

# On the shift of the fractional polarization peak position in the range of the glass transition

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## Abstract

Using the fractional polarization thermally stimulated discharge current technique the shift of the peak position in the temperature range of the glass transition of the amorphous phase for polyethylene terephthalate is analyzed. The difference between the temperature of maximum intensity of an elemental peak  $T_m$  and the polarization temperature  $T_p$  provides information about the contribution of the molecular mobility to the dielectric relaxation. The temperature of 363 K was identified as the lower limit at which the dielectric manifestation of the glass transition becomes significant and the temperature of 403 K represents the higher limit of dielectric manifestation of the glass transition. It is proposed that the dielectric transition temperature associated with the non-local  $\alpha$  relaxation is to be determined from the condition  $T_m = T_p$ . At this temperature the dipoles move equally fast during polarization or depolarization stage. The activation energy continuously grows and the pre-exponential factor significantly decreases as the polarization temperature increases. The relaxation time  $\tau(T_m)$  at the temperature of maximum intensity of an elemental peak decreases from 762 to 545 s as  $T_m$  increases from 356 to 391 K, demonstrating a narrow distribution of relaxation times. A structural change has been observed around 368 K.

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## 1. Introduction

Thermally stimulated discharge current (TSDC) method is largely used for investigating charge relaxation and molecular dynamics in various materials [1]. For the polar semicrystalline polymers the dielectric polarization is determined by dipoles orientation in the amorphous and in the crystalline regions and by space charge (SC) accumulated at different interfaces (electrode polarization and Maxwell–Wagner interfacial polarization) [1–4]. The high-resolution power of the TSDC, especially in the modification

known as the fractional polarization (FP) [5] (or windowing polarization or thermal sampling), allows the decomposition of a relaxation into individual components. All the thermal motions of the molecules are contributing to charge detrapping and transport.

The glass transition temperature  $T_g$  for polyethylene terephthalate (PET), chosen as a model material, changes from 341 K for the amorphous polymer to 398 K for crystalline and bioriented material [6], being very broad and weak in the last case. The  $\alpha$  relaxation associated with the glass transition is observed as a weak and broad dispersion in alternating current measurements [7–12]. It is partially masked by conductivity effects [9,10] and by the constraints imposed

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by crystallites upon the amorphous phase [7,8]. The global TSDC spectrum displays a broad peak in the  $T_g$  range and few shoulders have been identified using the partial heating technique [10,13–15].

The temperature of the maximum intensity of the FP peaks obtained at low temperature, in the range of the local (secondary)  $\beta$  relaxation, are in general about 10–20 K above the poling temperature. There is not an accepted explanation of the shift between the polarization temperature  $T_p$  and the temperature of the maximum intensity of an elemental peak  $T_m$ . It is considered that the appearance of FP maxima occurring at about  $(T_p + 10)$  K, for a heating rate  $b = 0.11$  K/s, can be explained if dipolar orientation with a relaxation time spectrum is assumed [16]. Little at the present time is known about the shift of  $T_m$  in respect with  $T_p$  when the temperature varies in the range of the glass transition where the non-local (primary)  $\alpha$  relaxation occurs.

The aim of this article is to analyze the variation of  $(T_m - T_p)$  for the elemental peaks obtained in the range of the glass transition of the amorphous phase for biaxially drawn semicrystalline polyethylene terephthalate by using the FP method. Elemental peaks have been obtained and the relaxation parameters computed by fitting the experimental data with an appropriate equation. It is proposed that the dielectric transition temperature associated with the non-local  $\alpha$  relaxation to be determined from the condition  $T_m = T_p$ . The results are explained considering the strong influence of the thermal agitation on the dielectric relaxation.

