current was measured, using a Keithley-617 electrometer, under short circuit conditions from -100 to 100°C and for a constant heating rate $\beta = 6$ °C/min. All the TSDC measurements were done under controlled helium atmosphere.

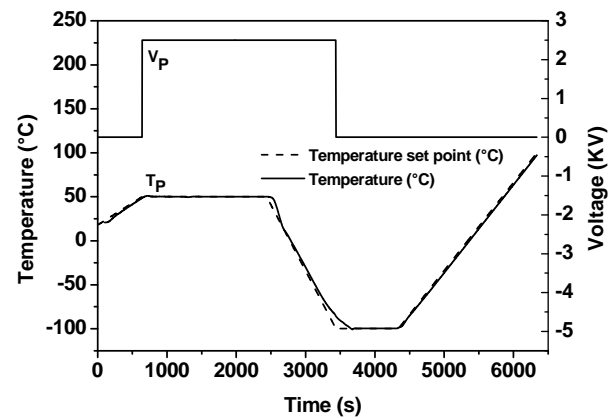


Fig. 1 Voltage and temperature protocol of TSDC measurements. Dotted and solid lines represent respectively the set point temperature and the measured temperature along the cycle.

3. EXPERIMENTAL RESULTS

3.1. Relaxation peaks in polyethylene

In the temperature range from -100 to 100°C, LDPE shows three relaxations processes located, in increasing temperature order, around -30°C (β), 50°C (α_1) and 65°C (α_2).

Fig.2 and Fig. 3 show respectively the plot of the TSDC at several applied polarization voltages for two polarization temperatures 25 and 50°C. In the TSDC spectra at $T_p = 25$ °C (Fig. 2), two relaxation peaks are observed. The first, called β is located at -30°C. The second peak, called α_1 , is located at 50°C and can be compared with the α peak revealed by thermo-mechanical spectroscopy [6]. One of the likely

mechanisms responsible for the α peak is molecular motions in crystalline or paracrystalline regions of the polymer. This leads to the release of trapped charges within the interface between the crystalline and amorphous regions [7]. Furthermore, the β and α peaks are located at the same temperatures as those labelled as C3 and C4 in the work of Mizutani et al [8]. These peaks are assigned to the presence of defects, acting as deep traps (0.8 to 1.4 eV) and located in the amorphous-crystalline interface [8], or in the crystalline region [9]. Moreover, the β and α relaxations are only observed in the case of LDPE with antioxidant [10], so the antioxidant most probably adds deep trapping levels and is also responsible for the polymer morphological change.

The TSDC spectra at $T_p = 50^\circ\text{C}$ (Fig. 3) shows a second peak of relaxation α_2 with an opposite sign, corresponding to an anomalous depolarization current. Usually, removing the applied voltage causes a discharge current of opposite sign compared to the charging current. This anomalous depolarization current has already been observed by Mizutani et al. [8].

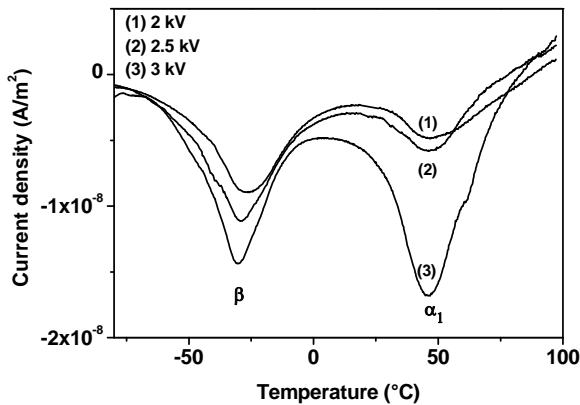


Fig. 2 TSDC responses of LDPE at $T_p = 25^\circ\text{C}$: evolution of the β and α_1 peaks with the applied voltage V_p .

