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Fragility index of drawn or annealed poly(ethylene terephthalate) films studied by thermally stimulated depolarisation currents

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Abstract

According to the 'strong-fragile' glass forming liquid concept, amorphous poly(ethylene terephthalate) (PET) must be classified as a 'fragile' supercooled liquid. In this work we show that the value of the fragility index of the glassy material (m_g) can be obtained by means of Thermally Stimulated Depolarisation Currents measurements. Experiments were carried out on different PET for which the molecular mobility of the vitreous domain was constrained by the existence of a crystalline phase. This crystalline phase was obtained in two different ways, i.e. by thermal cold crystallisation or by a uniaxial hot-drawing method. Depending on the degree of crystallinity, but whatever the nature of the crystalline morphology (spherulitic or oriented crystallites), it is found that the initial fragile character becomes stronger as the degree of crystallinity increases.

Keywords: Poly(ethylene terephthalate); Fragility; TSDC

1. Introduction

By maintaining a glass at a temperature below T_g for a given duration, its excess of configurational energy must decrease in order to reach more favourable thermodynamic states. After an infinite ageing duration the thermodynamic equilibrium defined by extrapolation into the glassy temperature domain of the liquid equilibrium curve must be reached. This well-known phenomenon, occurring for all glasses whatever their nature, is called physical ageing [1]. During physical ageing, cooperative molecular rearrangements will occur leading to a relaxation phenomenon, with as a consequence, a change over time of the physical properties of the glassy material. Whatever the physical property '*P*' considered, this time dependence can be written as

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -\frac{\Delta P}{\tau} \tag{1}$$

where τ is a relaxation time, known since the works of Tool [2] to be dependent on both the temperature (T) and the structure (ξ); $\tau = \tau(T, \xi)$. As the relaxation phenomenon is associated to an energy loss, it is convenient to analyse the variations with ageing of the material enthalpy (H) as this time dependent physical property, which is why calorimetric measurements are often performed for such studies of relaxation phenomena [3–5]. Among the different expressions available for the relaxation time which have been used for τ by means of calorimetric investigations, is the so called TNM relationship (for Tool–Narayanaswamy–Moynihan) [2,6,7]

$$\tau = \tau_0 \exp\left(\frac{x\Delta h^*}{RT}\right)\exp\left(\frac{(1-x)\Delta h^*}{RT_\mathrm{f}}\right) \tag{2}$$

The first exponential characterises the temperature dependence, while the second characterises the structure dependence by the quantity T_f which is defined on Fig. 1. In this equation, x is a partition parameter ($1 \geq x \geq 0$) called the Narayanaswamy or non-linearity parameter; and Δh^* an apparent activation energy. Theoretically, these two parameters are material constants. However, a glass kept at a temperature T_a for an infinite time will see its value of T_f decrease down to T_a, when the equilibrium is reached. Thus,

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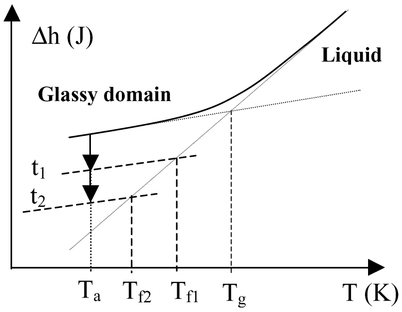

Fig. 1. Variation of the enthalpy of a glass-forming liquid vs. temperature. T_a is the ageing temperature, T_g the glass transition temperature measured by DSC and T_{fi} are the fictive equilibrium temperatures.

after an infinite ageing duration performed at $T_a = T_g$ we obtain

$$\tau(T_g) = \tau_0 \exp\left(\frac{\Delta h^*}{RT_g}\right) \tag{3}$$

On the other hand, the relaxation phenomena occurring in the liquid state can also be investigated independently of those observed in the glassy state. This is well established for instance with the works of Angell et al. [8] leading to the well-known 'strong-fragile' glass forming liquid concept. It was observed that for liquids the variations of the viscosity with the temperature are included between two borderline limits. An Arrhenius law can describe the first, leading to the 'strong' glass-forming liquid behaviour, while a Vogel Tamman Fulcher law must be used to describe the second, leading to the 'fragile' glass-forming liquid behaviour (Fig. 2). To study the molecular relaxation, a more appropriate scale is the shear relaxation time linked with the shear viscosity by $\tau = \eta/G_\infty$ where G_∞ is the shear modulus measured at high frequency. Because all the liquids are included between these two limits, a classification of the glass-forming liquids was proposed by using the definition of a fragility index m [8–10]

$$m = \left.\frac{\mathrm{d}\log_{10}(\tau)}{\mathrm{d}\left(\frac{T_g}{T}\right)}\right|_{T=T_g} \tag{4}$$