## 2. Experimental procedure

The samples used in these experiments were biaxially drawn sheets of PET of 8  $\mu\text{m}$  thickness supplied by industry. Circular pieces were dipped into a hexane bath for 2 min to reduce surface contamination. Disk specimens of 40 mm diameter were provided with two measuring electrodes of 25 mm diameter by evaporating silver at a pressure of  $2 \times 10^{-5}$  Torr. Measurements of TSDC, at a chamber pressure of  $5 \times 10^{-3}$  Torr, were made for a polarization fields of  $8.75 \text{ MV m}^{-1}$ . The fractional polarization peaks were recorded with the following polarization conditions. Isothermal polarization time  $t_p$  at selected temperatures  $T_p$ , followed by cooling to  $(T_p - 5)$  K in 2 min

with the electric field on. At  $(T_p - 5)$  K the electric field was removed and the sample was kept for  $t_s = 2$  min in short circuit. Further the sample was cooled down (0.5 K/s) at approximately  $(T_p - 50)$  K in short circuit. The method of measurements is described in a previous paper [4]. The temperature of measurements was varied over the range 293 to 463 K. A Cu-Constantan thermocouple mounted in the sample holder and adjacent to the film, allowed the temperature measurement with a precision of 0.1 K. The sample temperature was maintained constant to within  $\pm 0.1$  K. The current measurements were taken at a heating rate  $b = 1$  K/min. The linear heating rate was controlled by the computer and the difference between the prescribed and the measured temperature was always lower than 0.3 K. Prior to every TSDC measurements the sample was heated to 463 K to anneal out any thermal and electrical pre-history. It was kept there for a sufficient long time until the discharging current becomes insignificant. It was then slowly cooled down to room temperature. In this way, the sample is conditioned so that prior history does not influence the next measurements impairing repeatability and interpretation of results [17]. The degree of crystallinity determined by X-ray diffraction was 68% and it was found to be practically unchanged by the conditioning procedure.

## 3. Data analysis

The current density measured during a TSDC experiment can be written as [1]:

$$j(T) = \frac{P_0(T_p)}{\tau(T)} \exp\left(-\frac{1}{b} \int_{T_0}^T \frac{dT'}{\tau(T')}\right) \quad (1)$$

where  $P_0(T_p)$  is the equilibrium polarization produced during the polarization of the sample at  $T_p$ ,  $\tau(T)$  the relaxation time,  $b = dT/dt$  the heating rate and  $T_0$  the initial temperature. The maximum current occurs when [1]:

$$\frac{d\tau(T)}{dT} = -\frac{1}{b} \quad (2)$$

In what follows we will assume that for every elemental peak an Arrhenius-like dependence of the relaxation time on temperature is valid [18]:

$$\tau(T) = \tau_0 \exp\left(\frac{W}{kT}\right) \quad (3)$$

where  $\tau_0$  represents the relaxation time at infinite temperature,  $W$  the activation energy of dipole disorientation and  $k$  is the Boltzmann constant.

From Eqs. (2) and (3) it results:

$$\tau_0 \frac{W}{kT_m^2} \exp\left(\frac{W}{kT_m}\right) = \frac{1}{b} \quad (4)$$

where  $T_m$  is the temperature of maximum intensity of the FP peak. The pre-exponential factor  $\tau_0$  can be eliminated from Eq. (1) by using Eq. (4). It follows for the TSD current density:

$$j(T) = P_0(T_p) \frac{bW}{kT_m^2} \exp\left(\frac{W}{kT_m}\right) \exp\left[-\frac{W}{kT} - \frac{W}{kT_m^2} \exp\left(\frac{W}{kT_m}\right) \times \int_{T_0}^T \exp\left(-\frac{W}{kT'}\right) dT'\right] \quad (5)$$

Eq. (5) represents an improved form of Eq. (1). The number of adjustable parameters is reduced to 2, namely  $P_0(T_p)$  and  $W$ , allowing a better evaluation.  $T_m$  is determined from the experimental data.

The mean relaxation time of the process may be obtained from Eqs. (3) and (4) for  $T = T_m$  it results:

$$\tau(T_m) = \frac{kT_m^2}{bW} \quad (6)$$

By following the variation of  $W$ ,  $\tau_0$ ,  $\tau(T_m)$  and  $(T_m - T_p)$  when the polarization temperature  $T_p$  (and implicitly  $T_m$ ) covers the glass transition range, we can analyze the dielectric manifestation of the glass transition. The dielectric transition temperature corresponding to the non-local  $\alpha$  relaxation associated with the glass transition can be determined.