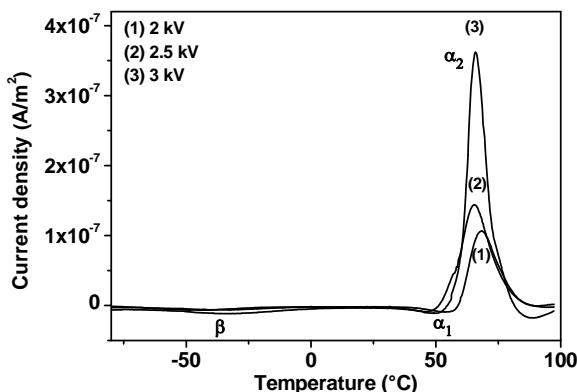


Fig. 3 TSDC responses of LDPE at $T_p = 50^\circ\text{C}$: evolution of the β , α_1 and α_2 peaks with the applied voltage V_p . In the configuration used, positive currents are anomalous discharge currents.

In a recent study on the impact of antioxidant on the

electrical properties of LDPE, Tebani et al. [10] have shown, using Pulse Electro-Acoustic (PEA) method, that negative charges are accumulated at both cathode and anode, after removing the applied voltage (Fig. 4). The α_1 and α_2 peaks were then interpreted as charge detrapping. The negative charges accumulated near the cathode, when evacuated from the bulk under short circuit conditions and temperature increase, are responsible for a normal discharge current (α_1 peak), while the negative charges accumulated near the anode and extracted through the anode are responsible for a positive, i.e. anomalous, discharge current (α_2 peak).

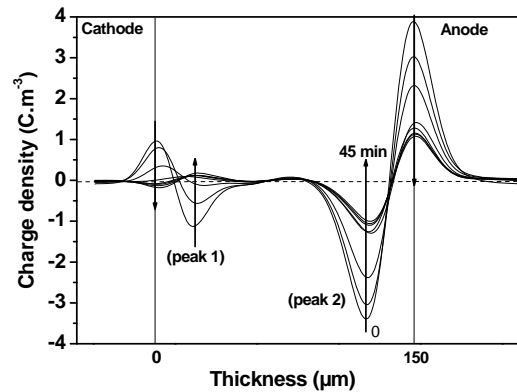


Fig. 4 Space charge profiles for LDPE-AO with antioxidant after different times in Volt off [10]. Polarization and measurements were achieved at 50°C .

3.2. TSDC with two temperature ramps

In order to separate the α_1 and α_2 peaks, TSDC measurements were conducted according to a partial heating method [11] and according to the protocol described in Fig. 5(a). After the polarization period at T_p and V_p followed by a rapid cooling, sample is heated a first time, from -100°C to 51°C . The upper temperature was selected according to curve (1) in fig. 5(b) and corresponds to the temperature at which the depolarization current sign is changing from negative to positive, after α_1 peak. The sample was then cooled to -100°C and reheated to 100°C with the same heating rate $\beta = 6^\circ\text{C}/\text{min}$.

During the first heating cycle, charges accumulated near the cathode, and responsible for the α_1 peak, were evacuated. During the second heating, only the positive α_2 peak is recorded with higher amplitude when compared to the α_2 peak recorded by classical TSDC measurement (dash line Fig. 5(b)). This last result seems to confirm that negative charges accumulated at the cathode and anode are responsible respectively for α_1 and α_2 peaks. The idea is now to drive these charges by the application of a small voltage during heating. A positive voltage application on the electrode that was previously anode should tend to drive negative charges from (pre-)cathode to (pre-)anode and as a consequence should increase the α_2 peak amplitude, while a negative

voltage should drive negative charges from (pre-)anode to (pre-)cathode and then decrease the α_1 peak amplitude. Indeed, it can be shown [12] that the external current essentially corresponds to the space-averaged transport current. If one hypothesizes that charges are trapped in a narrow region close to an electrode, then, their extraction through this electrode produces only a very small current (depending only on their distance from the electrode). Conversely, it is their transport in the dielectric bulk that produces a significant current.

