

THE T_g DISPLACEMENT MEASUREMENTS: A WAY TO FORESEE THE PHYSICAL BEHAVIOUR AND THE USE OF GLASSY POLYMERS

J. Grenet, J. M. Saiter, C. Vautier and J. Bayard

FACULTE DES SCIENCES DE ROUEN, LABORATOIRE L. E. C. A. P., B. P. 118, 76134, MONT-SAINT-AIGNAN CEDEX, FRANCE

The effect of ageing temperature (below T_g) on physical ageing of glassy PET has been investigated by differential scanning calorimetry. The position of the glass transition endotherm was found to be strongly dependent on the annealing conditions (time, annealing temperature). A single relaxation time model is proposed for the analysis of physical ageing.

The variations of the equilibrium relaxation time τ_{150} with annealing temperature allow the determination of the parameters of the model. Finally, using these constants, one can determine the thermal past and foresee the thermal future of unknown samples which are of prime importance in processes using temperatures around the glass transition temperature.

Keywords: T_g displacement, glassy polymers

Introduction

It is of prime importance to foresee the physical behaviour (i.e. evaluate the ageing) in the use of a material, particularly for glassy polymeric materials. It holds in standard use for wear and tear of things as well as in industrial processes where the material (or a preform of the final product) is heating (for softening) above its glass transition temperature (T_g) before the final forming process. Indeed, because of the lack of thermodynamic equilibrium in such glassy materials, relaxation processes occur during ageing at temperatures lower than T_g .

It is well known that the value of the glass transition temperature depends on many parameters such as the following:

- i) the nature of the polymer;
- ii) the thermal history (this includes preparation as well as ageing);
- iii) the different stresses and constraints (mechanical, illumination,...). However, in spite of the great number of parameters which influence the value of T_g ,

it is possible to use a judicious selection of experiments to approach ageing phenomena in glassy polymers by means of measurements of T_g . As number of changes in physical properties (optical, mechanical, thermal,...) are observed when the material is heating (or cooling) through the glass transition region, different methods could be used but the majority of them is connected with thermal analysis methods. Moreover all transitions which imply thermal exchanges will be more or less observable by DSC means and can be characterized by their energies and their temperatures.

The aim of this paper is to develop a method which, from DSC measurements, allows for glassy polymers an estimation of the thermal past and/or a prediction of the future. Experimental results presented here were carried out on polyethylene terephthalate (PET) glassy samples.

Sample preparation

The samples have been prepared by quenching ($\approx 10^2 \text{ deg}\cdot\text{s}^{-1}$) from the melt of a granule of PET directly into the sample pans of the calorimeter (Perkin Elmer, system 4). In order to obtain a good reproducibility in ageing studies, the same sample was used for a series of experiments. This is possible by cooling the sample, after heating it through the transition region, back to the ageing temperature. This thermal cycle (D→E→F→B→C in Fig. 1), called rejuvenation, leads to the restoration of the as-prepared state (no degradation was observed by thermogravimetry as well as X-ray diffraction). The glassy nature of the samples

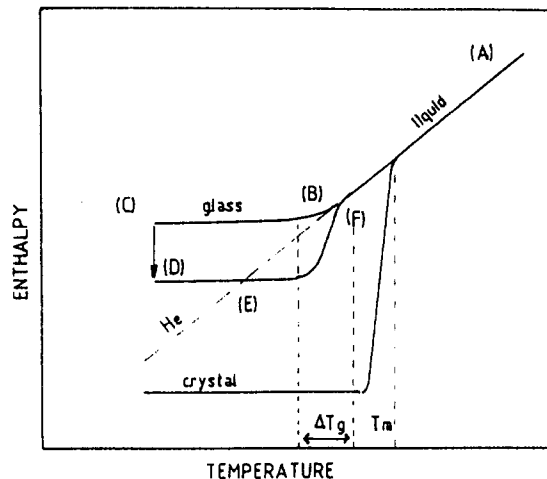


Fig. 1 Change of enthalpy during cooling (A→B→C), ageing (C→D) and reheating (D→E→F). ΔT_g indicates the range of variations of T_g

was probed by X-ray diffraction. Finally the value of the glass transition temperature is measured directly on the curve as shown in Fig. 2.