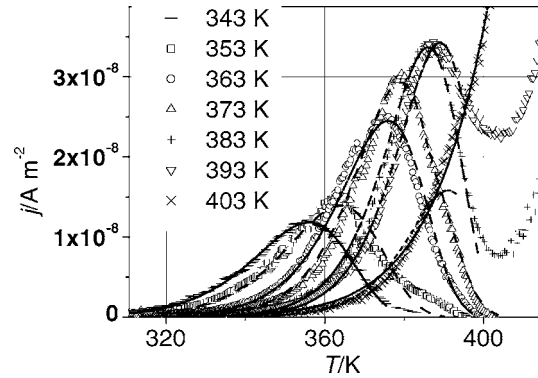


Fig. 1. Thermally stimulated discharge current (fractional polarization) for PET samples polarized for 30 min under a field of  $8.75 \text{ MV m}^{-1}$  at different temperatures. The dashed lines represent the best fitting curves obtained using Eq. (5). The full line represents the best fitting curve obtained using the initial rise method for a sample polarized at 403 K.

#### 4. Results and discussions

Fig. 1 displays the FP spectra for samples polarized for  $t_p = 30 \text{ min}$  and  $E_p = 8.75 \text{ MV m}^{-1}$  at seven temperatures  $T_p$  between 343 and 403 K. The dashed lines represent the best fitting curves obtained using Eq. (5). The values of the fitting parameters are presented in Table 1. For polarization temperatures higher than 373 K, a second relaxation is entering at high temperatures. For the sample polarized at 403 K the peak reduces to a shoulder around 391 K, but knowing  $T_m$  and using Eq. (5) it was possible to compute the peak parameters. The full line along the data measured for  $T_p = 403 \text{ K}$  (crosses in Fig. 1) represents the best fit obtained using the initial rise (IR) method (in this approximation the integral term in Eq. (1) is neglected).

Table 1

The results obtained from the fitting of experimental data to the theoretical model

$T_p$ (K)	$T_m$ (K)	Fitting to Eq. (5)				$\Delta\epsilon'$
		$W$ (eV)	$P_0(T_p)$ ( $\text{C m}^{-2}$ )	$\tau_0$ (s)	$\tau(T_m)$ (s)	
343	356	0.86	$1.72 \times 10^{-5}$	$1.1 \times 10^{-10}$	762	0.21
353	364	0.93	$2.6 \times 10^{-5}$	$9.6 \times 10^{-11}$	736	0.31
363	376	1.12	$4.1 \times 10^{-5}$	$6.2 \times 10^{-13}$	652	0.47
373	379	1.18	$4.9 \times 10^{-5}$	$1.3 \times 10^{-13}$	629	0.57
383	386	1.36	$5.0 \times 10^{-5}$	$9.7 \times 10^{-16}$	566	0.57
393	389	1.40	$5.0 \times 10^{-5}$	$5.4 \times 10^{-16}$	562	0.58
403	391	1.45	$2.1 \times 10^{-5}$	$1.1 \times 10^{-16}$	545	

Differential scanning calorimetry measurements on the same sample showed a broad and weak glass transition in the temperature range 353–393 K [9] and a small peak around 358 K. This peak was related with the physical aging undergone by the sample while it was stored at room temperature for a long time. The steep variation of the current in Fig. 1 around 368 K suggests that there is a structural modification around this temperature. The TSDC measurements on the same material combined with peak cleaning technique [4] revealed three shoulders in the same temperature range, namely at around 363, 368 and 378 K. It is an experimental fact that in most cases a FP peak is not completely clean of other influences. As long as these influences are small the peak can be considered as elemental. It is the case of the data presented in Fig. 1. The polarization parameters have been carefully chosen (i) to assure a complete filing of the states ( $t_p$  is higher than the mean relaxation time of every elemental peak and consequently the polarization at the end of  $t_p$  is at least 0.9 from the maximum expected value) [1], (ii) to have a reasonable high current for a relatively low heating rate (1 K/min), and (iii) to obtain a well-shaped elemental peak. The activation energies of 1.18 and 1.40 eV for the samples polarized at 373 K ( $T_m = 379$  K) respective 393 K ( $T_m = 389$  K) are in good agreement with the values determined using the IR method for the shoulders observed at 378 K ( $W = 1.21$  eV) and 398 K ( $W = 1.41$  eV) [4] for the same material.