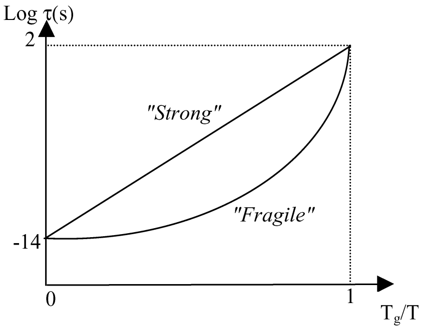

Fig. 2. Variation of the relaxation time vs. T_g/T for two glass-forming liquids.

The two borderline limits are reached for $m = 16$ and $m \geq 200$ for, respectively, 'strong' and 'fragile' glass-forming liquids [11,12]. By combining relationships (3) and (4) it follows that the fragility index can be easily determined if Δh^* is known according to

$$m = \frac{\Delta h^*}{\ln(10)RT_g} \tag{5}$$

The values of this fragility index have been determined successfully for many polymeric and inorganic glasses [13–15] and for some of them can be correlated to structural considerations, particularly when massive molecular groups are engaged [13,14].

The same process can be performed for the glassy state and as shown by Hutchinson [16] it is possible to define a fragility index for the glass by

$$m_g = xm \tag{6}$$

To determine experimentally the values of the different parameters stemming from the relationships presented above, thermal cycles are required in which the glass is heated to a temperature above its T_g, cooled back to the annealing temperature T_a, aged for t_a, heated again to above T_g and so on. This procedure works very well as long as the material does not exhibit any irreversible chemical (post cure for instance) or physical (cold crystallisation) transformations. When such phenomena exist, it could be tempting to work with many different samples and perform the ageing outside the DSC oven, but generally too much data scattering occurs to hope to get significant results. As a consequence this calorimetric method cannot be brought into play and an alternative one is needed. This is precisely the situation if the goal is to determine the fragility index of drawn or annealed poly(ethylene terephthalate) films (PET).

For this material, as the kinetics of crystallisation are slow, a wholly amorphous material can be easily obtained by rapid quenching from the melt. On the other hand, an annealing performed above the glass transition temperature could induce different degrees of 'cold' thermal crystallisation with the existence of a spherulitic superstructure. Moreover, it is also possible to create a crystalline phase in the material by uni or multi-axial drawing [17]. Indeed, when initially amorphous PET films are uniaxially drawn at a temperature above the glass transition temperature (70 °C), it is established that a strain-induced crystalline (SIC) phase (which can reach 40% in mass for the extreme deformation) and a fiber texture can appear above a critical value of the draw ratio λ [18]. From X-ray poles figures analysis we have shown that for PET, a SIC phase appears with a weak crystalline texture in a first time, while for higher values of the draw ratio, the drawing tends to align the crystallites with the draw direction (rather than increase the degree of crystallinity). An extra texture where the planes of the phenyl rings are quasi-parallel to the film surface is also observed for the highly drawn sample [18].

For these semi-crystalline drawn samples, a DSC study of the amorphous phase to determine the values of the fragility index appears very difficult because of the very small temperature gap between glass transition and thermal cold crystallisation and also because of possible strain relaxations induced by a high temperature treatment (in regard to T_g).

Recently, it was proposed to approach this fragility concept by means of depolarisation current measurements [19,20]. Using a zero entropy prediction model [19], a good correlation was apparently found between the results obtained by Thermally Stimulated Depolarised Current (TSDC) and DSC. Experiments were performed on a series of side chain liquid crystalline polymers using the elementary spectra for TSDC investigations and the Cowie–Ferguson [21] method for DSC measurements. In this work we propose to determine the values of the fragility index for different drawn or annealed PET by an alternative TSDC method.