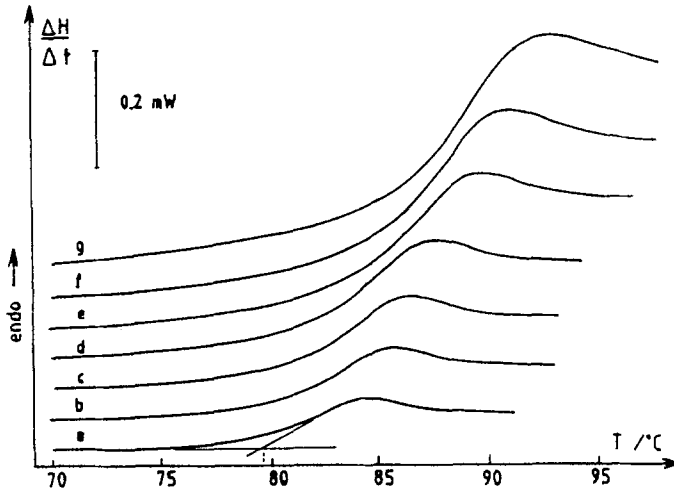


Fig. 2 Determination of T_g on a DSC curve for various heating rates: a) $r=15 \text{ deg}\cdot\text{min}^{-1}$; b) $r=20 \text{ deg}\cdot\text{min}^{-1}$; c) $r=25 \text{ deg}\cdot\text{min}^{-1}$; d) $r=30 \text{ deg}\cdot\text{min}^{-1}$; e) $r=40 \text{ deg}\cdot\text{min}^{-1}$; f) $r=50 \text{ deg}\cdot\text{min}^{-1}$; g) $r=60 \text{ deg}\cdot\text{min}^{-1}$. T_g is obtained from the intercept of the slope on the left-hand part of the peak with the base line

Methods and models

The main parameter which characterizes an ageing process is the relaxation (or retardation) time τ which occurs in the relaxation equation:

$$\frac{\partial H}{\partial t} = -\frac{H - H_e}{\tau} + C_{pg} \cdot r \quad (1)$$

where H is the current enthalpy, H_e the equilibrium enthalpy (when the ageing is achieved), t the time, r the heating rate and C_{pg} the heat capacity in the glassy state. Other authors use several time constants or distribution of time constants [1–3], but it has been shown [4] that, if the range of annealing temperatures used during the relaxation process studies is close to T_g , a single relaxation time is a good approximation.

We consider, hereafter, a simple model using a single relaxation time which separates the temperature dependence $F(T)$ and the structural variation $G(S)$ (co-operative effects). In this model, used in many previous works [4–6] the relaxation time could be given by [7–9]:

$$\ln \tau = \ln a - b \cdot T - c \cdot (H - H_e) \quad (2)$$

where the constants a , b , c depend on the material. Moreover, in a first approach, we may suppose that the difference ΔC_p between the specific heats in the liquid and in the glassy states is independent of the annealing temperature (T_a), annealing duration and heating rate; then a linear relationship exists between the variation of enthalpy and the variation of temperature:

$$H - H_e = \Delta C_p \cdot (T_f - T) \quad (3)$$

T_f is the 'fictive' temperature (for which the curve $H(T)$ followed during heating reaches the extrapolated equilibrium curve $H_e(T)$).