Additional peak assignments are obtained by noting the dependence of the current maxima on the magnitude of the polarization field strength  $E_p$ . For relaxations at  $T_g$  and below, the majority of literature indicates that the current always scales linearly with  $E_p$ . Fig. 2 shows four elemental peaks obtained for the sample polarized for 10 min at 373 K under different polarization voltages. For  $U < 70$  V, the current scales linearly with the field. For  $U = 70$  V, there are small deviations and for  $U = 100$  V, there are important deviations meaning that there are contributions from space charge. To keep these contributions as low as possible, but to obtain well-shaped peaks, the polarization voltage was 70 V for all experiments excepting that presented in Fig. 2 for 100 V.

The equilibrium polarization  $P_0(T_p)$  can be related to the dielectric strength (or dielectric increment)  $\Delta\epsilon'$  measured for a given relaxation process [1,2]

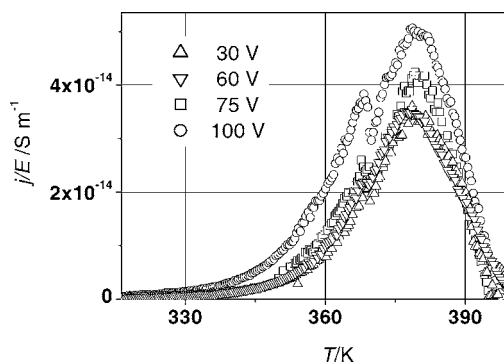


Fig. 2. The fractional polarization signal for samples polarized for 10 min at 373 K under different applied voltages to observe the dependence on the applied field.

$\Delta\epsilon' = P_0(T_p)/\epsilon_0 E_p$  where  $\epsilon_0$  is the permittivity of free space and  $E_p$  the electric field strength during polarization. Using the values of polarization obtained by fitting (see Table 1) the values for  $\Delta\epsilon'$  have been determined and are presented in Table 1. The dielectric increment can be determined as well from the AC dielectric relaxation measurements. Fig. 3 shows the dielectric increment determined from AC measurement at three frequencies and from the TSDC measurements. There is a good agreement between the values obtained using the two methods emphasizing the advantage of using Eq. (5) and the dipolar origin of the measured current (in good agreement with data in Fig. 2).

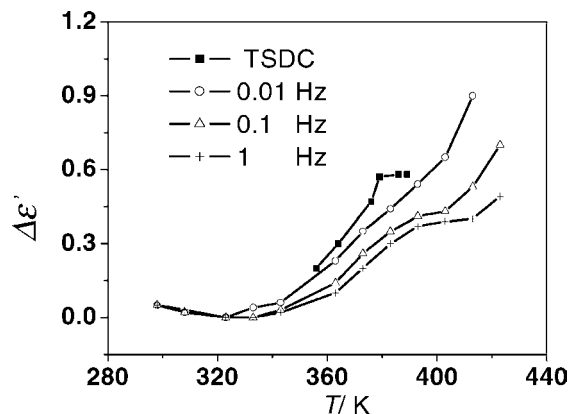


Fig. 3. The variation of dielectric strength (or dielectric increment)  $\Delta\epsilon'$  with temperature.

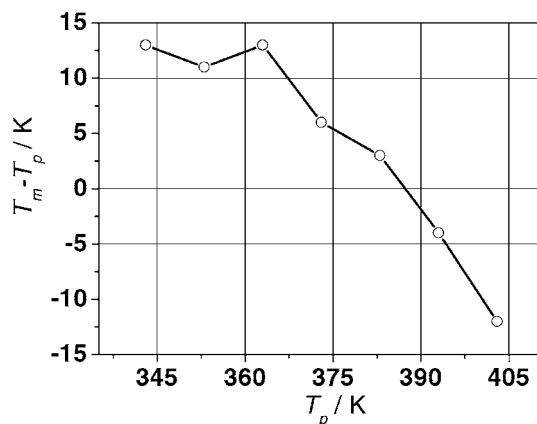


Fig. 4. The difference between the temperature of the maximum intensity of the peak and the polarization temperature vs. the polarization temperature.

