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THE GLASS TRANSITION
Correlation of DSC and TSDC investigations

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Abstract

This work deals with a comparison of data obtained from differential scanning calorimetry (DSC) and thermally stimulated depolarization current (TSDC) investigations. Measurements were performed on various poly(ethylene terephthalate) films: a wholly amorphous, a thermally crystallized and drawn samples.

For each specimen, the TSDC complex spectra, resolved into elementary ones, led to the determination of the classical compensation temperature (T_c). The glass transition temperature (T_g) and the fictive equilibrium temperature (T_f) were determined by means of DSC. It appears that T_c is different from T_g and very close to T_f.

Keywords: compensation temperature, DSC, fictive temperature, poly(ethylene terephthalate), thermally stimulated depolarization current

Introduction

The structural relaxations occurring in a vitreous material (a polymer for instance) in the glass transition region can be studied with different techniques, such as differential scanning calorimetry (DSC) and thermally stimulated depolarization current (TSDC) [1].

The dielectric manifestation of the glass transition, called the α-transition, appears in a temperature range characterized by a maximum of the depolarization current at T_α. The value of T_α depends not only on the material, but also on the experimental method of measurement. Comparison of different data concerning T_α requires a knowledge of all the parameters which influence its value (the heating and cooling rates [2], the ageing duration [3], etc.) and also a knowledge of the temperature range of the α-peak (onset, middle, maximum, etc.). Elementary TSDC analysis performed on the α-transition allows determination of the relaxation time $\tau(T)$ defined from

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$$\tau(T) = \tau_c \exp\left\{\left(\frac{\Delta H}{R}\right)\left[\left(\frac{1}{T}\right) - \left(\frac{1}{T_c}\right)\right]\right\} \tag{1}$$

where ΔH is an apparent activation energy and R is the ideal gas constant. At the compensation temperature T_c, all the relaxational processes are presumed to exhibit the same relaxation time τ_c [4].

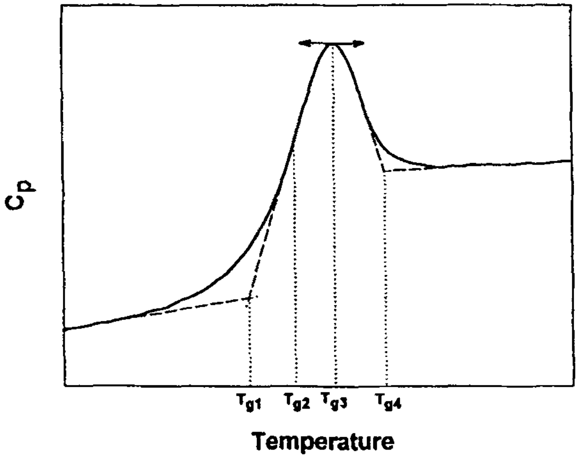

Fig. 1 The different ways to determine a value of the glass transition [5]: T_{g1} is the temperature at the beginning transition; T_{g2} is the temperature at the inflexion point; T_{g3} is the temperature at the maximum of the C_P curve; T_{g4} is the temperature at the end of the transition

On the other hand, in DSC experiments the reabsorption of heat in aged samples heated through the T_g range reveals itself: i) as an endothermic peak whose height increases with increasing ageing time, ii) and as a variation of the heat capacity C_p. The literature gives (at least) four ways to determine a value of T_g (Fig. 1) [5], and the remarks made for T_α remain valid [6, 7]. From calorimetric investigations performed in the glass transition range, it is very interesting to determine the value of the fictive temperature T_f', defined by Tool [8] (Fig. 2). When the samples are analysed immediately after cooling (no ageing), T_f' is very close to T_f. This temperature, defined in Fig. 2, is the temperature which separates the glassy and the liquid states [9]. Hence, at this temperature the relaxation time is the same for both states and it is frequently defined [10] by

$$\tau = \tau_o \exp\left(\frac{x\Delta h}{RT}\right)\exp\left(\frac{(1-x)\Delta h}{RT_f}\right) \tag{2}$$

where Δh is an apparent activation energy, and x is a structural parameter ($0 \leq x \leq 1$). This expression includes structure and temperature effects on the re-

