The effect of charge trapping on final thermally stimulated discharge currents in polyethylene naphthalate (PEN)

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Abstract. The aim of the work presented in this paper was to analyse final thermally stimulated discharge current that appeared at the end of discharging process, when the temperature was increased from 100 to 180°C. This current exhibit two probable peaks. To fit the experimental data, two Gaussian components were used: the first one centred at 128°C near \( T_g \) and the second one at 150°C associated to pre-melting of crystallites. The sample (gold metallised PEN film 25 µm thick) was submitted, prior to this process, to 72MV/m DC field during ten thousand seconds. The DSC analyse showed a \( T_g \) at 128°C and an endothermic peak at 150°C. These results imply that the trapped space charge cannot release from the sample and require an increasing of temperature. Above \( T_g \), the molecular motion facilitates the de-trapping process.

1. Introduction
Due to their excellent electrical properties, polymers are widely used as electrical insulators. However, in particular conditions, especially under high electrical field, their insulating properties may be affected, as the space charge composed of trapped charge carriers, can have a drastic effect on dielectric properties, which influence tremendously the reliability of apparatus and systems where they are integrated. Indeed, this charge can increase the local electrical field and subsequently cause breakdown of the insulator.

The aim of this work was to make a correlation between the trapping of space charge and transient currents, by comparing the results obtained by three techniques. The material used in this study was the polyethylene naphthalate (PEN) which gives high performance films with excellent thermal mechanical and electrical characteristics.

Measurements were done in a large temperature-range including the glass transition temperature \( T_g \) so as to analyze the effect of polymer state, glassy or rubbery, on electrical properties.

2. Material
Polymers are currently used as dielectrics in a wide range of electro-technological applications. Since the polyethylene naphthalate (PEN) gives high performance films with physical, thermal and chemical characteristics better then those of polyethylene terephthalate (PET), it is used as a substitute for the latter in a large number of applications, particularly in film capacitors.

The PEN film of 25 µm thickness, and 1.36 g/cm³ density was provided by Dupont de Nemours Luxembourg. The PEN sample was prepared with gold evaporated electrodes, 2 cm in diameter, on
both sides of the sample. The chemical structure of PEN is reported in figure 1.

3. Experimental and method

3.1. Transient current technique
A DC voltage was applied to a sample at a constant temperature, and the charging current was measured up to three hours. The voltage was then removed and the discharging current of the short-circuited sample was recorded for three hours, according to the experimental setup [1]. The experimental cell was connected to a vacuum pump and a gas cylinder. This allowed to control the nature of the gas inside the cell, and to remove the moisture from the sample. A temperature controller connected to the heating element was located inside the cell. Hewlett Packard stabilized power supply (HP6525ADC) was used to deliver DC voltages up to 4000V. The current was measured by Keithley 617 programmable electrometer driven by a microcomputer. A high voltage relay switches from polarization when the sample was exposed to the voltage, to depolarization when the sample was grounded.

A new technique combining isothermal charging and discharging with non-isothermal discharging measurement proposed by Neagu et al [2], was used. In the second step of the experiment, the sample was heated at a constant rate of 2.4°C/min, from a charging temperature $T_c$ to a final temperature $T_f = 180^\circ$C. The current recorded was called "final thermally stimulated discharge current" or "non-isothermal discharging current".

3.2. DSC analyse
The thermal analysis of PEN samples was obtained by using the TA instruments (Differential Scanning Calorimeter, DSC Q10 t). DSC thermograms were recorded from 30 to 300°C by a constant heating rate of 10°C/mn under a nitrogen atmosphere to avoid thermal degradation. The obtained data was analyzed by TA Universal Analysis Software.

4. Isothermal currents

4.1. Charging Currents
Isothermal charging current, at different temperatures between 100 and 150°C, under a DC field of 72x10^6 V/m, are presented in figure 2. These results showed an anomalous behavior. Indeed, instead of monotous decrease, a rise after few minutes of polarization [3] was observed, which was generally attributed to space charge effect.