Fig. 4 shows the variation of  $(T_m - T_p)$  versus  $T_p$ . The difference  $(T_m - T_p)$  is  $\cong 12.5$  K as  $T_p$  increases from 343 to 363 K. It decreases from 13 to  $-12$  K as  $T_p$  increases further from 363 to 403 K. For  $T_p = 387$  K,  $(T_m - T_p)$  is zero. There is a general observation that the current maxima of an elemental peak obtained by FP, especially in the temperature range of the  $\beta$  relaxation, occurs always quit accurately 10 K above  $T_p$ , for  $b = 0.11$  K/s [16]. This behavior is explained in terms of dipole orientation processes having a continuous relaxation time spectrum [16]. The data in Fig. 4 show that as  $T_p$  increases in the interval from 343 to 363 K the difference  $(T_m - T_p)$  is about 12.5 K. We will consider first this interval. A possible explanation of the observed behavior is as follow. The peak position is determined by the increase of the mobility of the dipoles, that become free to rotate, and progressively exhaustion of the induced polarization. During polarization the field aligns the dipoles. During heating, at each temperature including  $T_p$ , a part of the dipoles rotate to the initial positions and generate a discharging current but some of them will need a higher energy to return to the initial position. In order to disorientate those dipoles it is necessary to heat up the sample meaning that, in general,  $T_m$  is higher than  $T_p$ . The low heating rate of 1 K/min (the typical heating rate for FP measurements is 7 K/min [5,16,18]) was purposely chosen to account for the fact that the dipoles do not disorientate instantaneously. If the heating rate is high, the dipoles do not have sufficient

time to disorientate and it is evident that  $T_m > T_p$ . It is well known that if  $b$  increases the peak shifts to higher temperatures [1]. Actually the mean value of  $\tau(T_m)$  for the data presented in Table 1 is 636.4 s meaning that even  $b = 1$  K/min is too high and the dipoles do not have sufficient time to disorientate as long as the thermal agitation is low, meaning for  $T < T_g$ .

As  $T_p$  increases approaching  $T_g$ , there is an increase of the number of oriented dipoles, assuming that the formation conditions are chosen so that the degree of filling produced by polarizing field approaches the maximum value [1] and a strong increase of molecular mobility. For  $t_p = 30$  min (usually in FP experiments  $t_p = 2$  min [5,16,18]) and a mean relaxation time of 636.4 s about 94% of the dipoles are oriented. During heating the dipole disorientates faster, the current increases faster and consequently the interval between  $T_m$  and  $T_p$  diminishes. The number of dipoles that can be aligned by the field is limited, for the given temperature range, as results from the value of  $\Delta\epsilon'$  in Fig. 3. Consequently the difference  $(T_m - T_p)$  progressively decreases when  $T_p$  increases. From the data in Fig. 4, it results that for  $T_p = 387$  K,  $(T_m - T_p)$  is zero. As the temperature further increases the thermal agitation increases, the dipoles disorientate faster and the difference  $(T_m - T_p)$  is negative.

In the light of the above discussion 363 K represents the lower temperature at which the dielectric manifestation of the glass transition becomes significant (the dipole (dis)orientation is speeded up) and 403 K represents the higher limit of dielectric manifestation of the glass transition (for higher  $T_p$  the thermal energy is so high that the dipoles in the amorphous part can not longer be frozen). At 387 K,  $T_m - T_p = 0$  meaning that the dipoles move equally fast during polarization or depolarization stage. This temperature gives the position of the  $\alpha$  peak for the material for a heating rate of 1 K/min. At this temperature the number of dipoles aligned by the field is maximum, a fact that can be important for the applications of this material as dipolar electret. For  $T_p = 403$  K a new relaxation process becomes dominant and the  $\alpha$  relaxation is observed as a small shoulder around 391 K. The apparent activation energy determined by the IR method (neglecting the contribution from the previous peak) was 0.96 eV. It is lower than 1.45 eV computed assuming that the current is determined by the first relaxation process (showed by the dashed line superimposed on



the crosses in Fig. 1), meaning that only the fast components of the new relaxation process are involved.