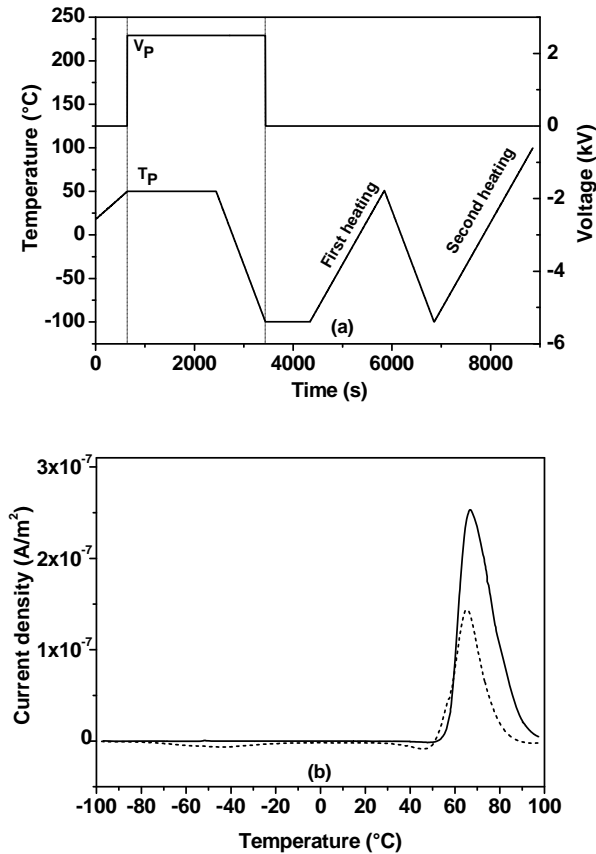


Fig. 5 (a) Voltage and temperature protocol for partial heating method (b) TSDC responses without partial heating (dashed line) and after partial heating to 51°C (solid line).

3.3. Driving voltage during temperature ramp

In this study, samples were first polarized with $V_p = 2.5$ kV at 50°C. After cooling to -100°C under applied voltage, the sample was reheated using a constant heating rate $\beta = 6$ °C/min. The originality here is to apply a small positive or negative driving voltage during the temperature rate. Hence, three different tests have been performed following voltage protocols described in Fig. 6(a). Test 1 corresponds to the classical TSDC protocol where the sample is under short circuit during heating ramp. In Test 2, a positive voltage of 50 V is applied during heating, while in Test 3 the driving voltage is -50V.

As expected, a positive driving voltage leads to an increase of α_2 peak magnitude (curve (2), Fig 6). Furthermore the magnitude of the α_1 peak in this case is near zero. When the driving voltage is negative, an increase in α_1 peak amplitude and a decrease in α_2 peak amplitude are observed (curve (2) Fig 6.). These results can be interpreted and explained by a negative charge detrapping process, where a positive driving voltage enhances the transport and extraction of negative charges from the pre-cathode, and a negative driving voltage enhances charge transport and extraction from the pre-anode.

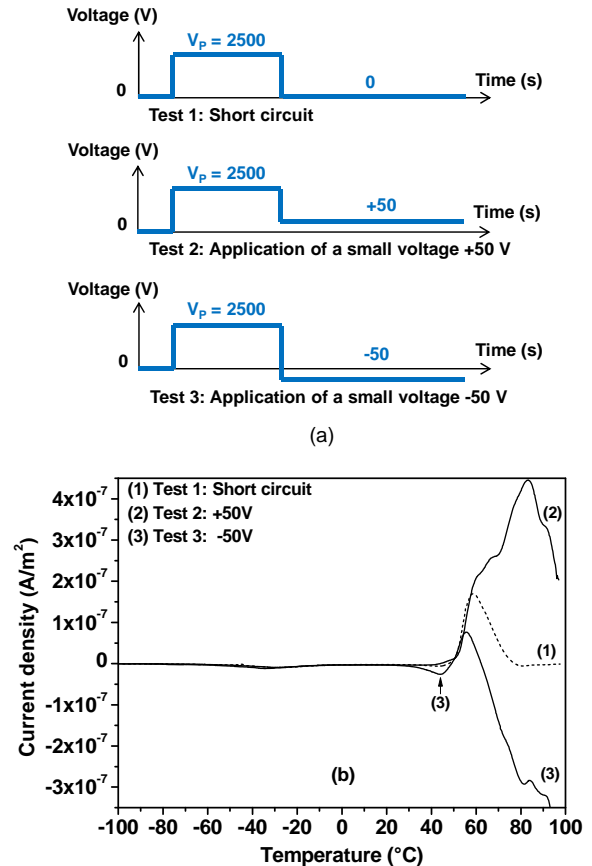


Fig. 6 TSDC measurements under driving voltage applied to LDPE at $T_p = 50^\circ\text{C}$ and $V_p = 2.5$ kV: (a) Voltage protocols; (b) TSDC spectra for different driving voltages.