Several works have reported the existence of these peaks with different polymers, like polyethylene (PE) [4-5], polyethylene terephthalate (PET) [6] and polypropylene (PP) [7]. In PEN very few [8] references cited this behavior. The charging current peak is similar to that given by Many and Rakavy [9] relating to transient SCLC (space charge limited current). It appears at time $t_p$:

$$t_p = 0.786 \frac{d}{\mu F}$$ (1)
where \( F \) is the applied field, \( d \) the sample thickness, \( \mu \) the carrier mobility and \( \varepsilon \) the permittivity of the polymer. This time was related to the transit time of a space charge between electrodes.

4.2. **Discharging Currents**

Figure 3 shows typical discharging current measurement subsequent to the charging current displayed in figure 2. It can be noticed that the discharging current present a monotonous decrease, suggesting a dependence on time given by the Curie-Von Schweidler law [9]:

![Charging Current](image1)

![Discharging Current](image2)

**Figure 2.** Isothermal charging current in gold metallised PEN at different temperatures.

**Figure 3.** Isothermal discharging current in gold metallised PEN at different temperatures.
with $n$ an exponent close to unity. Neagu [10] suggested that the isothermal discharging current described by this power law for the whole glass transition temperature range, is due to the space charge released from the deeper traps existing in the amorphous volume. On the other hand, it should be noticed that the absorption current is not the mirror image of the discharging one. This suggests that the dipolar mechanism was not the predominant process. Mechanisms of dipolar origin are generally predominant at short time and low field [9].

5. **Final thermally stimulated discharge currents**

The isothermal discharging current (figure 4) becomes low but there is still space charge trapped in the sample. Subsequently the sample is heated up at a constant rate and the released current is recorded. Figure 4 presents the results obtained for a sample charged at 100°C under an electric field of 72 MV/m for 4000 s and isothermally discharged during 4000s. The non-isothermal discharging current was obtained for a heating rate of 2.4°C/min from 100 to 180°C. The variation of temperature as a function of time was linear. That allow us to represent the variation of current $I$ as a function of temperature $T$. A high increase of the current was observed. An increase in temperature seems to release some of the trapped charges. Two peaks were obtained: the first one located at $T_1 = 128°C$ near $T_g$ and the second one, which appears as a shoulder on the first one, at $T_2 = 150°C$.

5.1. **Analysis of $I(T)$ spectra**

The procedure used to fit the $I(T)$ spectra is illustrated in figure 4. We have found that the experimental data can be properly fitted by a superposition of two Gaussian profiles: One described the release of space charge related with the relaxation in the glass transition temperature range, while the other takes into account the detrapped charge from deeper traps associated to the premelting of crystallites. The fitting parameters are summarized in table 1.

The charge involved in the discharging step can be calculated using equation 3:

$$Q = \int_{100}^{180} \frac{I_{d} dT}{b} = \frac{A}{b}$$ (3)
Table 1. The Gaussian fitting parameters of a $I(T)$ spectra (figure 4) corresponding to a 2.4°C/min heating rate.

| Peak | Center $T_i$ (°C) | Area $A$ (A.°C) | Width (°C) | Height (A) | Charge $Q$ (nC) |
|------|-------------------|-----------------|-----------|------------|----------------|
| 1    | 128               | $2.0 \times 10^{-10}$ | 14.3      | $1.1 \times 10^{-11}$ | 5.0           |
| 2    | 150               | $1.6 \times 10^{-10}$ | 19.7      | $6.6 \times 10^{-12}$ | 4.0           |

where $b$ is the heating rate and $A$ the Gaussian profile area.

Finally, the charge $Q_1$ was obtained by simple integration of the Gaussian profile peaked at $T_i=128°C$. With a similar procedure the charge $Q_2$, associated to the second curve, was also estimated. These charges are less than 1% of the charge $CV = 0.6 \mu C$ on the capacitor for $V = 1800V$ and $\varepsilon_r = 3$.

5.2. Heating rate effect
The heating rate is generally an important parameter for non-isothermal measurements. It can give the possibility to investigate charge detrapping and transport mechanism. With the aim to examine if the temperatures of the peaks are related the measuring conditions, the experiments were repeated in identical conditions but with higher heating rate.

The final thermally stimulated discharge current obtained with a sample charged at 100°C under an electric field of 72 MV/m for 4000s, and isothermally discharged during 4000s, for a heating rate of 4.8°C/min from 100 to 180°C, is displayed in figure 5. These experimental data can also be fitted by two Gaussian profiles, the first one peaked at 132°C and the second one at 151°C. The fitting parameters are reported in table 2.