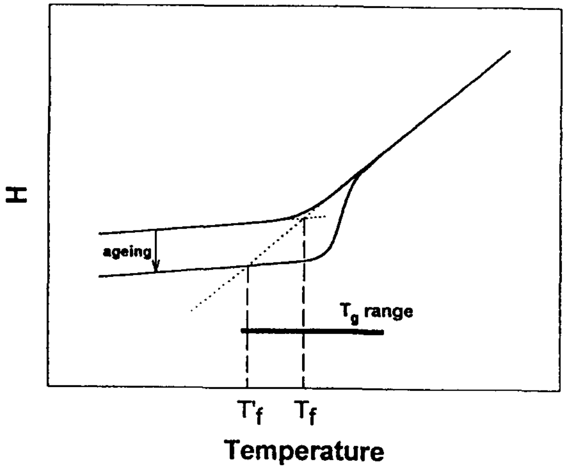

Fig. 2 Enthalpic diagram showing the fictive temperature as defined by Tool [8]

laxation time. Other expressions for τ have been proposed, but it has been shown that they are similar [11].

For a given material (that takes into account the cooling rate used to obtain the glass), the values of T_c and T_f can be regarded as constant parameters. Thus, it is tempting to compare T_c and T_f instead of T_c and T_g as is usually done [12]. This work deals with such a comparison of the T_c and T_f values obtained for different poly(ethylene terephthalate) (PET) samples, with the aim of clarifying the phisycal significance of the compensation temperature. The samples were prepared in such a way that the relative contributions played by cooperative and kinetic effects on the relaxation time values are modified.

Experimental

Sample preparation

To obtain samples with different structures, we performed different thermomechanical treatments on the same material. Experimental measurements were made on PET films with a thickness of 0.5 mm. The original films were isotropic and amorphous, as judged from birefringence, density and X-ray diffraction measurements, and were used in this form for the amorphous state (sample A). On annealing of the film at 130°C for 30 min, a semi-crystalline sample consisting of semi-crystalline spherulites included in an amorphous matrix was obtained (sample B). The degree of crystallinity X_c determined from the melting and crystallization enthalpies [13] was 26%.

Uniaxially deformed samples were obtained by means of an Instron tensile machine equipped with a heating chamber. After isothermal annealing for 15 min at 100°C, the samples were drawn at this temperature with a strain rate of 0.14 s^{-1}. The working temperature (100°C), which lay between the glass transition temperature and the crystallization temperature, allowed a homogeneous draw and did not lead to additional thermal crystallization. Then, to freeze structural relaxation, the sample was cold air-quenched down to room temperature. The draw ratio λ was calculated from the ratio of the extended length to the original one, determined from the displacement of inked marks. To limit the molecular mobility of the chains, an oriented amorphous sample with a medium draw ratio $\lambda=2.5$ (sample C) was prepared. A sample with a structure composed of a rigid amorphous phase and a strain-induced crystalline phase was also prepared (sample E). It had a high draw ratio ($\lambda=6$) and a degree of crystallinity $X_c=36\%$ [13]. Finally, to create a crystalline phase from an oriented structure, a sample drawn to $\lambda=2.5$ was reheated at 10°C min^{-1} up to 110°C, and then quenched back to room temperature (sample D, $X_c=21\%$) [13].

To avoid the drastic effect of the plasticization due to moisture sorption [14], before the preparation the samples were dried for 2 weeks at room temperature in a vacuum desiccator in the presence of P_2O_5. The sample preparation is outlined in Table 1.

