

# The study of weak molecular movements in nonpolar materials by decorating the structure with space charge

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The ac dielectric relaxation technique allows to investigate the molecular dynamics by studying the dipoles movement under ac field. The Thermally Stimulated Discharge Current technique allows to investigate the molecular dynamics by studying the dipoles movement under dc field. There is a permanent challenge to use electrical methods to characterize molecular movement in nonpolar materials. It is demonstrated in this paper that the Final Thermally Stimulated Discharge Current technique can be used to investigate the molecular movements in nonpolar dielectrics. By controlling the isothermal charging and/or discharging times the structure is "decorated" with space charge trapped in different traps. During the heating of the sample two types of peaks have been observed. The apparent peak, located 5 to 30 K above the charging temperature, is appropriate to study space charge injection/movement/trapping/detrapping. The peaks for which the difference between the temperature of the maximum current of the peak and the charging temperature is higher than about 30 K can be used to study the weak molecular movements and structural transformation in nonpolar materials.

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## 1. Introduction

Detailed information on molecular motions in polymers can be obtained using the so-called Dynamic Mechanical Analysis (DMA) [1]. Differential Scanning Calorimetry (DSC) may also be employed, since molecular motions are thermally activated within certain characteristic temperature regions [1]. In addition, melting processes in the polymer's crystalline phase are easily detected with DSC. The ac dielectric relaxation (DR) technique allows to investigate the molecular dynamics by studying the dipoles movement under ac field [2]. There is always a contribution from the movement of electrons and ions, especially at low frequency and/or high temperature [3,4]. The thermally stimulated discharge current (TSDC) method is very sensitive to both dipolar and space charge (SC) effects [5-8]. It is assumed that in the variant known as fractional polarization of TSDC (FPTSDC) the current is mainly determined by dipoles randomization. Conversely, the experimental conditions can be chosen so that the measured current is determined by the movement of detrapped SC [9-10]. In this respect, the sample is isothermally charged at  $T_c$  for a time  $t_c$  and subsequently discharged for a time  $t_{di}$  to allow the depolarization of the lowest activation modes. The ratio  $t_c/t_{di}$  controls the energetic and spatial distribution of the trapped charge which "decorate" the structure. If the trapping time is long,  $t_{di}$  can be very large, the isothermal discharging current becomes very low but there is still SC trapped in the sample. To analyze this SC, the sample is heated up at a constant heating rate and the released current is recorded. This is the Final Thermally Stimulated Discharge Current (FTSDC) technique recently proposed by us [9,10].

The aim of this article is to reveal the use of the FTSDC method to investigate the molecular dynamics in

Teflon FEP, an excellent insulator and a nonpolar material. We will report on the behavior of the FTSDC peaks and on the possibility to use the SC trapping/detrapping to observe the weak molecular movements in nonpolar materials.

## 2. Experimental

Measurements, under a pressure of  $5 \times 10^{-3}$  Torr, were carried out with semicrystalline Teflon FET films of  $12.5 \mu\text{m}$  thickness for charging fields lower than  $20 \text{ MV m}^{-1}$  and in the temperature range from 60 to 320 K. Teflon FEP is a copolymer of tetrafluoroethylene (PTFE) -  $\text{CF}_2\text{-CF}_2$ - with hexafluoropropylene (HFP)  $\text{CF}_3\text{CF=CF}_2$ . The samples of 3 cm diameter were provided with vacuum evaporated silver electrodes (2.5 cm diameter). The electrical current in the circuit was measured with an electrometer (Keithley 617) and recorded using an X-Y recorder. The electrometer was coupled to a PC for data acquisition and analysis. The sample temperature was maintained constant to within  $0.1 \text{ }^\circ\text{C}$ . The linear heating/cooling rate was controlled by a computer and the difference between the prescribed and the measured temperature was always lower than  $0.2 \text{ }^\circ\text{C}$  within the temperature range of interest. The FTSDC was measured usually up to 320 K using a constant heating rates of  $5 \text{ K/min}$ . Before measurements the samples were kept in a desiccator until they were required for use.