Using ageing time, annealing temperature and heating rate as parameters, the proposed method which leads to the different constants of the material, requires two kinds of experiments:

Dependence of T_g on heating rate

During heating or cooling, at different rates r , of samples of the same age, we could assimilate the continuous change of temperature to a series of instantaneous small variations ΔT followed by an isothermal hold of duration $\Delta t = \Delta T / r$. The structure will readily relax to its equilibrium state if the relaxation time is smaller than Δt ; when τ is larger than Δt the structure will remain in the glassy state. So we may define the glass transition temperature T_g as the temperature where the relaxation time τ becomes comparable with the isothermal hold Δt and consequently $r \cdot \tau(T_g)$ is constant. Thus

$$\ln r = -\ln a + b \cdot T_g + c \cdot (H - H_e) + \text{constant} \quad (4)$$

and (with Eq. (3))

$$\ln r = b \cdot T_g - c \cdot \Delta C_p \cdot T_g + c \cdot \Delta C_p \cdot T_f + \text{constant} \quad (5)$$

The last term depends on ageing duration, but for the same ageing T_f is constant. So

$$\frac{d \ln r}{d T_g} = b - c \cdot \Delta C_p \quad (6)$$

Figure 3 shows the good agreement between this model and the experimental results. When the measurements are carried out with cooling from the liquid state, this method leads to $d \ln r / d T_g = b$ (because, in this case, the departure from the liquid equilibrium vanishes for temperatures greater than T_g).

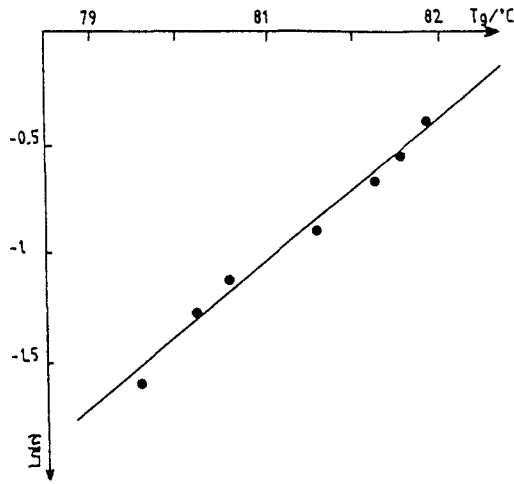


Fig. 3 Change of T_g against logarithm of heating rate

Dependence of T_g on heating

In this case, the heating rate and the annealing temperature are kept constant. As in the above section, the variations of H and of T_g are linked by the linear relationship

$$H_2 - H_1 = (b - c \cdot \Delta C_p) \cdot (T_{g1} - T_{g2}) / c \tag{7}$$

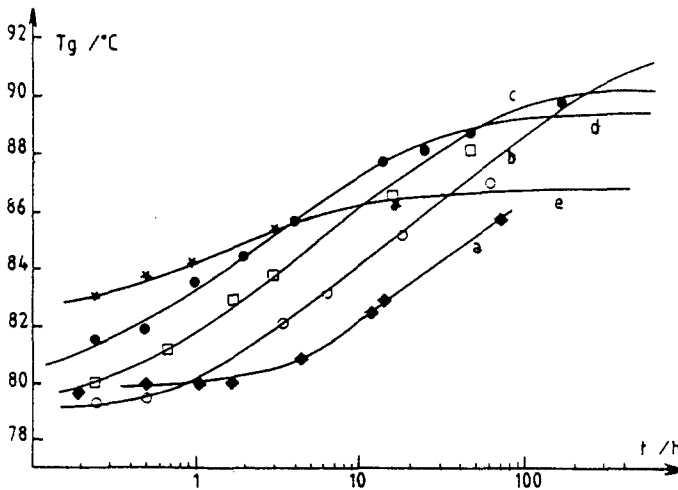


Fig. 4 Displacements of T_g with ageing time for various annealing temperatures ($r=20 \text{ deg}\cdot\text{min}^{-1}$):
 a) $T_a=50^\circ\text{C}$; b) $T_a=55^\circ\text{C}$; c) $T_a=60^\circ\text{C}$; d) $T_a=65^\circ\text{C}$; e) $T_a=70^\circ\text{C}$