At this stage however, we cannot fully conclude on the reason for having two peaks in depolarization current: either it is linked to the specific position of the charges in the dielectric and related induced field settled by poling prior to TSDC measurement, or there are two populations of charges of different nature, being e.g. injected electrons at the cathode and anionic charges adjacent to the anode. If a single kind of carriers were at the origin of the double peak, then it should be reproduced by modelling charge transport during a TSDC run. Besides, this task would also help in exploiting TSDC for extracting relevant transport

parameters. In the following, we present preliminary results obtained in an attempt to model TSDC based on electronic carriers transport.

4. SIMULATION RESULTS

4.1. Model

The model used to simulate TSDC measurements has been widely described in [12] [13]. We only briefly recall the temperature-dependent processes. Two kinds of carriers are considered in the model: electrons and holes. They can be either trapped or mobile. Mobile carriers are associated with an effective mobility μ that we consider of hopping type:

$$\mu_{e,h}(x,t) = \frac{2d\nu}{E(x,t)} \exp\left(\frac{e \cdot w_{\mu e,h}}{k_B T(t)}\right) \sinh\left(\frac{eEd}{2k_B T(t)}\right) \quad (1)$$

where d is the distance between traps, E the electric field, an e the elementary charge. ν is the attempt to escape frequency, k_B the Boltzmann constant, w_{μ} the hopping barrier height and T the temperature.

Deep trapping is described through a single trapping level for each kind of carrier. Charge carriers have a given probability to escape from traps by overcoming a potential barrier, w_{tr} . This is accounted for by the detrapping coefficients D_i of the form, for each kind of carrier:

$$D_{e,h}(t) = \nu \cdot \exp\left(\frac{-e \cdot w_{tr e,h}}{k_B T(t)}\right) \quad (2)$$

The recombination of carriers is accounted for considering different coefficients S_i for the several electron-hole pairs. Carriers are provided by charge injection at the electrodes and are extracted without any barrier. We have supposed that charges are injected at the electrodes according to a modified Schottky law:

$$j_{e,h}(t) = AT^2(t) \exp\left(-\frac{w_{e,h}}{k_B T(t)}\right) \left(\exp\left(\frac{e}{k_B T(t)} \sqrt{\frac{eE_{elect}}{4\pi\epsilon}}\right) - 1 \right) \quad (3)$$

where A is the Richardson constant, $w_{e,h}$ are the injection barriers for electrons and holes and ϵ is the dielectric permittivity. The time and space dependent equations to solve and the numerical schemes used are given in [12].

4.2. Simulation results

The objective of this simulation is to further understand the TSDC profiles obtained during a temperature ramp when a voltage is applied. In that goal, the three experimental tests described in Fig 6(a) are reproduced in the simulation. The parameters used are those given in [13]. No further attempt has been made to 'fit' the present TSDC results, and we are aware that this set of parameters mainly gives positive charges inside the dielectric [13]. The simulated TSDC profiles should however give the same dynamics as what is observed experimentally, the only difference being the sign of the current.

Fig 7 shows the simulated TSDC profile as a function

of temperature obtained for the short circuit protocol. The current density is negative, as we are dealing with positive charges. Anyway, the TSDC profile shows a single peak, centered at around 64°C. No TSDC peak is observed in simulation at temperatures less than 0°C, as the model does not include polarization processes.

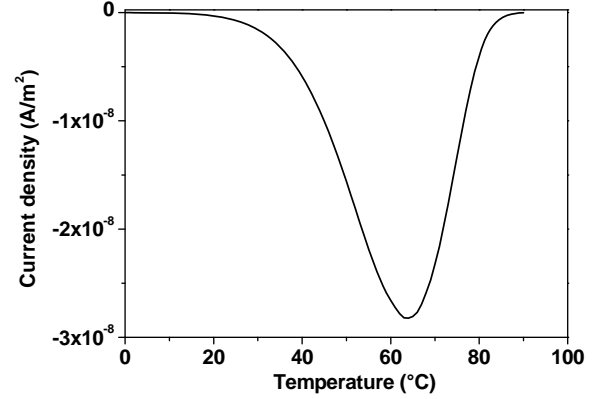


Fig. 7 TSDC spectrum predicted by the model under short circuit conditions for $T_p=50^\circ\text{C}$, $V_p=2.5\text{kV}$ with model parameters given in [13].