## 3. Measurement technique

Fig. 1 presents the measuring protocol giving the evolution with time  $t$  of the electric field  $E$ , the

temperature  $T$  and the current during the isothermal charging current (ICC), the isothermal discharging current (IDC), the FTSDC and the final isothermal discharging current (FIDC) experiments.  $T_i$  represents the initial temperature at which the sample is charged and at which the IDC is measured.  $T_f$  represents the final heating temperature and usually it is close to the maximum temperature at which the material is still stable or the maximum temperature at which the experimental setup can be heated. During the ICC a step voltage is applied for a time  $t_c$  and the charging current is measured.

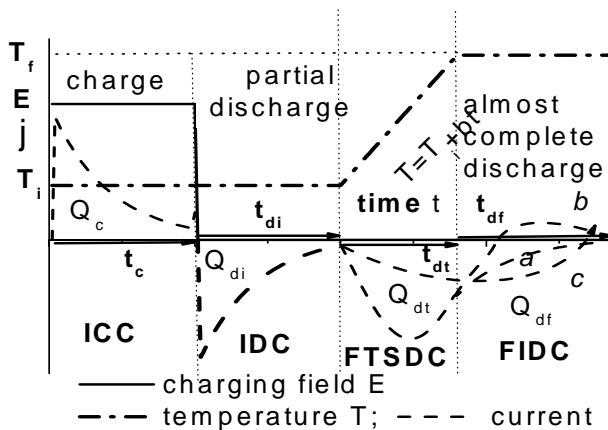


Fig. 1. The variation of temperature, electric field and current with time during the four steps of proposed technique.

It is recommended to choose  $t_c$  so that

$$\mu(T)Et_c < L/3 \quad (1)$$

where  $\mu(T)$  is the apparent or trap-modulated mobility and  $L$  sample's thickness. If  $t_c$  is short we expect that only the surface states are charged for low or moderate fields. As  $t_c$  increases more and more bulk states are involved in the charging process. If  $t_c$  is very long it is possible that the injected charge penetrates very deep into the sample and the efficiency of the measurement of the discharging current will decrease [6,7]. At  $t = t_c$  the applied voltage is removed and the current released from the sample is 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 measured current gives information primarily about polarization. It is very likely that there is a component of the current determined by a spontaneous and field-assisted detrapping of the trapped SC. The time  $t_{di}$  must be equal or higher than  $t_c$  because (i) the driving field is low, (ii) the trapping time can be long and (iii) the charge moves slowly. If  $t_{di}$  is short only the less persistent charge is removed, in other words only the shallow traps at the surface or close to the surface are discharged. As  $t_{di}$  increases the charge from deeper surface

and bulk traps is removed. The shape of the ICC and the IDC and the values of the total charge measured during the ICC ( $Q_c$ ) and during the IDC ( $Q_{di}$ ) provide information about charging and discharging mechanisms and trapping/detrapping processes. As long as the charging and discharging currents are similar and  $Q_c \cong Q_{di}$  the trapping process is not important. During the first two steps (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.

In a usual TSDC experiment a non-equilibrium state is frozen. During the heating of the sample the charge (dipolar or interfacial) relaxes in the field of the frozen charge and generates a current whose maximum is usually 10 to 25 °C above the poling temperature, as observed using the windowing polarization [8]. The movement of the released charge is significantly dominated by the trapped charge and we can talk about an interaction between dipolar and space charge.

The situation changes when the new proposed technique is used. At the end of selective charging the sample is heated in order to analyze the charge trapped in deep traps. During the heating of the sample a current is measured which gives an image of the field-assisted-charged traps which are now mainly detrapped by thermal movement and structural movements. It is obvious that by choosing experimental conditions, namely 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 [6,7].

