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# Effect of macromolecular orientation on the structural relaxation mechanisms of poly(ethylene terephthalate)

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## Abstract

In this work we used Dielectric Spectroscopy (DS) and Thermally Stimulated Depolarisation Currents (TSDC) analysis to obtain values of fragility indexes as defined in the 'Strong-fragile' glass former liquid concept. DS and TSDC measurements have been performed on a series of polyethylene terephthalate (PET) samples with various degrees of macromolecular orientations. These orientations have been obtained by means of uniaxial drawing performed above the glass transition temperature. Samples with draw ratios $\lambda=1$, $\lambda=2$ and $\lambda=5$ have been obtained. From TSDC measurements, the fragility index of the glassy state ($m_g$) can be obtained, while DS measurements allow to reach the fragility index value of the liquid-like state ($m$). Furthermore, for low draw ratio, the material is practically wholly amorphous and its liquid state can be classified as 'fragile' glass forming liquid while for semi-crystalline PET (draw ratio $\lambda=5$), it is shown the remaining amorphous phase becomes stronger (m varies from 170 to 60 and $m_g$ varies from 81 to 21).

*Keywords:* PET; Drawing; TSDC

## 1. Introduction

The glass transition in non-crystalline materials is actually one of the most difficult and unsolved problems in solid state physics. The glass transition, which is associated to important changes in thermodynamic properties (as heat capacity), is not a true thermodynamic phase transition and must be seen as a kinetic event [1–2]. Consequently, a glass must be understood as a frozen liquid or as a liquid with a very high viscosity. The phenomenological approach of the glass transition based on the variations of the viscosity (or relaxation time) with temperature has shown that all glass-forming liquids exhibit log $\tau$ versus $T_g/T$ variations included between two bordering limits. This approach, known as the 'fragility concept' or 'strong-fragile glass forming liquid concept', proposed by Angell [3], allows the definition of a fragility index $m$ [4]. This is a measure of the rate at which the relaxation time $\tau$ (or related properties) decreases with the increasing temperature around $T_g$. A low value for $m$ ($\approx 16$) characterises a 'strong' glass-forming liquid, which exhibits an Arrhenian temperature dependence of $\tau$ (observed for example for rigid network systems [5]), while a 'fragile' glass-forming liquid with a high $m$ value ($\approx 250$) exhibits an important sensitivity of its properties with the temperature. In this case, this dependence could be fitted by a Vogel–Tamman–Fulsher relationship [6–8] (observed for example for linear polymeric materials [9–10]). The fragility concept has often been used to characterise wholly amorphous materials: inorganic glasses [11], thermoplastics [9], polymer networks [12], liquid-crystalline polymers [10]. Otherwise, what are the effects of a crystalline phase on the molecular mobility of the remaining amorphous fraction when analysed in view of this fragility concept? For a semi-crystalline polymer, the polymer chains conformational mobility pertaining to the amorphous phase is often restricted close to the crystallites. Moreover, the glass transition in semi-crystalline polymers not only depends on the degree of crystallinity but also on its microstructure (crystallites or spherulites [13]).

For this purpose, Polyethylene terephthalate (PET) is

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particularly interesting because important and continuous changes in its microstructure can be achieved experimentally. For instance, it can be found wholly amorphous at room temperature (by quenching from the melt) and by controlling its cooling, its heating or its drawing, a semi-crystalline structure can be obtained [14]. Alves et al. [15] have recently determined the relaxation times of the cooperative conformational rearrangements of the amorphous phase of semi-crystalline PET when the crystalline phase is induced by annealing. They distinguish two different fractions in the amorphous phase with two different conformational mobilities. As far as we know, any work using the fragility concept concerns semi-crystalline PET in which the crystalline phase is induced by a uniaxial drawing have been published. In this case we called the crystalline phase as the strain induced crystallised phase (SIC phase).

From an experimental point of view, calorimetric methods can be used for a wholly amorphous PET, because the $\Delta C_p$ ($T_g$) jump (characteristic from the glass transition) is high enough to be detected. For drawn materials, $\Delta C_p$ values decrease drastically and cannot be correctly estimated. To overcome this difficulty we have shown [14] that values of fragility indexes can be obtained on these drawn samples by means of Thermally Stimulated Depolarisation Currents (TSDC) measurements. In the present work, we propose to analyse, in regard with the fragile concept, TSDC and Dielectric Spectroscopy (DS) results obtained on amorphous and semi-crystalline drawn PET.