2. Experimental

2.1. Material and samples preparation

PET films ($\bar{M}_{\bar{n}}$ of 31000 g/mol) are isotropic and amorphous judging from birefringence, density and X ray diffraction measurements. Undrawn semi-crystalline samples are obtained after an annealing at $T = 120$ °C for various durations included between 5 min and 24 h. Drawn semi-crystalline samples are obtained from the following procedure. Before the drawing period, the films are kept in the heating chamber of a tensile machine at 95 °C for 5 min to allow a homogenous distribution of temperature. Then, the films are uniaxially drawn at a strain rate of 0.14 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. Finally, different samples are cut from the drawn materials and the draw ratio λ, equal to the ratio of the extended length over the original length, is measured. It was found that λ varied from 1 to 6. Finally, undrawn and drawn samples are stored before experiments under vacuum in the presence of P_2O_5 at 20 °C in order to avoid moisture sorption.

2.2. Methods

TSDC measurements, described in detail elsewhere [22], were performed by means of an apparatus developed in our laboratory [23]. At a polarisation temperature T_p just above the glass transition (classically $T_p = T_g$ endset), samples were submitted to an electric field ($E = 10^6$V/m) for 2 min. The temperature was then lowered to -150°C. Then samples were short circuited and the depolarisation current I was measured during annealing up to 150 °C at 10 °C/min to obtain a complex spectrum. The relaxation time $\tau(T)$ of the dielectric manifestation of the glass transition can be obtained by a procedure referred as the Bucci method [24] and using the following relationship

$$\tau(T) = \frac{1}{q}\frac{\int_T^{T_\infty} I(T')\mathrm{d}T'}{I(T)} \qquad (7)$$

where T_∞ is the temperature at which the transition considered is achieved (in this case the temperature where the current above the peak reaches practically nil value), q is the heating rate and $I(T)$ the current at the temperature T. Calorimetric investigations are performed with a Perkin–Elmer DSC7 calorimeter. It is calibrated for temperature and energy at 10 K min^{-1} under nitrogen atmosphere using indium and zinc standards. The DSC curves presented in this paper have been normalised to 1 mg of matter.

3. Results

The TSDC and DSC signals obtained for an amorphous PET are superimposed on Fig. 3. The dielectric manifestation of the glass transition is evidenced by a depolarisation current peak called α peak which exhibits a maximum at the temperature $T_\alpha = 66$ °C. The calorimetric manifestation of the glass transition is evidenced by the endothermic ΔC_p step (close to 0.32 J g^{-1} K^{-1}). For this DSC curve, the glass transition temperature can be determined as the onset one (T_g onset = 72 °C) or by the so-called mid point ($T_g = 74$ °C). We may notice that even if the two experiments have been performed on samples having the same thermal history

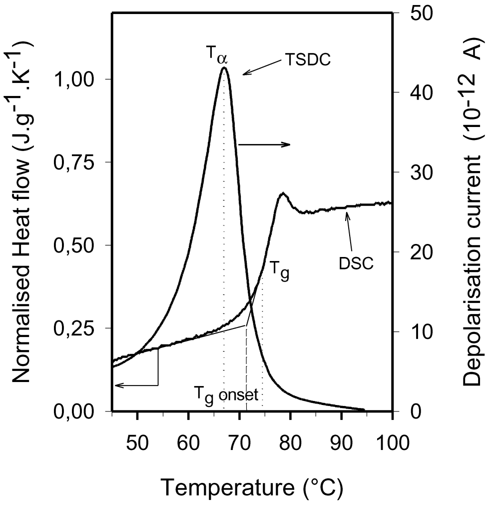

Fig. 3. TSDC and DSC curves in the glass transition region for an amorphous and undrawn PET. The experimental set of condition of TSDC is: $T_p = 80$ °C, $T_d = -150$ °C, the electric field is 10^6 V m^{-1}, the heating and the cooling rates are 10 °C min^{-1}. For DSC the heating rate is 10 °C min^{-1}.

and with the same heating rate, the dielectric and the calorimetric signals of the glass transition do not occur at the same temperature. It is apparently shifted to a lower temperature for the dielectric results.