The first observation is that the heating rate does not affect significantly the appearance and the localization of peaks. On the other hand the height of the two peaks increases with $b$. Indeed, doubling the heating rate induced a more than doubling of the peak heights. But there is a less change in the charge values $Q_1$ and $Q_2$ as indicated in tables 1 and 2. In fact, the heating rate of 2.4°C/min is still high to permit the observation of the two peaks. Consequently, an increase of $b$ will not affect largely the $I(T)$ spectrum. Contrarily, the situation where $b$ is increased from low values can exhibit a significant effect as mentioned by Neagu [11] in the case of PET films. It can also be noticed that the ratio of the height of the first peak to the second one is practically equal to ratio of the two heating rates,

$$\frac{H_1}{H_2} = 2.0 \quad \text{and} \quad \frac{H_1}{H_2} = 1.7 .$$

6. Differential Scanning calorimetry
The DSC thermogram of sample was given in figure 6. As the temperature increases, the glass transition, and the melting of PEN can be observed successively. The DSC thermogram of the semi-crystalline PEN shows a $T_g$ (glass transition temperature) at about 128°C, and $T_m$ (melting temperature) at 267°C. A small endothermic pre-melting peak was also observed at $T_{pm} = 150°C$. The presence of double melting peak was already reported [12] in PEN.

These experiments have allowed us to calculate the degree of crystallinity using the equation:

$$\chi(\%) = 100 \frac{\Delta H_m - \Delta H_c}{\Delta H_f} = 44\%$$

where $\Delta H_m$ and $\Delta H_c$ were respectively crystallization and melting enthalpy. $\Delta H_f = 103.4 \text{ Jg}^{-1}$ was a melting enthalpy of 100% crystalline PEN.
Table 2. The Gaussian fitting parameters of a $I(T)$ spectrum (figure 5) corresponding to a 4.8°C/min heating rate.

| Peak | Center $T_i$ (°C) | Area $A$ (A.°C) | Width (°C) | Height (A) | Charge $Q$ (nC) |
|------|-------------------|-----------------|------------|------------|-----------------|
| 1    | 132               | $3.8 \times 10^{-10}$ | 10.9       | $2.8 \times 10^{-11}$ | 4.8             |
| 2    | 151               | $2.6 \times 10^{-10}$ | 15.0       | $1.4 \times 10^{-11}$ | 3.3             |

7. Discussion
The increase of a non-isothermal discharge current is related to detrapping of space charge. The release of charges may be a result of increased motion of the polymer chains at the higher temperature, especially near $T_g$. Indeed, it is well known that glass transition temperature is associated with chain segment cooperative motion induced by diffusive rearrangement of main chain portions [13].

The peaks are localized at two temperatures which are in good concordance with DSC analysis and current-field $J(F)$ characteristics presented in previous works [14]. It would be noticed that this temperature (150°C) was presented by industrials as the maximal temperature of use. The two peaks suggest that there are, at least, two sorts of traps in which charges may be trapped. The first sorts of traps are shallow ones and the second types are deep ones. These traps can be of chemical or physical nature. According to Patsch [15], they may be foreign molecules, carbonyl groups or even polarized states that are able to capture a charge via self-trapping.

On the other hand, the charge concerned may be trapped in different sites associated with amorphous region, amorphous-crystalline boundaries and crystalline region, since the polymer studied is semi-crystalline.

In previous works [1] we have shown that, above 150°C, the shape of isothermal charging current change with temperature reflecting that at low temperature the charge is trapped mainly in the amorphous region but for higher temperature the charge penetrate into the sample and is trapped in the crystalline region [16].
8. Conclusion
These results implies that, after isothermal discharging there was still space charge trapped which cannot release from the sample and require an increasing of temperature. Indeed, the peak in non-isothermal discharge current at $T_g$, indicate that the change of polymer state, from glassy to rubbery, favor molecular motion and then facilitate the space charge detrapping process. The second peak was associated to premelting of crystallites.

9. References
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Acknowledgements
We wish to thank the Laboratoire de Génie Electrique (Toulouse) for providing us with sample.