Table 1 Sample preparation

Sample	Draw ratio/λ	Thermal process	Degree of crystallinity X_c/%
A	–	–	0
B	–	annealed at 130°C during 30 min	26
C	2.5	–	0
D	2.5	reheated at 10°C min^{-1} up to 100°C	21
E	6	–	36

Experimental procedure

Largely described elsewhere [15], the TSDC measurements were performed by means of an apparatus developed in our laboratory [16]. Elementary TSDC spectra were obtained by the following method:

The sample was submitted to the same field ($E=10^6$ V m^{-1}) for 2 min at temperature T_p (polarization temperature). The temperature was then lowered to $T_d=T_p$–5°C, and a short circuit was performed for 2 min. The sample was finally cooled (in short circuit) to $T_o=T_p$–40°C. The depolarization current I (in amperes) was measured during annealing up to T_p at 10°C min^{-1}. The conductivity σ (in siemens per metre) was used instead of current, as normalized quantity ($\sigma=I/E.S$ where S is the surface area of the sample). Use of the same procedure with increasing T_p allows exploration of all the α-transition.

Enthalpic analysis was performed with the help of a Perkin-Elmer DSC 7 apparatus. Calibration was based on the determination of the temperature and enthalpy of fusion of indium. Calorimetric measurements were made under a nitrogen atmosphere at a heating rate of 10°C min^{-1}. All the enthalpic curves presented are normalized to 1 mg. To compare TSDC and DSC data under the best conditions, the same thermal cycles were performed on the samples studied by TSDC and DSC, respectively.

Results

For the different samples, the data measured by DSC are reported in Table 2. The respective DSC curves are regrouped in Fig. 3. Among the different thermal phenomena which could occur during the heating of a polymer, only the glass transition was observed in the temperature range scanned. The endothermic peak which appeared in the cases of samples A and C was due to a sub-T_g relaxation (ageing) prior to analysis, while for the other samples only a change in C_p indicated the glass transition.

Table 2 Experimental DSC and TSDC data obtained on the different samples of PET

Sample	T_{g1}/°C	T_{g2}/°C	ΔC_p/J $g^{-1}K^{-1}$	T_f/°C	T_α/°C	T_c/°C
A	75	79	0.36	76	72	76
B	77	83	0.18	88	78	86
C	76	79	0.32	77	75	75
D	77	84	0.21	81	82	83.5
E	102	119	0.11	120	103	119

According to the method proposed by Moynihan [17], the value of T_f reported in Table 1 is the temperature for which the area (from T_1 to T_2) under the experimental $\Delta C_p(T)$ curve is equal to the shaded area shown in Fig. 4.

The α-transition is clearly observable in the different complex spectra (Figs 5 and 6). For sample B, an extra peak appears at a temperature higher than T_p. This transition, called ρ, is attributed to space charges [15]. For samples C, D and E, a pre-α-peak, called α′, was observed. It has been shown that this last transition appears as soon as anisotropy is induced in the sample [18]. The different parameters obtained from these experiments are also reported in Table 2. Figure 7 shows elementary spectra obtained by TSDC on sample B. Only the beginning of each peak was resolved, to avoid any additional structural relaxations due to the thermal cycles necessarily performed to obtain the elementary spectra. Due to the narrowing of the T_p–T_d windows, each elementary spectrum was considered to be characteristic of entities relaxing with the same relaxation time constants. According to the Debye equation:

$$J(t) = \frac{dP(t)}{dt} = -\frac{1}{\tau(T)}P(t) \tag{3}$$

the rate of change of the polarization at any time of the depolarization process, $J(t) = dP(t)/dt$, is proportional to the remaining polarization $P(t)$. The relaxation time $\tau(T)$ was obtained from $J(T)/P(T)$, where $J(T)$ is the measured density current at temperature T, and $P(T)$ is the surface area of the discharge peak from T to infinity. According to Eq. (1), the compensation temperature T_c was deter-

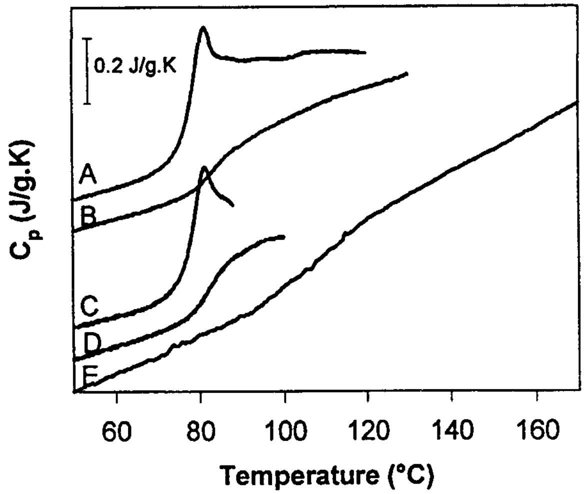

Fig. 3 C_P curves obtained on the samples A–E. The curves are shifted on the C_P axis for legibility