Complex TSDC spectra of drawn or annealed PET are shown on Figs. 4 and 5. For drawn samples (Fig. 4), the α mode appears from -30 to $+120$ °C. For $\lambda < 3.8$, an increase of T_α and a diminution of the area under the peak are observed when λ increases while the shape of the peak remains the same. For $\lambda > 3.8$, the shape of the α peak becomes different: a first peak is observable at 30 °C and a second at 90 °C. The magnitude of the highest temperature peak (which corresponds also to the glass transition) is drastically weaker than for undrawn sample. The first peak is generally attributed to localised motions of aromatic cycles for anisotropic polymers [25]. The same remarks can be made for the results concerning annealed samples as evidenced by the curves shown on Fig. 5.

A previous study has shown that different crystalline phases appear during the drawing (strain-induced crystallites) or during the annealing (spherolites). Whatever the nature of the crystalline phases, an induced rigid amorphous fraction which cannot participate in the glass transition occurs [26,27].

As usual, the degree of crystallinity X_c of the samples can be obtained by DSC from the fusion and the cold crystallisation peaks according to the following equation

$$X^* = \frac{\Delta H_c^0 - \Delta H_c}{\Delta H_c^0}\frac{\Delta H_f}{\Delta H_f^0} \tag{8}$$

where ΔH_f is the measured enthalpy of fusion of a given sample, ΔH_f^0 is the calculated enthalpy of fusion of a wholly crystalline material ($\Delta H_f^0 = 140$ J/g for PET [28]) and ΔH_c is the enthalpy of the cold crystallisation observed during the heating of the sample. So, using this relationship and the DSC data, we have determined the degree of crystallinity for drawn and for annealed PET (Table 1). The degree of crystallinity is found to be practically nil for draw ratio $\lambda < 2$. Above this critical draw ratio X_c increases with λ up to $\lambda = 5$. For the highest draw ratio, X_c is found to be constant and presents a value close to 40% (w/w). For annealed PET samples, the degree of crystallinity increases from zero to 28% for annealing time included between 0 and 25 min. For higher annealing times, the degree of crystallinity is found constant (28%). As expected, the degree of crystallinity that can be reached with the drawing process is higher than with annealing.

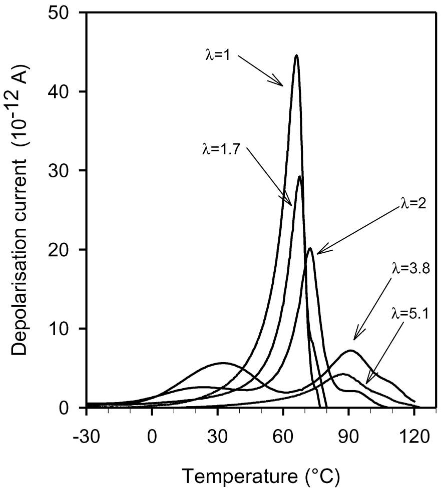

Fig. 4. TSDC curves for different drawn PET (the draw ratios are indicated on the figure). The experimental set of conditions: the polarisation temperature is just above T_g and the depolarisation temperature is -150 °C, the electric field is 10^6 V m^{-1}, the heating and the cooling rates are 10 °C min^{-1}.

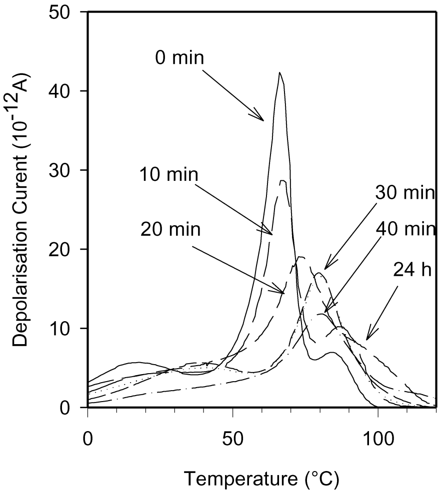

Fig. 5. TSDC curves for different annealed PET (the times are indicated on the figure). The experimental set of conditions: the polarisation temperature is just above T_g and the depolarisation temperature is -150 °C, the electric field is 10^6 V m^{-1}, the heating and the cooling rates are 10 °C min^{-1}.