Fig 8(a) shows the simulated TSDC spectra for the three experimental protocols of Fig. 6(a). The application of a negative driving voltage enhances the transport and extraction of positive charges at the anode. As a result, the absolute value of the current density will be increased compared to the short-circuit case. This is what is observed for the TSDC of Test 3 compared to the one of Test 1. On the contrary, the application of a small positive driving voltage enhances the transport and extraction of positive charges towards the cathode. In this case, the current density related to the application of a positive driving voltage is of opposite sign compared to the one of Test 1, hence decreasing the TSDC, which tends to zero and becomes positive with the temperature ramp.

The absolute values of the simulated current densities are always increasing with temperature, whereas the experimental TSDC shows a maximum in absolute value. An explanation is that the model enables an injection of charges during TSDC measurements, depending on the electric field at the electrodes. This 'conduction part' to the TSDC is possibly over-estimated in the model. However, when adding the TSDC of Tests 2 and 3 (Fig. 8(b)), the conduction part due to charge injection is nearly annihilated, and the result is roughly twice the simulated TSDC of Test 1, which is an expected result if one suppose that the area under the TSDC is proportional to the stored charge. Though results are promising, refinements are necessary, especially as regards the temperature dependence of model parameters.

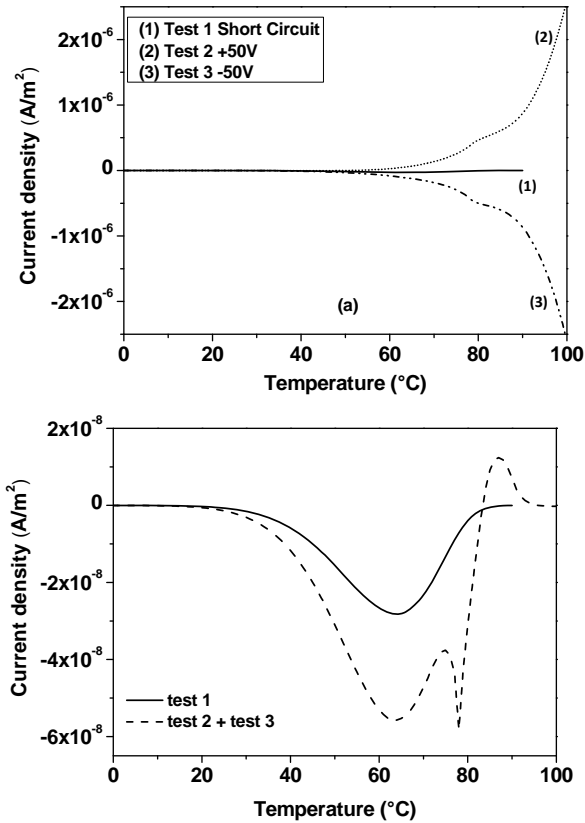


Fig. 8 (a) TSDC profiles vs. temperature for the three experimental tests described in Fig. 6(a). (b) Comparison of TSDC profile from Test 1 and the addition of TSDC from Test 2 and 3.

Although the simulated space charge pattern is positive at the beginning of the ramp-up, the model is able to give the same trend as what is observed experimentally.

CONCLUSION

By using different variants of TSDC experiments, namely partial heating and superposition of a driving voltage during TSDC measurements, we have shown, in the light of previous space charge measurements, that the α_1 and α_2 depolarization peaks observed in the range 30 to 70°C in TSDC of LDPE actually correspond to the release of negative charges, located respectively close to the electrodes that were cathode and anode during polarization. It is not possible at this time to decide if the carriers are of the same nature or not. TSDC modelling using a transport model has been initiated in order to unravel the actual nature of this double population of charges.

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