## 2. Experimental

### 2.1. Material and samples preparation

Poly(ethylene terephthalate) films of $\bar{M}_n = 31,000\ \text{g mol}^{-1}$ for its number-average molecular weight and of $\bar{M}_w = 62,000\ \text{g mol}^{-1}$ for its weight-average molecular weight are isotropic and amorphous judging from birefringence, density and X ray diffraction measurements. Drawn semi-crystalline samples are obtained using the following procedure. Before the drawing period, the films are kept in the heating chamber of a tensile machine at 95 °C during 5 min to allow a homogenous temperature distribution. Then, the films are drawn uniaxially at a strain rate of $0.14\ \text{s}^{-1}$ in the tensile machine. The drawing temperature (95 °C) is chosen between the glass transition temperature and the cold crystallisation temperature of PET to allow homogeneous drawing and to avoid thermal crystallisation. After drawing, the material is cold air-quenched down to room temperature in order to freeze in its structural state. Then, different samples are cut from the drawn materials and the draw ratio $\lambda$, equal to the ratio of the extended length over the original length, is measured. Finally, undrawn and drawn samples are stored before experiments under vacuum in the presence of $P_2O_5$ at 20 °C to avoid moisture sorption.

### 2.2. Methods

Dielectric measurements were performed by means of a dielectric analyser (Thermal Analysis Instrument DEA 2970), with a frequency range between 0.05 and 1000 Hz, from 40 to 150 °C by steps of 5 °C. The samples studied were of 25 mm diameter and 0.5 mm thickness disks for undrawn PET (lower thickness for the other samples). For each measuring point, real and imaginary part of the dielectric permittivity as well as the temperature and the frequency were recorded.

TSDC measurements, described in detail elsewhere [16], were performed thanks to an apparatus developed in our laboratory. At a polarisation temperature $T_p$ just above the glass transition (classically $T_p = T_g$ endset), samples were subjected to an electric field ($E = 10^6$ V/m) during 2 min. Then, the temperature was lowered to −10 °C, samples were short circuited and the depolarisation current '$I$' was measured during heating up to 150 °C at 10 °C/min to obtain a complex spectrum. The relaxation time $\tau(T)$ of the glass transition dielectric manifestation can be obtained by different formalisms. Alegria et al. had shown that the α relaxation can be analysed with the Kohlrausch–Williams–Watts (KWW) equation [17]:

$$Q(t) = Q_0 \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{1}$$

where

$$Q(t) = \int_t^{\infty} I \, dt,$$

$Q_o$ is the value of the initially stored charge, and $\beta$ is a parameter accounting for the non-Debye character of the α relaxation. For PET it had been shown that $\beta$ is close to 0.5 [18]. From the time derivative of Eq. (1), $\tau$ can be written as:

$$\tau = \beta \frac{Q}{I} \left[\ln \frac{Q_0}{Q}\right]^{[1-1/\beta]} \tag{2}$$

The sample optical anisotropy is measured by birefringence at room temperature and by using a spectrophotometric method [19]. Calorimetric investigations are performed with a Perkin Elmer DSC7 calorimeter. Its calibrations in temperature and energy are achieved at $10\ \text{K.}\ \text{min}^{-1}$ under nitrogen atmosphere using indium and zinc as standards.

## 3. Results

Birefringence is due to a difference between the principal refractive indices within a material and its variations can be interpreted in regard of the average macromolecule orientations. Depending on the authors, the maximum values of $\Delta n$ proposed in literature for PET are spread between 0.212 [20] and 0.290 [21] for the crystalline phase

