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## The study of molecular movements in dielectrics using isothermal and non-isothermal current measurements

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**Abstract.** The electrical methods used to study the molecular movements in dielectric materials are based on the movement of the dipoles, which are parts of the component molecules, under a convenient external applied *DC* or *AC* electric field. We have proposed recently a combined isothermal and non-isothermal measuring protocol to analyze charge injection/extraction, transport, trapping and de-trapping in low mobility materials. During an electric polarization process or an electric charging process, besides the polarization process, electric charge is injected into the material. This charge is partially transported and partially trapped in the material, depending on the material properties and on the experimental conditions. As a consequence of the charge trapping process, the structure is *decorated* with space charge and during the subsequent thermally stimulated discharge current experiment we are observing an *apparent peak* and *the genuine peaks* that are related to dipole randomization and charge de-trapping determined by the molecular movements. The aim of this paper is to present a combined measuring protocol that allows to separate the apparent peak and the genuine peaks in polar and non-polar dielectric materials. The method is very sensitive, very selective and allows to reveal, in a single run, details that are not observed when other electrical and non-electrical techniques are used.

### 1. Introduction

For characterization of the dielectric materials and for a better understanding of the connection between their structure and their properties, it is necessary to use more and more sensitive methods to study the molecular movement at low dimensional scale approaching the nanometric scale. Detailed information on molecular motions in polymers can be obtained using the so-called Dynamic Mechanical Analysis [1], Differential Scanning Calorimetry (DSC), *AC* dielectric relaxation technique [2-6], etc. As concerns the electrical methods, there is always a contribution from the movement of electrons and ions, especially at low frequency and/or high temperature. Traditionally, the electrical methods used to study the molecular movements are based on the movements of the dipoles that are parts of the molecules [2-6]. In the case of the Thermally Stimulated Discharge Current method (TSDC) a *DC* field is applied to orientate the dipoles. Even in the case when the Windowing Polarization (WP) method is applied [4,5] the peaks are quite broad and the measured current is determined by the detrapped space charge (SC) and by dipole randomization. In our opinion the peaks are quite broad because during the charging step too much charge is injected into the sample. To overcome this difficulty we have proposed a combined protocol to analyze charge injection/extraction transport, trapping and detrapping in

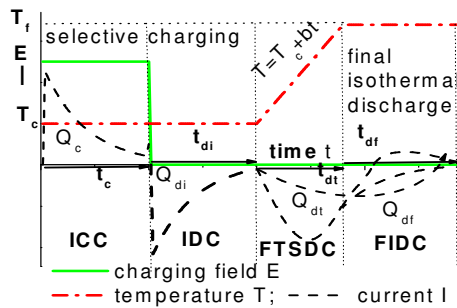


Figure 1. Schematic of the measurement protocol for the employed technique: variation of temperature, electric field and electric current with time during the four different steps.

low-mobility materials [7-9]. The combined protocol consists of four measuring steps: the isothermal charging current (ICC), the isothermal discharging current (IDC), the final thermally stimulated discharge current (FTSDC) and the final isothermal discharging current (FIDC) technique. The experimental conditions can be chosen so that the FTSDC and the FIDC are mainly determined by the movement of detrapped SC.

The aim of this article is to reveal the use of the FTSDC technique as a method to investigate the molecular dynamics in polar and non-polar materials. The method allows to separate the *apparent peak* from the *genuine peaks* related to polymer chain vibrations and structural changes and to reveal fine details not always observed by other methods.

## 2. Experimental

### 2.1. Measuring protocol

Figure 1 presents schematically the measuring protocol, giving the evolution with time  $t$  of the electric field  $E$ , the temperature  $T$  and the electric current  $I$  during the ICC, IDC, FTSDC and the FIDC measurements.  $T_c$  represents the initial temperature at which the sample is charged and at which the ICC and the IDC are measured.  $T_f$  represents the final heating temperature and the temperature at which the FIDC is measured. During the ICC measurement a step voltage is applied for a time  $t_c$  and the isothermal charging current is measured. At  $t = t_c$  the applied DC voltage is removed and the current released from the sample is isothermally measured during the IDC step for a time  $t_{di}$ . During this step it is expected that the polarization charge vanishes almost completely so that the IDC gives information primarily about the rapid polarization mechanisms related to the local movement of the molecular dipoles and/or the induced dipoles determined by SC polarization effects at the electrode-sample interface or in the bulk. The time  $t_{di}$  must be equal or higher than  $t_c$  because (i) the driving field is low during discharging current measurement, (ii) the charge trapping time can be long and consequently the current is low.