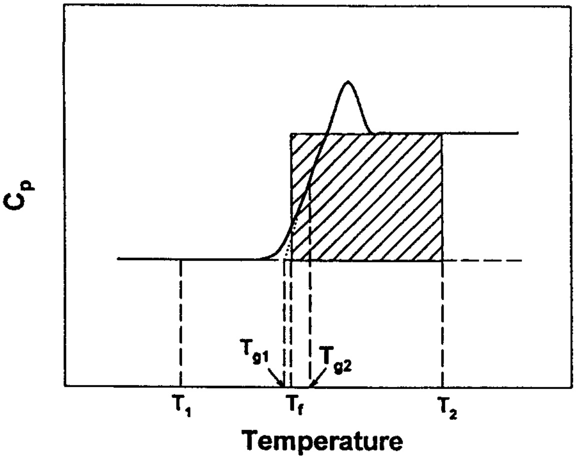

Fig. 4 Determination of the fictive temperature following the Moynihan method [17]

mined for each sample from the variations in lnτ with $1/T$. Fig. 8 exemplifies the linear dependence of lnτ on $1/T$; the values of T_c are read as the average intersection of the extrapolated lines corresponding to each elementary spectrum and are given in Table 2.

Discussion

For samples A and C, the similar position and height of the endothermic peak and the similar variation of the heat capacity C_p occurring during the glass