($\Delta n_c$) and between 0.200 [22] and 0.275 [23] for the amorphous phase ($\Delta n_a$). The birefringence data are displayed in Fig. 1 and the lines are solely included to facilitate visualisation of changes over the draw ratio ($\lambda$). For PET samples, the maximum observed for $\Delta n$ ($\Delta n = 0.23$ for $\lambda$ greater than 5) is very close to the literature values showing the orientation developed by the drawing has practically reached its maximum. Differential Scanning Calorimetry (DSC) studies had been previously performed and the degrees of crystallinity were calculated [24]. Fig. 1 shows the variations of this crystallinity degree with the draw ratio and it is found that up to $\lambda = 2.5$, the initial degree of crystallinity of drawn PET samples is negligible. For these drawn polymers, the amorphous phase is only oriented. Then, it raises with $\lambda$ until $\lambda = 5$. For the highest draw ratio, $X_c$ remains practically constant and close to 40%. It is of interest to note that the variations of the birefringence and of the degree of crystallinity are very similar. The shift (in $\lambda$) between the two data series can be explained by the existence of a SIC phase appearing in PET when the molecular orientation is large enough, i.e. the draw ratio is above a critical value (given between $\lambda = 2$ and 3 as a function of the material and the drawing process). To perform relaxation measurements we have limited the samples to $\lambda = 1$ (wholly amorphous), $\lambda = 2$ (wholly amorphous and oriented structure) and $\lambda = 5$ (strain induced crystallised material).

Fig. 2 shows, as an example, the temperature dependence of the dielectric loss factor $\varepsilon''$ obtained for different frequencies on a drawn PET ($\lambda = 5$). For the other samples, the same kind of curve is obtained. We observe a classical behaviour, i.e. the dielectric loss peak shifts to lower temperatures with decreasing frequencies. For these peaks characterising the $\alpha$ relaxation (dielectric manifestation of the glass transition), and for each frequency $f$, two parameters can be easily obtained: a characteristic temperature (taken at the peak maximum) and a relaxation time $\tau$ defined by:

$$\tau = 1/2\pi f \tag{3}$$

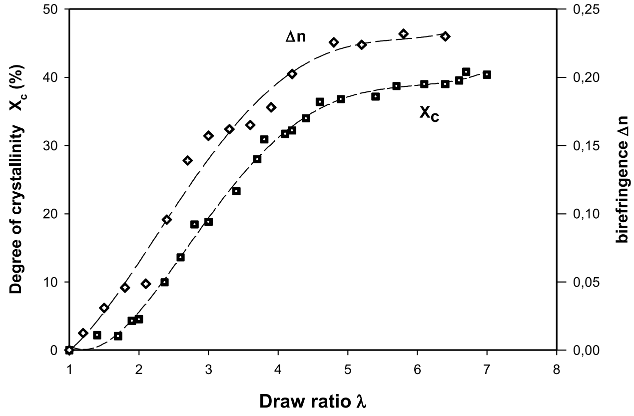

Fig. 1. Variations of the crystallinity degree $X_c$ (■) and of the birefringence $\Delta n$ (◇) with the draw ratio.

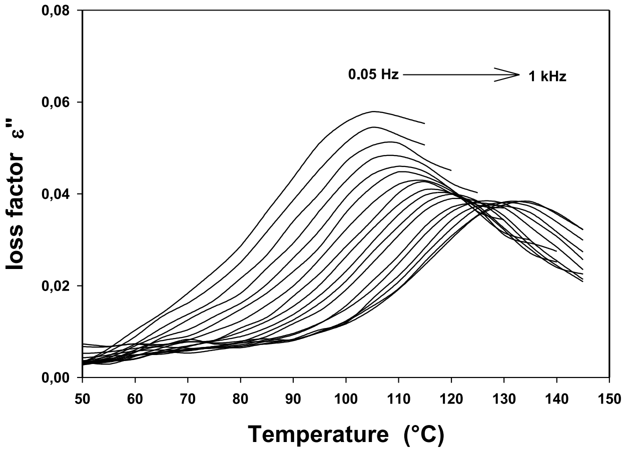

Fig. 2. Example of temperature dependence of the dielectric loss $\varepsilon''$ obtained for different frequencies (included between 0.05 and 1000 Hz), on a $\lambda = 5$ drawn PET.

For the different PET samples, the variations of log $\tau$ versus $1/T$ can be done (Fig. 3) and fitted by the Vogel–Tamman–Fulsher relationship [6–8]:

$$\tau = \tau_0 \exp \frac{B}{(T - T_2)} \tag{4}$$

The pre-exponential factor $\tau_0$, the activation energy $B$ and the temperature $T_2$ have been determined and are reported in Table 1. Two kinds of variations are observable: For $\lambda = 1$ and 2, the observed curvature indicates these data can be fitted by the VTF equation. For $\lambda = 5$ the variations are quasi-linear and in consequence an Arrhenius law must be used:

$$\tau = \tau_0 \exp \frac{\Delta E}{RT} \tag{5}$$

The parameters $\tau_0$ and $\Delta E/R$ are reported in Table 1. Thus, undrawn and weakly drawn samples can be classified has 'fragile' while highly drawn samples exhibit a 'strong' behaviour.