It is a common practice in a TSDC experiment to stop the heating process after a peak was recorded and many times in spite of the fact that there are clear evidences that another peak emerge at higher temperatures. An opposite situation is the one when we are forced to stop the heating at a high temperature  $T_f$  at which the sample is still stable. Actually the trapping time could be high, in respect with the heating rate, even at high temperature. It is judicious to use a low heating rate especially to be sure that we are dealing with thermal equilibrium processes but the lower limit is imposed by experimental considerations [6,9]. Under these circumstances it is advisable to continue the measurements at high temperature. This is the Final Isothermal Discharging Current (FIDC) step in Fig. 1.

#### 4. Experimental results

Fig. 2 displays a global thermogram measured for a sample charged at 320 K for 2 min under a field of 10 MV m<sup>-1</sup> and cooled under the field to 80 K. A very broad band is observed in the range from 100 to 220 K, a narrow and sharp band around 300 K, a broad relaxation around 250 K

and a weak relaxation around 80 K. These relaxations are related to SC detrapping in Teflon FEP because the material is nonpolar.

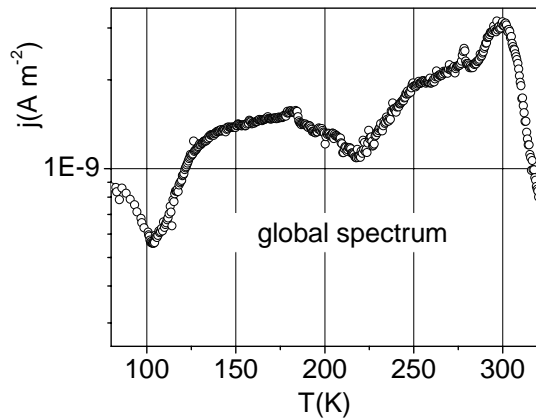


Fig. 2 The global thermally stimulated discharge current spectrum for a sample charged at 320 K.

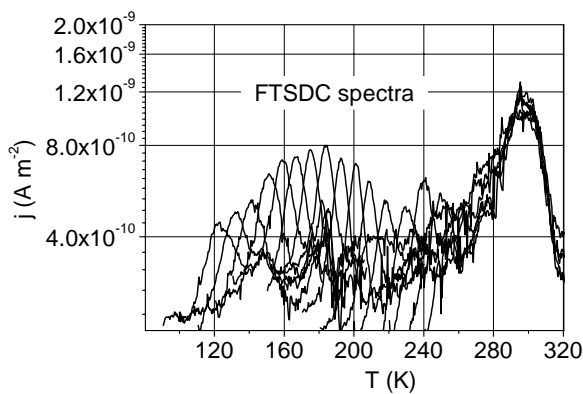


Fig. 3 The FTSDC for different charging temperatures from 90 to 270 K.

The fine structure of the global thermogram in Fig. 2 can be analyzed using the FTSDC technique [9,10]. Fig. 3 shows the FTSDC peaks obtained for different polarization temperatures from 90 to 270 K. The charging field was  $20 \text{ MV m}^{-1}$  and the charging time  $t_c = 30 \text{ min}$  was equal with the isothermal discharging time  $t_{di}$ . To better observe the individual thermograms in Fig. 3, Fig 4 displays the FTSDC measured for  $T_c$  from 90 to 120 K. The charging field was  $20 \text{ MV m}^{-1}$  and the charging time  $t_c = 30 \text{ min}$  was equal with the isothermal discharging time  $t_{di}$ . Fig. 5 displays the FTSDC measured for  $T_c$  from 190 to 270 K using similar experimental conditions as for the data in Fig. 3. Every individual thermogram in Fig. 4 consists of three contributions. The first and more intense contribution (starting from lower temperature) represents the apparent peak, whose position changes significantly with  $T_c$  [6,7]. In all cases the apparent peak's position and magnitude primarily reflects the field-assisted charge trapping/detrapping mechanisms and secondarily it reflects the local molecular movement. The second contribution, centered around 146 K, is partially masked by the apparent

peak. The third contribution, centered around 180 K, shifts very little to higher temperature with increasing  $T_c$  but the maximum current intensity increases significantly. It is important to underline that this narrow relaxation is observed even when  $T_c = 90 \text{ K}$ , i.e. for a very high difference between  $T_c$  and the maximum current temperature  $T_m$ , indicating that the peak is related to SC detrapping. The peak shape suggests that it is related to a sharp structural movement.  $T_m$  indicates precisely the temperature where the molecular movement is stronger. Consequently, it results that to study SC injection/movement/trapping/detrapping it is appropriate to study the apparent peaks. To study the molecular movement it is indicated to analyze the contribution for which the difference  $T_m - T_c$  is higher than about 30 K.