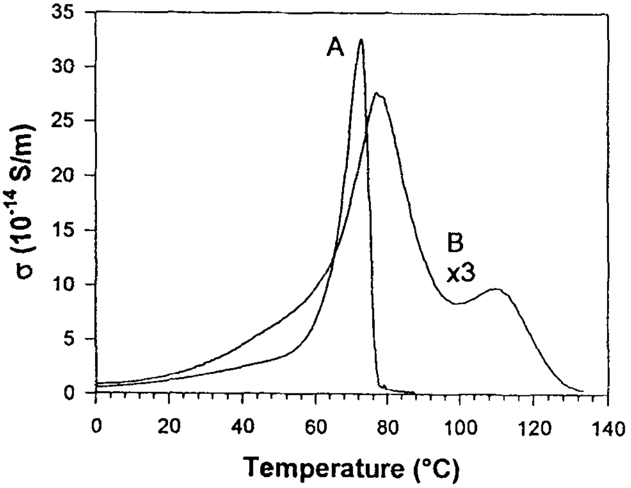

Fig. 5 Complex TSDC spectra obtained on the samples A and B

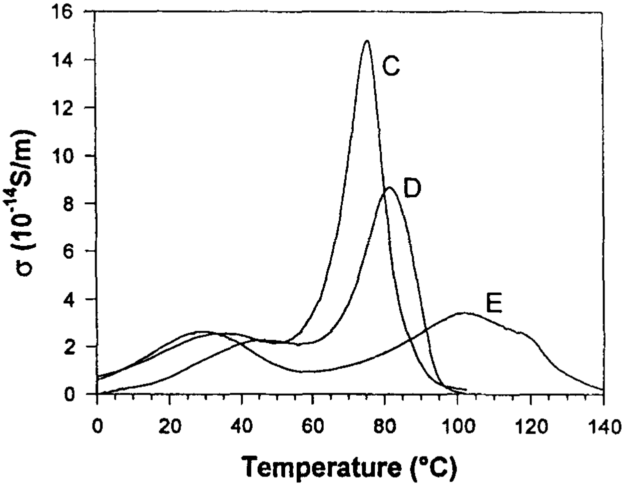

Fig. 6 Complex TSDC spectra obtained on the samples C, D and E

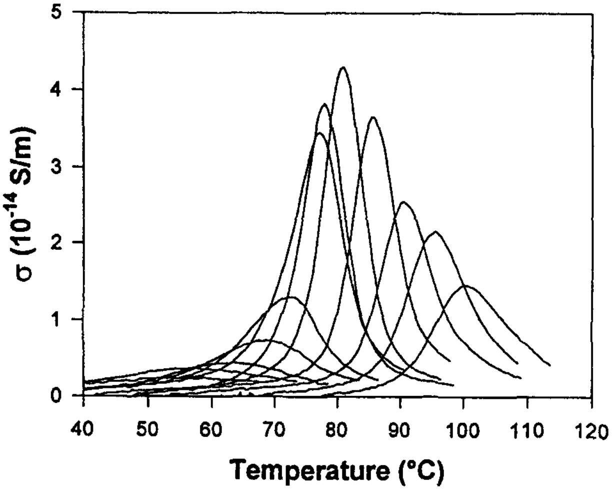

Fig. 7 Elementary TSDC spectra obtained on the sample B

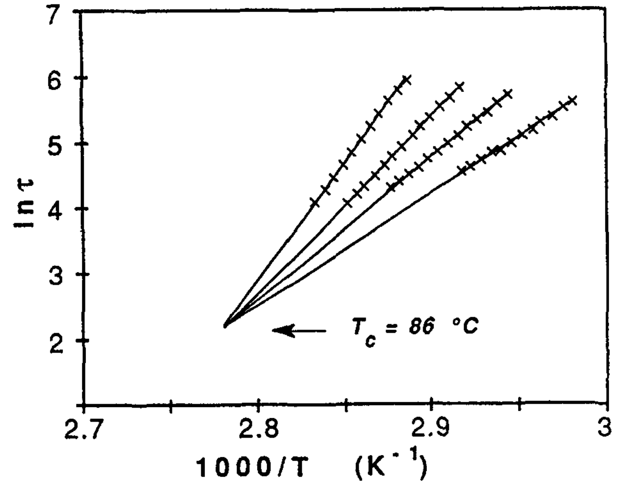

Fig. 8 Determination of the compensation temperature from the variations of ln(τ) *vs*. T^{-1} for sample B

transition show that the sub-T_g ageing occurs in the same way. Thus, there is no real difference between a wholly amorphous and a weakly drawn state as far as no contraints act on the macromolecular chains. This is confirmed by the similar values for the fictive temperature T_f and the compensation temperature T_c calculated from the TSDC spectra. At the end of the transition of sample C, a decrease in the C_p signal is observed. This is the beginning of the exothermic peak accompanying the crystallization of sample C. This peak is not observable for sample A. Indeed, the position of the crystallization peak decreases with increasing draw ratio [19].This is the only difference observable between the two samples and this difference does not affect the thermal behaviour of the amorphous state below T_g.

It is tempting to compare the thermally semi-crystallized samples B and D. They differ principally in mechanical drawing prior to crystallization ($\lambda = 1$ and $\lambda = 2.5$, respectively). Except for the already-mentioned influence of the drawing on the shift of the crystallization zone, the amorphous phase exhibits the same behaviour, and it is not surprising to determine similar values for T_{g2}, ΔC_p, T_α and T_c for the two samples. However, the presence of a rigid amorphous phase (widely developed by Wunderlich [20]) linked and surrounding the crystalline zones is revealed by the widening of the glass transition zone (T_{g2}–T_{g1} is larger for semi-crystalline samples than for amorphous ones). The decrease in ΔC_p observed for samples B and D is due to the presence of the crystalline structure induced by the thermal treatment. Finally, the most drawn sample E displays great differences from the others: i) a smaller value of ΔC_p, ii) an important shift of the glass transition towards higher temperatures, and iii) a wide transition zone.