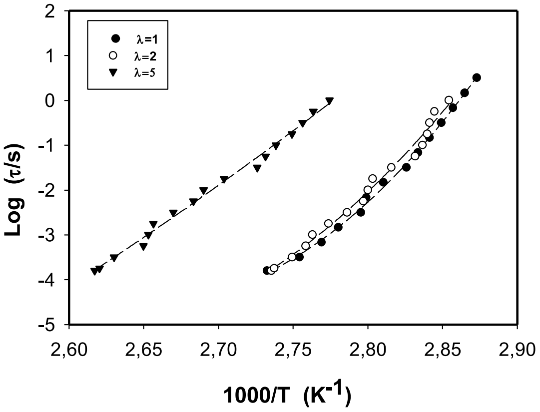

Fig. 3. Values of log $\tau$ obtained from Eq. (2) and reported for each characteristic temperature. The dashed line corresponds to the fit of the variation of log $\tau$ versus 1000/$T$.

Table 1
Different parameter values obtained from the VTF or the Arrhenian fit procedure performed on the $\log(\tau)$ versus $1000/T$ curves

| | $\lambda=1$ | $\lambda=2$ | $\lambda=5$ |
|---|---|---|---|
| $\log(\tau_0)$ | $-12.5$ | $-12$ | $-64$ |
| $B$ (K) | 1012 | 951 | / |
| $T_2$ (°C) | 315 | 316 | / |
| $m$ | 142 | 160 | 66 |
| $\tau$ $(T_g)$ | 16 | 40 | 600 |
| $T_g$ (°C) | 74 | 73 | 75 |
| $\Delta E/R$ (kK) | / | / | 53 |
| $m_g$ | 81 | 72 | 30 |

The TSDC manifestation of the glass transition is evidenced by a depolarisation current peak called α peak which exhibits a maximum at the temperature $T_\alpha=69$ °C for $\lambda=1$. Some of the TSDC spectra of drawn PET are also shown in Fig. 4. For $\lambda=2$, an increase in $T_\alpha$ and a decrease in the area under the peak are observed, while the shape of the peak remains the same. For $\lambda=5$, the shape of the α peak becomes different: the magnitude of the α peak is drastically weaker than for undrawn sample. The calculation of a fragility index $m_g$ by means of TSDC measurements is completely described in a previous paper [14]. Following relationship (2), the first part of the work consists in calculating the variations of the relaxation time $\tau$ with the temperature. Using the data presented in Fig. 4 and relationship (2), this first step can be done easily. The results are reported on Fig. 5. Two types of curves can be observed: for weakly drawn samples $\lambda=1$ and 2 the slopes are steeper than for highly drawn samples (strain induced crystallised). The relaxation phenomena occurring in the glassy state are known to be dependent on the temperature and the structure, this dependence is for instance described by the non-linearity parameter called '$x$' occurring in the well known Tool–Narayanaswamy–Moynihan (TNM) relationship [25–27]. A value of $x$ close to unity indicates that the relaxation time mainly depends on the temperature effects, while at the opposite a value of $x$ close to 0 indicates that the structure governs the relaxation process. For a large part of the polymers, values of $x$ between $x=0.3$ and 0.6 are obtained. For the sample with $\lambda=5$ the material is deformed enough to limit the effect of the structure on the global relaxation phenomena, this is evidenced by the quasi-linear variation of the relaxation time with the temperature. The effects of the structure on the relaxation time vanish. For low $\lambda$ values ($\lambda=1$ or 2), the amorphous phase is not constraint enough and remains free to relax, the effects of the temperature and of the structure remain in action, the dependence of the relaxation time with the temperature exhibits a clear curvature.