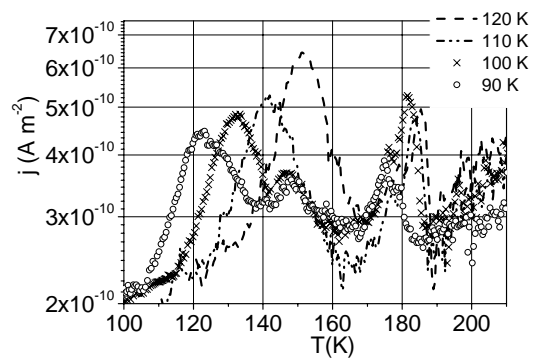


Fig. 4. The FTSDC for different charging temperatures to observe the apparent peaks and the relaxations around 146 and 180 K.

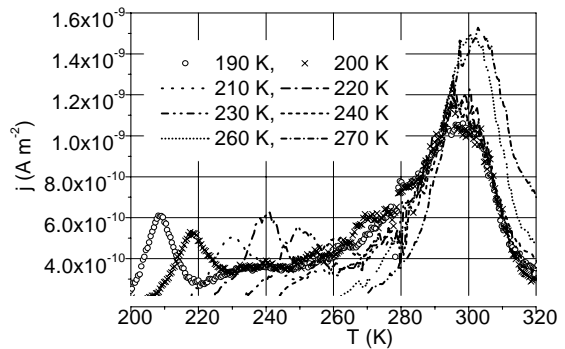


Fig. 5. The FTSDC for different charging temperatures to observe the apparent peaks and the relaxations around 240 and 300 K.

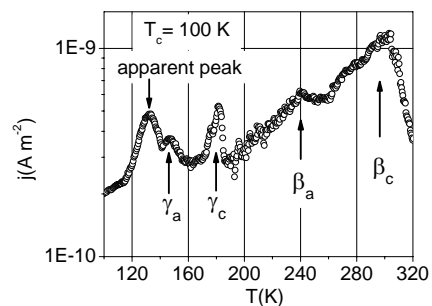


Fig. 6. The FTSDC for  $T_c = 100 \text{ K}$  to observe the apparent peak and the four relaxations.

The data in Fig. 6 shows the thermogram for  $T_c = 100$  K. This figure clearly demonstrates the sensitivity and the selectivity of the FTSDC method. Besides the apparent peak at 133 K four other relaxations are observed around 146, 175, 240 and 298 K.

## 5. Discussion

To be possible to identify the observed relaxation and to ascribe them to different molecular movements we will present the relaxation reported in literature to date for Teflon FEP. Dielectric relaxation in Teflon FEP can presumably result only from the presence of polar impurities attached to the polymer chains. The ac dielectric data show a relaxation around 94 K [11,12], a relaxation around 160 K [13] and a broad relaxation around 219 K [14]. The relaxation observed below 120 K in the dielectric data, but not in the ultrasonic data, is independent of polymer density and HFP content [11,12].

The Dynamic Mechanical Analysis data at a frequency of 1 Hz for 75  $\mu\text{m}$  thick films showed a broad peak for the phase shift  $\tan\delta$  between the real part and the imaginary part of the shear modulus around 193 K [15]. High resolution low frequency DMA at 0.1 Hz for polytetrafluoroethylene showed a peak around 177 K that was identified with the  $\alpha$  relaxation [15]. DMA also show narrow peaks at the phase transitions near 293 and 308 K [15].

Differential Scanning Calorimetry measurements show an endothermic peak at approximately 190 K [14]. A broad, thickness-dependent, but not so well-defined region of energy consumption between 273 to 423 K is related to glass I transition [14].