During the IDC step, for short times, the depolarization of the lowest activation mode (characterized by a lower value for the relaxation time) takes place. Consequently, the measured current density, which is the time derivative of the polarization, is mainly determined by polarization decay. It is very likely that there is a component of the current determined by a spontaneous and field-assisted detrapping of the trapped space charge. In the presence of trapping, the charge decay process is controlled by the trapping time. For longer trapping times, the current decays very slowly and for a long time period. The shape of the ICC and the IDC provide information about charging and discharging mechanisms and trapping/detrapping processes. During the first two steps (the ICC and IDC) a thermally and field-assisted selective charging takes place. The ratio  $t_{di}/t_c$  controls actually the energetic and spatial distribution of the trapped charge. At the end of the selective charging the stored charge is trapped at a mean depth into the material below a certain energy level. This trapped charge will be analysed in the next two steps.

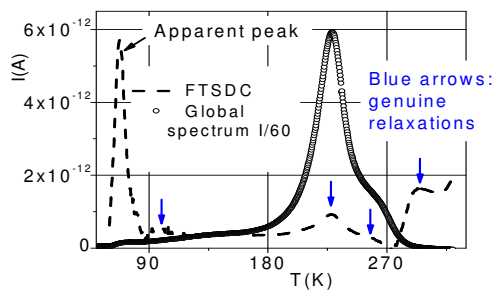
In a usual TSDC experiment a non-equilibrium state is frozen. During the heating of the sample the charge (dipolar or interfacial) relaxes and generates a current whose maximum is usually 10 to 25 K above the poling temperature, as observed using the WP [4].

The situation changes when the new proposed technique is used. At the end of selective charging the sample is heated at a linear heating rate in order to analyze the charge trapped in deeper traps. During the heating of the sample a current is measured which gives information

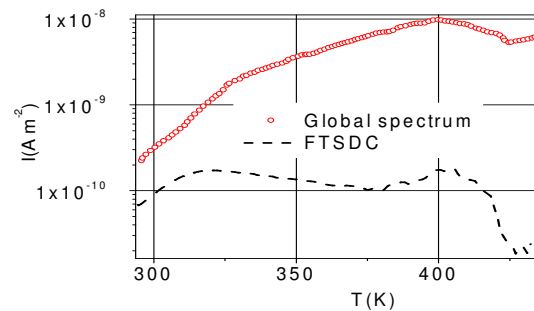
about the field-assisted-charged traps which are now mainly detrapped by thermal movement and structural movements. It is obvious that by choosing the experimental conditions, namely the charging field, charging temperature, work function of the electrodes, environmental atmosphere,  $t_c$  and  $t_{di}$  we can focus on certain states and valuable information about trapping sites and transport mechanism can be obtained [6-9]. The first and more intense contribution (starting from lower  $T$ ) represents the *apparent peak*, because the peak position changes significantly with experimental conditions [10]. The temperature of the maximum current of an apparent peak is dependent on  $T_c$ ,  $t_c$ ,  $t_{di}$  and on the heating rate.

### 2.2. Experimental measurements

Measurements, under a pressure of  $5 \times 10^{-3}$  Torr, were carried out on polar poly(vinylidene fluoride) (PVDF) films of 30  $\mu\text{m}$  thickness and semicrystalline non-polar Teflon FET films of 12.5  $\mu\text{m}$  thickness. The samples of 3 cm diameter were provided with vacuum evaporated silver electrodes (2.5 cm diameter). The charging field was lower than  $80 \text{ MV m}^{-1}$  and the temperature range from 60 to 320 K and from 273 to 440 K, respectively. The electrical current in the circuit was measured with an electrometer (Keithley 6517A). The electrometer was coupled to a PC for data acquisition and analysis. The sample temperature was maintained constant to within  $0.05^\circ\text{C}$ . The linear heating/cooling rate was controlled by a computer. Before measurements, the samples were kept in a desiccator until they were required for use.