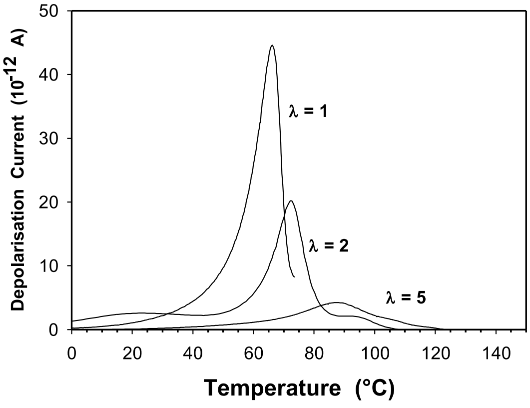

Fig. 4. Variations of log $\tau$ versus $1000/T$ and corresponding fit curves for three draw ratio (for $\lambda=1$ and 2, VTF fit, for $\lambda=5$, Arrhenian fit).

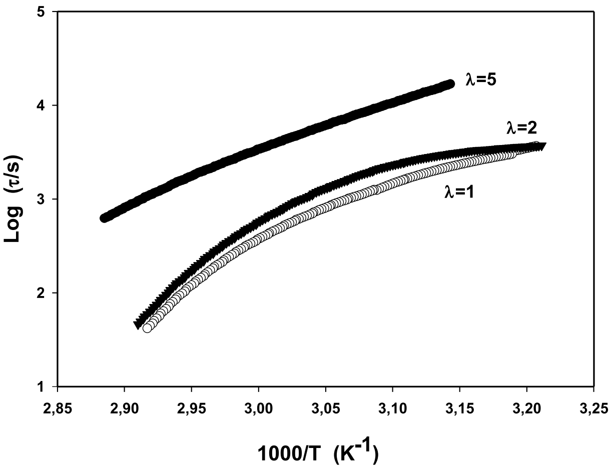

Fig. 5. TSDC spectra for three draw ratios.

So, as for dielectric studies, the TSDC manifestation of the glass transition seems to be influenced by the presence of a crystalline phase.

## 4. Discussion

The calculation of the fragility index $m$ can be done for TSDC and SD techniques according to [12] and using the following equation:

$$m=\frac{d(\log(\tau))}{d(T_g/T)_{T=T_g}} \tag{6}$$

That highlights the problem of the $T_g$ value choice. This is a difficult problem linked to the fact that the observed glass transition is a kinetic and not a thermodynamic phase change. For most of the glass forming liquid, $T_g$ is the temperature for which the relaxation time $\tau(T=T_g)$ is 100 s [28]. Nevertheless, as already mentioned by Angell [28], depending on the nature of the units engaged in the relaxation process and depending on the technique used to investigate the glass transition, the relaxation time at $T_g$ for different materials can cover values included between $10^{+2}$ and $10^{-3}$ s. The lowest values being generally observed for the simplest molecular structures engaged in the relaxation process.

In Fig. 6 are reported the variations of log $\tau$ versus $1000/T$

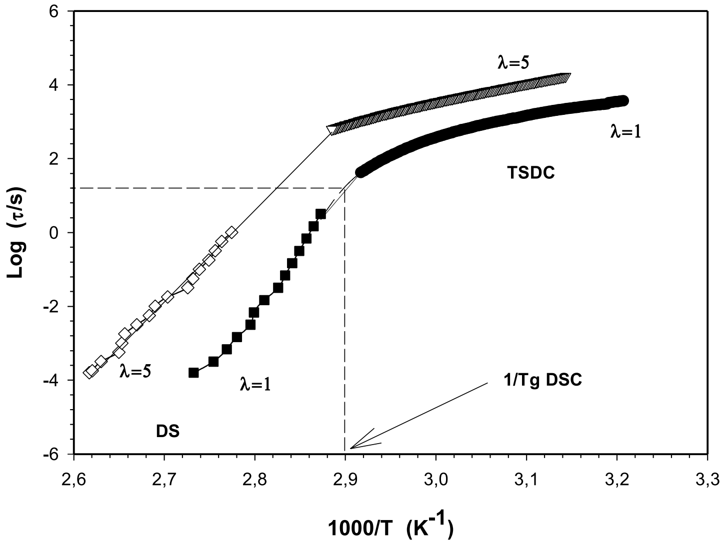

Fig. 6. Values of log $\tau$ obtained from Eq. (1) and reported as a function of 1000/$T$ for two draw ratios.