Table 1
Fitting parameters A, B and T_0 (from Eq. 6), degree of crystallinity X_c (%) obtained from DSC data and values of m_{CDTS} calculated from Eq. (4)

Polymer	A	B (K^{-1})	T_0 (K)	X_c (%)	m_{CDTS}
Drawn PET $\lambda = 1$	3.2	8150	320	0	81
$\lambda = 1,7$	3	10000	325,5	2	78
$\lambda = 2$	3	10500	332,5	4.5	72
$\lambda = 3,8$	3	9000	348	29	40
$\lambda = 5,1$	3	8000	345,5	38	29,5
$\lambda = 6,2$	3	6000	346	40	21
Annealed PET $t = 0$	2.9	10300	328	0	81
$t = 5$ min	3	10350	330	1	74
$t = 10$ min	3	10200	331	9	63
$t = 15$ min	2.8	10200	338	25	41
$t = 20$ min	2.9	9700	336	25.5	35
$t = 25$ min	3.1	9000	338	28	33
$t = 30$ min	2.9	9500	342	28	28
$t = 35$ min	2.9	9000	342	28	28
$t = 40$ min	2.9	9400	342	28	27
$t = 24$ h	3	8800	342	28	24

4. Discussion

Our objective is the calculation of a fragility index by means of TSDC measurements. Following relationship (4), the first part of the work is to calculate the variations of the relaxation time τ with the temperature. Using the data presented on Figs. 4 and 5 and relationship (7) this first step can be done easily. The results are reported on Figs. 6 and 7. The curvatures are indicative of non-Arrhenius behaviour. Two types of curves can be observed: for weakly drawn samples $\lambda \leq 2$ or weakly annealed samples ($t \leq 10$ min), the slopes are steeper than for highly crystallised samples (strain induced crystallised $\lambda > 2$ or annealed $t \geq 20$ min samples). So, as for DSC, the TSDC manifestation of the glass transition seems to be influenced by the presence of a crystalline phase.

The second part of the work is to normalise in a reduced T_g/T scale the X-axis. That opens the problem of the choice of a value of T_g. This is a difficult problem linked to the fact that the observed glass transition is a kinetic effect and not a thermodynamic phase change. First we propose to analyse the results obtained for a wholly amorphous PET, which presents the advantage of having been widely studied, so all the values of the parameters occurring in the different relationships (2)–(6) have already been estimated by means of DSC measurements [29]. These values are reported in Table 2. By means of the equal area method as proposed by Moynihan [7], the value of T_g (as defined on Fig. 1) can be easily determined from a DSC curve and we find $T_g = 74.5$ °C, which is reasonable comparing to other values proposed in the literature. For the TSDC signal, it could be tempting to use T_α (the temperature of the current peak maximum) but there is no specific reason to choose T_α rather than another temperature. When measurements are carried out by TSDC, where is localised the glass transition as defined previously on Fig. 1? We have only one experimental evidence fact: the dielectric TSDC manifestation of the glass transition occurs at lowest temperature than the calorimetric DSC one. This could be due to an equivalent frequency shift factor as often proposed to explain the dependence of the dielectric signal on the frequency. Following Van Turnhout [22], the calculation of the equivalent frequency is given by

$$f_e = \frac{E_a q}{2\pi R T_m^2} \tag{9}$$

where E_a is the activation energy of the relaxation process, q the heating rate, R the gas constant and T_m the temperature of the TSDC current maximum. Using DSC (Table 2) and TSDC data [26], the equivalent frequency for TSDC and DSC are found similar and close to 10^{-2} Hz. So, TSDC and DSC signals do not appears at the same temperature not because there is a equivalent frequency shift but because the nature and the time response of the experimental probes are different: for TSDC a depolarisation current peak resulting from cooperative motions of dipoles is detected, while for DSC we observe a heat flow step related to cooperative conformational rearrangements of segments of the macromolecular chains. The reorientation of the dipoles starts as soon as the cooperative motions create enough freedom for charge transfers, then when the temperature increases, and reaches T_g (DSC), the dipolar relaxation is not observable because all the dipoles have been disoriented despite that cooperative motions of molecular units can exist yet. Thus

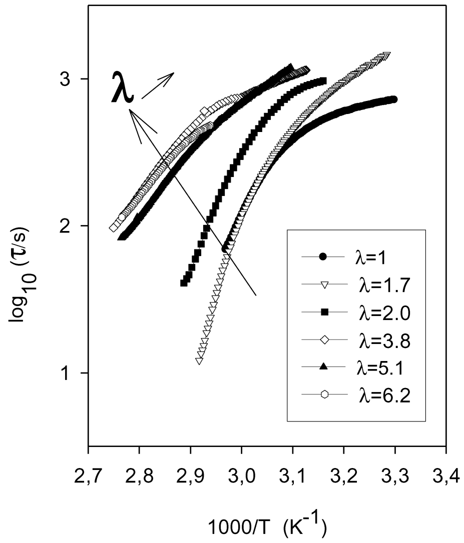

Fig. 6. Variations of $\log_{10} \tau$ with $1/T$ (the relaxation time in seconds is calculated from Eq. (5) for different drawn samples).