**Figure 2.** The global spectrum (circles) and the FTSDC for PVDF at low temperature.



**Figure 3.** The global spectrum (circles) and the FTSDC for PVDF at high temperature.

### 3. Experimental results and discussion

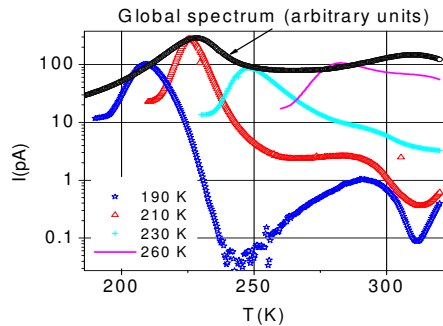
Figure 2 displays, by circles, the global spectrum measured for a PVDF sample charged at 273 K for 10 min under a field of  $40 \text{ MV m}^{-1}$  and cooled under the field to 60 K. Two broad relaxations are observed in the range from 200 to 300 K. The fine structure of the global thermogram in figure 2 can be analyzed using the FTSDC technique. The FTSDC measured for  $T_c = 90 \text{ K}$  and  $t_c / t_{di} = 5 \text{ min}/10 \text{ min}$  is displayed by a dotted line in figure 2. The first and more intense contribution (starting from lower  $T$ ) represents the *apparent peak*, whose position is around 68 K. Four *genuine* relaxations can be observed around 100, 230, 260 and 290 K. By an appropriate choice of the experimental conditions any of these genuine relaxations can be further analysed.

Figure 3 displays, by circles, the global spectrum measured for a PVDF sample charged at 393 K for 10 min under a field of  $10 \text{ MV m}^{-1}$  and cooled under the field to 293 K. The broad peak observed around 400 K is the *apparent peak*. The FTSDC measured for  $T_c = 293 \text{ K}$  and  $t_c / t_{di} = 5 \text{ min}/10 \text{ min}$  is displayed by a dotted line in figure 3. Two relaxations can be observed around 310 and 400 K. We can conclude that the FTSDC method is more selective and allows observation and separation of the elementary relaxations to a temperature resolution of approximately 30 K.

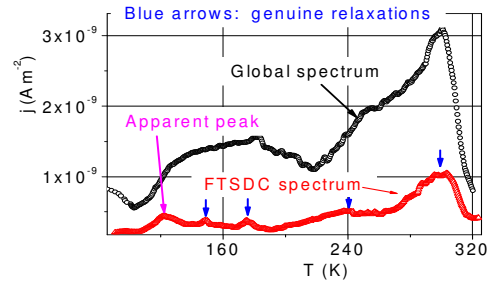
A comparison of data in figures 2 and 3 indicates that the method is more selective at low temperatures. This is a consequence of the fact that the sample resistivity is higher at lower temperatures and the charge involved in the charging process is lower.

Figure 4 displays the global spectrum measured for a PVDF sample charged at 320 K for 2 min under a field of  $80 \text{ MV m}^{-1}$  and four FTSDC thermograms to observe the broad relaxation in the range of 200 to 300 K. The *apparent peak* becomes broader as  $T_c$  gets closer to a genuine relaxation and the genuine peaks are not observed as individual relaxations. The situation becomes

similar with the broad peaks observed in AC measurements or when the traditional TSDC technique is used. This happens because by increasing  $T_c$  more SC is injected and trapped into the sample in deeper superficial and bulk traps. This charge will be released at higher and higher



**Figure 4.** The global spectrum and four FTSDC thermograms to observe the overlap of the genuine peaks as  $T_c$  is close to them.



**Figure 5.** The global spectrum (circles) and the FTSDC for Teflon, a non-polar material, at low temperatures.

temperatures with the consequence that the genuine relaxations will overlap. Consequently, to have a good selectivity and to separate the apparent peak from the genuine peaks or the genuine peaks between them, we have to choose  $T_c$  sufficient low in respect with the temperature of a genuine relaxation.

Figure 5 displays, by circles, the global spectrum measured for a Teflon sample charged at 300 K for 10 min under a field of  $60 \text{ MV m}^{-1}$  and cooled under the field to 60 K. Two broad relaxations are observed in the range from 120 to 320 K. The fine structure of the global thermogram in figure 5 can be analyzed using the FTSDC technique. The FTSDC measured for  $T_c = 100 \text{ K}$  and  $t_c / t_{di} = 15 \text{ min}/30 \text{ min}$  is displayed by triangles in figure 5. Besides the apparent peak around 120 K, four relaxations around 146, 180, 240 and 300 K can be observed. Because Teflon is a non-polar material we conclude that even the apparent peak is mainly determined by SC detrapping.

#### 4. Conclusions

The Final Thermally Stimulated Discharge Current technique is very selective and very sensitive allowing to separate the apparent peaks from the peaks related to polymer chain vibrations or the structural changes and to reveal fine details not always observed by other methods. It allows to observe and to separate the elementary relaxation in a temperature range of about 30 K. The method can be applied for polar and non-polar materials. The relaxation parameters for local and collective molecular movements can be determined by analyzing the experimental thermograms.

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