From the data in Table 1, it can be observed that there is a distribution in activation energies and a broad distribution in pre-exponential factors. The relaxation time at the temperature of maximum intensity of the peak  $\tau(T_m)$ , computed using Eq. (6), decreases from 762 to 545 s as  $T_m$  increases from 356 to 391 K. The mean relaxation time is 636.4 s. The decrease of  $\tau(T_m)$  is correlated with the decrease of  $(T_m - T_p)$  actually with the modification of the type of dipoles aligned by the field. This variation of the relaxation time describes (i) the distribution of the relaxation times, and (ii) the increase of the molecular motion as  $T_p$  approaches  $T_g$ . It must be emphasized that there is big variation of  $\tau_0$  and a significant variation for  $W$  but  $\tau(T_m)$  do not change significantly, proving a narrow distribution of relaxation times. Although  $\tau(T)$  varies in good agreement with Arrhenius law underlying the fact that there are mono-energetic processes,  $\tau(T_m)$  changes less from one relaxation process to the nearby one. Using the mean relaxation time of 636.4 s the equivalent frequency of the TSDC experiment can be determined as  $f = 1/(2\pi\tau(T_m)) = 2.5 \times 10^{-4}$  Hz. It is generally assumed that  $f \approx 10^{-3}$  Hz [1–3,5,16,18].

The relaxation of the charge carriers can be characterized by using the Maxwell relaxation time  $\tau_M = \epsilon_0\epsilon'/\sigma$ , where  $\sigma$  is the conductivity. We have computed the electric conductivity at the end of the polarization time and, knowing the real part of dielectric permittivity at the same temperature at 0.01 Hz [9], we have computed the Maxwell relaxation time  $\tau_M(T_p)$ . It varies in large limits from 35,300 to 16.9 s as  $T_p$  varies from 343 to 403 K. It is interesting to compare  $\tau(383) = 566$  s (see Table 1) and  $\tau_M(383) = 243$  s and to observe that around  $T_g = 387$  K the two values are of the same order of magnitude meaning that the dipoles, which are parts of the molecular chains, relax almost similar with the free charge carriers, supporting the above supposition that for  $T_m = T_p$  the dipoles moves equally fast during charging or discharging. This means that at this temperature the polymer is in the rubbery state.

The values obtained for  $W$  and  $\tau_0$  suggest a compensation behavior:  $W$  increases and  $\tau_0$  decreases. Using the data in Table 1 or by extrapolating the Bucci-Fieschi-Guidi lines [19] it was not possible to define a compensation point. This result is in agree-

ment with a recent observation [20] showing that it is not possible to have a precisely defined compensation point.

The variation of  $(T_m - T_p)$  with  $T_p$  (Fig. 4) provides accurate information about the dielectric  $\alpha$  relaxation peak associated with the glass transition. Further work is in progress to optimize the values of  $b$  and  $t_p$  in respect with the mean relaxation time  $\tau(T_m)$ .

## 5. Conclusions

The difference  $(T_m - T_p)$  changes with  $T_p$  and provides information about the dipole mobility and the stimulation of relaxation process by the cooperative molecular movement around  $T_g$ . For  $T_p = 387$  K,  $T_m - T_p = 0$  meaning that the dipoles move equally fast during polarization or depolarization stage. This temperature is attributed to the non-local  $\alpha$  relaxation associated to the glass transition.  $T = 363$  K represents the lower temperature at which the dielectric relaxation start to be controlled by the glass transition and 403 K represents the higher limit of dielectric manifestation of the glass transition. The mean relaxation time is 636.4 s and the equivalent frequency of the TSDC experiment is  $2.5 \times 10^{-4}$  Hz. There is a distribution in activation energies and a broad distribution in pre-exponential factors but a narrow distribution of relaxation times. A steep variation of the current was observed at around 368 K suggesting that there is a structural change around this temperature.

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