The molecular origin of charge trapping in Teflon FEP is still not fully understood. Three different levels of the molecular structure are considered as possible sites for charge trapping: (i) suitable atoms or bonds of the macromolecules themselves, (ii) microscopic "cages" formed by selected atoms of neighboring polymer chains, and (iii) crystalline or amorphous regions or their interfaces. During the ICC steps the traps are filled with SC. At the end of the IDC (step 2 in Fig. 1) only the charge trapped in shallow traps is removed. We can say that during the first two steps the structure is decorated with SC. The current measured during the FTSDC is generated by the charge detrapped from deeper traps. SC detrapping should be very closely related to local molecular motion. The measured current implies the release of the charge carriers from traps and the subsequent transport of these carriers from their place to electrodes. There are two types of peaks. The first and the more intense contribution represents the apparent peak, whose position change significantly with  $T_c$ . The apparent peak position and magnitude primarily reflects the field assisted charge trapping/detrapping mechanisms and secondarily it reflects the local molecular dynamics. The second contribution is centered at temperatures much higher than the charging temperature. Consequently, it results that to study SC injection/movement/trapping/

detrapping it is appropriate to study the apparent peaks. To study the molecular movement and phase transitions it is indicated to analyze the contribution for which the difference  $T_m - T_c$  is higher than about 30 K.

The  $\gamma$  relaxation in polymers is attributed to local motions of aliphatic segments involving at least four chain atoms [11]. In Teflon and Teflon FEP a relaxation around 180 K have been observed in DMS, DSC and ac measurements. The sharp peak around this temperature in Fig. 4 is an indication that this relaxation can be identified with a relaxation in the crystalline fraction, the  $\gamma_c$  relaxation. The ac dielectric relaxation in this temperature region is an indication that there is SC trapped at the crystalline-amorphous interface. The peak around 146 K is reported for the first time in this paper. The peak is partially masked by the apparent peak. This relaxation was not clearly observed in other experiments because it is very weak. We suggest that this is the  $\gamma_a$  relaxation.

The data in Fig. and 5 demonstrate the complexity of the  $\beta$  relaxation in Teflon FEP. An accepted hypothesis is that the  $\beta$  relaxation in PTFE involves oscillations of the chain segments around the chain axes in the crystals [16]. The complex peak around 300 K is associated with the well observed crystal disordering transitions at 292 and 303 K in PTFE. We suggest that this is the  $\beta_c$  relaxation. The weak relaxation around 240 K was attributed to a shift of the  $\beta$  relaxation region in PTFE to lower temperatures when the HFP component is added [16]. The shape of this peak suggests that it is not related to a crystal disordering transition but to polar impurities attached to the polymer chains. It is very likely that the  $\beta$  relaxation has two components and this is the  $\beta_a$  relaxation. It is the merit of the FTSDC technique that is very sensitive and very selective and allows us to observe all this weak relaxations. The data in Fig. 6 show that by charging the sample at 100 K we can observe all the molecular movements from 100 to 320 K, 320 K being the upper limit of the working temperature for our experimental setup.

## 6. Conclusions

The FTSDC technique is very selective and very sensitive allowing to separate the apparent peak from the peaks related to polymer chain vibrations and structural changes and to reveal fine details not always observed by another methods. Four relaxations have been identified for Teflon FEP in the temperature range from 100 to 320 K. These relaxations are only partially observed by use of the DMA, DSC or DR technique. The relaxations are related to molecular movement in the crystalline fraction or in the amorphous fraction. The sharp peaks are associated to molecular movements in the crystalline fraction and the broad peaks are associated to molecular movements in the amorphous fraction. As concern the selectivity the technique allows, i.e., to separate the two peaks around

146 and 180 K, in the low temperature range where the peaks are very broad and overlap when other dielectrical techniques are used. As concern the sensitivity, charges (obtained by time integration of the FTSDC) well below 10 pC can be detected. This means a variation of about 0.0004 for the real part of permittivity for our experimental conditions.

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