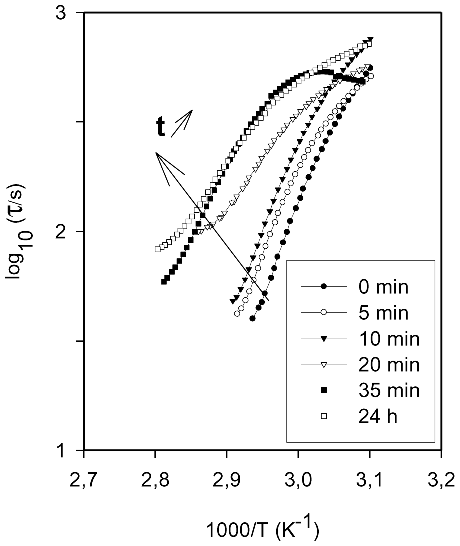

Fig. 7. Variations of $\log_{10} \tau$ with $1/T$ (the relaxation time in seconds is calculated from Eq. (5) for different annealed samples).

Table 2
DSC parameters for an amorphous PET from Refs. [29] and [32]

x	$\Delta h^*/R$ (kK)	m	$m_g = mx$	T_g (°C)
0.49	133	166	81	74

when using TSDC measurements we have to renormalize the x axis with the value of T_g obtains by DSC.

Nevertheless this corresponds for the TSDC signal to a domain of temperature for which the magnitude of the depolarisation peak does not allow the calculation of the corresponding relaxation time. To overcome this difficulty, we have used an electrical model whose time constant exhibits the same temperature dependence as that observed for polymers during TSDC measurements [30]. This electrical model was determined by means of an electrical simulator (PS–PICE) and its validity was demonstrated by comparing simulated and experimental results obtained on different kinds of polymers [31]. With this simulator, the variation of the relaxation time with the temperature can be described for a PET by

$$\log_{10} \tau = A - 0.43 \exp\left(B\left(\frac{1}{T_0} - \frac{1}{T}\right)\right) \quad (10)$$

Using this simulator, it is now possible to fit the TSDC data and to extrapolate the variations of the relaxation time to a wider domain of temperature including T_g. Table 1 collects the parameters obtained after each fit and Fig. 8 illustrates the fitting obtained for $\lambda = 1$. The calculation of the fragility index as proposed in relationship (4) can be done at T_g and we found, for amorphous PET, a value of 81.

On the other hand, the value of the TSDC relaxation time at T_g is of the order of 2 s. This value of relaxation time seems small compared to the $\tau(T_g) = 100$ s observed for a major part of the glass forming liquid [8]. Nevertheless, this value is not absurd because as already mentioned by Angell [8], 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 can cover, for different materials, 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. For PET, using relationship (2), it is possible to determine the value of τ_{T_g} if τ_0 and Δh^* are known. The value of $\Delta h^*/R = 133$ kK [32] have been obtained by the classical protocol which consists to determine the value of T_g for different values of the cooling rate [7], the value of Ln $\tau_0 = -379$ have been determined by means of a fitting procedure [33]. With these values we obtained $\tau_{T_g} = 25$ s which reinforces the idea of a value of τ_{T_g} lower than 100 s for PET.

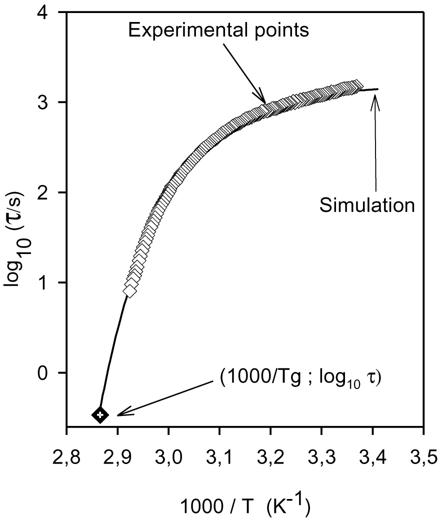

Fig. 8. Variations of $\log_{10} \tau$ with $1/T$ for the $\lambda = 1$ sample. The curve is calculated from Eq. (9) and the associated parameters are in Table 1. The dot for which $T = T_g$ is indicated on the curve.