These results are characteristic of a strain-induced crystallized sample [19]: the relaxation of the amorphous phase of the sample is hindered by the crystalline phase, and the thermal and mechanical treatments lead to the stiffness and the anisotropy of the amorphous phase. Thus, the high value of T_{g2} (or T_α) is due to the disappearance of the unconstrained or flexible amorphous phase, while the large amplitude of the transition is due to the constriction of the molecular chains.

For all the samples (characteristic of various amorphous states: flexible, linked to crystallites or very constrained), the calculated temperatures T_f and T_c, which are independent of the kinetic effects (as heating rate [2]), are very close together. Accordingly, for the glass transition, the compensation and the fictive temperatures have the same physical meaning. This is not surprising as, by definition, in TSDC the compensation temperature is the temperature at which all the relaxational processes have the same time constant, and on the other hand the fictive temperature, defined as the intercept of the glassy equilibrium curve and the rubbery equilibrium curve, can be regarded as the <ideal> T_g, i.e. the temperature where all the glassy relaxational processes have the same time constant. These remarks are applicable to other polymeric materials too [21].

Conclusions

Investigations carried out on the glass transition of various amorphous states of PET (flexible, linked to crystallites, and strongly drawn) show the dependence of the characteristic parameters of the glass transition on the structure. For each amorphous state, a comparison of the TSDC and DSC results reveals that the compensation temperature and the fictive thermodynamic equilibrium temperature, which allows avoidance of the heating rate effect, are identical.

References

1 B. B. Sauer, R. Beckerbauer and L. Wang, J. Polym. Sci., Polym. Phys., 31 (1993) 1861.
2 C. Cabot, M. Jutigny, E. Dargent, J. Bayard, J. M. Saiter and J. Grenet, Cal. Therm. Anal., 26 (1995) 215.
3 A. Bernes, G. Teyssedre and C. Lacabanne, Cal. Therm. Anal., 26 (1995) 185.
4 B. B. Sauer and P. Avakian, Polymer, 33 (1992) 4682.
5 J. Perez "Physique et mécanique des polymères amorphes", Tec & Doc Lavoisier, Paris 1992.
6 C. T. Moynihan, A. J. Easteal, J. Wilder and J. Tucker, J. Phys. Chemistry, 78 (1974) 2673.
7 J. Grenet, J. M. Saiter, C. Vautier and J. Bayard, J. Thermal Anal., 38 (1992) 557.
8 A. Q. Tool, J. Am. Ceram. Soc., 29 (1946) 240.
9 J. M. G. Cowie and R. Fergusson, Polymer, 34 (1993) 2135.
10 O. S. Narayanaswami, J. Am. Ceram. Soc., 54 (1971) 491.
11 J. M. Saiter, A. Assou, J. Grenet and C. Vautier, Phil. Mag. B, 64 (1991) 33.
12 C. Lacabanne, A. Lamure, G. Teyssedre, A. Bernes and M. Mourgues, J. Non-Cryst. Solids, 172–174 (1994) 884.
13 E. Dargent, thèse d'université, University of Rouen, Mont-Saint-Aignan, France, 1994.
14 D. Langevin, J. Grenet and J. M. Saiter, Eur. Polym. J., 30 (1994) 339.
15 J. Van Turnhout, "Thermally stimulated discharge of polymer electrets", Elsevier, Amsterdam 1975.
16 J. J. Santais, Thesis, CNAM, Rouen, France, 1992.
17 C. T. Moynihan, A. J. Easteal, M. A. Debolt and J. Tucker, J. Amer. Ceram Soc., 59 (1976) 12.
18 E. Dargent, J. J. Santais, J. M. Saiter, J. Bayard and J. Grenet, J. Non Cryst. Solids, 172–174 (1994) 1062.
19 E. Dargent, J. Grenet and X. Auvray, J. Thermal Anal., 41 (1994) 1409.
20 S. Z. T. Cheng, R. Pan and B. Wunderlich, Macromol. Chem., 189 (1988) 244.
21 C. Cabot, E. Dargent, M. Jutigny, J. M. Saiter, J. Bayard and J. Grenet, presented at the 1st International Conference on Mechanics of Time Dependent Materials, Ljubljana 1995.