for an undrawn and wholly amorphous PET ($\lambda=1$) and for a semi-crystalline sample ($\lambda=5$) from data obtained by TSDC and DS. The $\lambda=1$ PET presents the advantage of having been widely studied, so all the parameter values have already been estimated by means of DSC measurements [14]. As we may see, the temperature domains for which the data are collected with these two techniques are complementary. Every data series fitted with the ad hoc formula (relationship (4) for DS and a similar relation described in a previous paper [14] for TSDC) intersected each other at a temperature of 74 °C and at a relaxation time of 16 s. This temperature is very close to the glass transition temperature determined by DSC (72 °C) (according to the following protocol: $T_g$ is estimated at the mid point of the $\Delta C_p$ jump for a rejuvenated material heated and cooled at the same rate in such a way that any endothermic peak of relaxation occurs). This result shows that TSDC, DS and DSC techniques give converging data with a unique value $T_g=$ 74 °C and a characteristic relaxation time of 16 s at $T_g$ for a wholly amorphous PET. The same method used for the other samples leads to the data reported in Table 1. We find that $\tau(T_g)$ increases from 16 to $\approx$600 s for $\lambda=5$. So, different relaxation time values at $T_g$ are obtained (one decade of variations is found in this work) for quasi-identical values of the glass transition temperature.

For TSDC, a depolarisation current peak resulting from dipoles cooperative motions is detected in the temperature range of the glass transition observed by DSC. The dipoles reorientation starts as soon as the cooperative motions create enough freedom. The data reported in Figs. 5 and 6 are obtained from the first part of the TSDC curves; as example for $\lambda=1$ the TSDC signal is exploited between 40 and 69 °C, maximum of the curve. Thus, it is clear that the TSDC data concern relaxation phenomena occurring in the glassy state [14], while DS data concern relaxation phenomena occurring in the liquid like state. Finally, we may say that the profile of the relaxation time variations presented in Fig. 6 is typical of the glass transition region and was also observed by means of creep and dynamical mechanical analysis [2].

From the knowledge of the $T_g$ value, it is now possible to calculate the fragility indexes from the TSDC and the DS data (reported in Table 1) at the ad hoc value of $\tau(T_g)$. The TSDC fragility index is the one characterising the glassy state ($m_g$ as defined by Hutchinson [29] $m_g=xm$, where $0\leq x\leq 1$ is the non-linearity parameter) and the DS fragility index is the one characterising the glass forming liquid ($m$). The values of $m$ and $m_g$ are reported in Table 1. For $\lambda=1$ and 2, the values of $m$ close to 150 correspond to a 'fragile' behaviour. By means of calorimetric measurements, the value of the fragility index was found equal to $m=166$ for $\lambda=1$ [14] which is similar to our value. For these weak draw ratios, the degree of crystallinity is negligible (a wide angle X ray diffraction study have shown, on the same drawn samples [30] that the SIC phase appears only at $\lambda=2.8$). For the same range of draw ratio, the values of $m_g$ is also quasi-constant at $m_g=80$, leading for the non-linearity parameter to a value of $x\approx 0.5$. This is an acceptable value since the literature proposed $x=0.49$ [31]. Thus, no drastic variation on fragility is observed by changing the molecular orientation from $\lambda=1$ to 2.

For high draw ratio, ($\lambda=5$), $m$ values are lower and close to 66 while $m_g$ decreases to 30 holding the value of $x$ around 0.5. We find that the behaviour of the stretched material goes toward a 'strong character' which is consistent with the Arrhenian variations of $\ln(\tau)$. Fragility is strongly linked with the intra and intermolecular interactions existing in the material [31]. Strong materials have covalent predominant interactions ($SiO_2$, $GeO_2$ rigid network) while materials with a fragile behaviour (PP, CNH) have Van Der Waals predominant interactions. For our polymers composed of linear macromolecular chains, no drastic modifications in the covalent bonds occur. Thus, we find a change in the fragility behaviour can be obtained thanks to the drawing, by modifications of the Van Der Waals interactions.

## 5. Conclusion

By changing Van Der Waals interactions of a PET by drawing and using different experimental techniques and procedures (dielectric spectroscopy, TSDC and calorimetry) we have shown that the value of the relaxation time $\tau(T_g) = 100$ s is not an universal value. In particular, we found that deviation from this rule clearly appears for fragile materials. We have also shown that the knowledge of the true $\tau(T_g)$ value allows the correct calculation of fragility index value. By this way, the same value for $m$ is obtained by DSC and DS experiments. The orientation imposed by the drawing modifies the fragility of the material only if a strain induced crystalline phase is present in the sample. In this case, the fragility index decreases drastically.

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