Finally, the comparison of the value of the fragility index found by means of TSDC and DSC measurements shows immediately that this is m_g that is determined by TSDC and no m (Table 2).

At this point of the discussion, our results show that it is possible to determine a value of fragility index by means of TSDC experiments, but this fragility index is the one characterising the glassy state and not the glass forming liquid. This result is consistent with the fact that the depolarisation current peak characteristics of the glass transition is observed at a temperature below the calorimetric glass transition and thus the observed relaxation are characteristic of the glassy state rather than the liquid state. With this procedure, it is now possible from TSDC measurements to determine the value of the fragility index m_g for all the other samples and to analyse their variations as a function of the degree of crystallinity. Fig. 9 shows these variations and we may observe that amorphous and undrawn PET exhibit a value $m_g = 81$ and thus can be considered as 'fragile' materials. For weakly drawn ($\lambda < 2$) and until a crystalline structure does no occur, m_g is above 72; these materials can also be considered as 'fragile'. This last value is also obtained for a PET annealed for 5 min. PET remains wholly amorphous under these conditions. For samples annealed for 10 and 15 min, the thermal crystallisation reaches 9 and 25% respectively, and the value of m_g decreases down to 63. It is legitimate to suppose that this is due to the appearance of the crystalline phase. In the case of strain-induced crystallised films ($\lambda > 2$), m_g decreases down to 20 when λ reaches a value of 6. These very weak

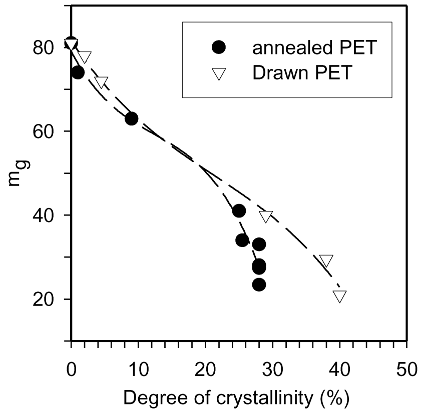

Fig. 9. Variations of the fragility index m_g with the degree of crystallinity.

values indicate that these highly drawn materials must be considered as 'strong' materials. It is interesting to note that for annealing time >20 min the values of m_g continue to decrease although the degree of crystallinity remains constant and lower to the degree obtained for the highest drawn materials.

In the semi-crystalline drawn PET, the amorphous phase is highly anisotropic due to the drawing, and the presence of small crystallites limits the size of the amorphous domain. One part of the amorphous phase, (called the rigid amorphous phase) that is linked to the crystalline domains, cannot relax at the glass transition of the material [27]. So, the structural units of the glassy phase are more bonded (the magnitude of the inter-chains van der Waals bonds increases due to the mechanical constraints) which is consistent with the evolution from a 'fragile' to a 'strong' character as soon as a crystallisation occurs and as the drawing ratio increases. The same arguments explained the results obtained for a semi-crystalline annealed PET, as the rate of crystallinity increases, a larger part of the amorphous phase is linked to the crystalline lamellas and the behaviour becomes increasingly stronger, although in this situation the amorphous phase remains isotropic. The last point is that for annealed time greater than 25 min although the degree of crystallinity has reached its maximum the fragility index continues to decrease (from $m_g = 33$ to 20), this indicates that a modification of the mobility in the amorphous phase remains possible.

5. Conclusion

Wholly amorphous PET is a 'fragile' material and we have shown that the fragility index m_g can also be calculated from TSDC measurements. When the amorphous phase becomes constrained by a crystalline phase, m_g values decrease and reach values characteristic of 'strong' materials. This is due to the inter-chain interactions which become more important. The fact that the amorphous phase is oriented in a draw direction does not appear to be an important factor for the fragility of the amorphous phase. On the other hand, the percentage of crystalline phase modifies drastically the value of m_g. An increase of X_c decreases the fraction of the amorphous phase able to relax at T_g (the mobile amorphous fraction) and it follows that the nature of the relaxation turns to a 'strong' behaviour.

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