For two ageing duration t_1 and t_2 (H_1, H_2, T_{g1}, T_{g2} respectively), the glass transition is reached when the relaxation times are equal. Then the variations of T_g (Fig. 4) with time can be described by

$$\frac{d \Delta T_g}{dt} = - \frac{\Delta T_g \cdot \exp([b - c \cdot \Delta C_p] \cdot \Delta T_g)}{\tau_{iso}} \quad (8)$$

with $\tau_{iso} = a \cdot \exp\{-b \cdot T_g\}$ and $\Delta T_g = T_{ge} - T_g$ (T_g and T_{ge} are respectively the glass transition temperatures after an ageing duration t and after complete ageing). The curves in Fig. 4 obtained by fitting the experimental results and the Eq. (7) lead to the isothermal relaxation time τ_{iso} . The changes of $\ln \tau_{iso}$ with annealing temperature enable the determination of $a = 8 \cdot 10^{41}$ h and $b = 0.27 \text{ K}^{-1}$ (Fig. 5). Other material constants $c = 0.11 \text{ gJ}^{-1}$ and $\Delta C_p = 0.54 \text{ Jg}^{-1} \text{ K}^{-1}$ are obtained from the heating rate dependence measurements and by calorimetric means.

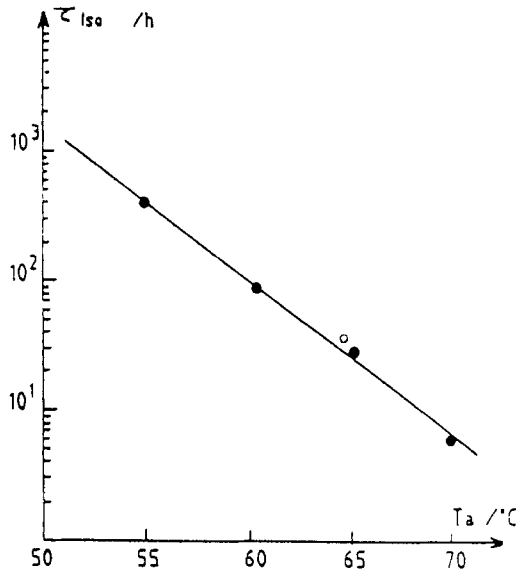


Fig. 5 Change of the equilibrium relaxation time τ_{iso} against annealing temperature

Figure 6 shows the variations of the initial glass transition temperature T_{gi} (fresh sample) and of the equilibrium value T_{ge} with the annealing temperature. The initial T_{gi} increases with the temperature T_a while the equilibrium value T_{ge} decreases. It is clear that these variations lead to a limit for T_a (when $T_a \approx T_{ge} \approx T_{gi}$); indeed the higher is T_a , the lower is the equilibrium value. For the lowest ageing temperatures, the relaxation phenomena are so long that measurements are not possible compared with the experimental time and for the highest

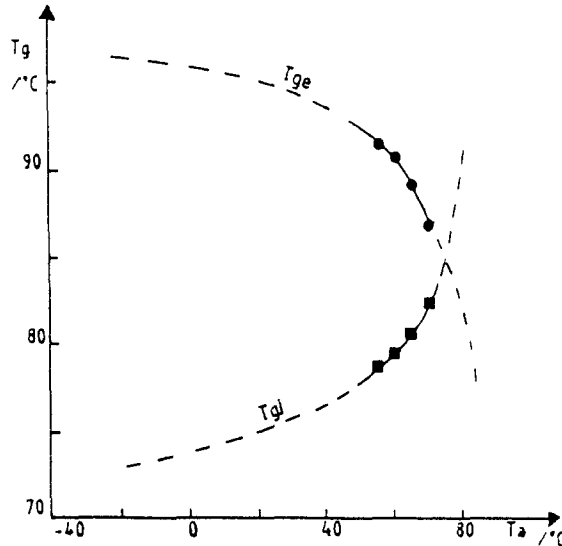


Fig. 6 Variations of the initial and of the equilibrium glass transition temperatures with annealing temperature. Curves are extrapolated behaviours

T_a the material relaxes so fast that the measurements cannot be considered to be significative.

Applications

Let us consider a batch of glassy PET preform of unknown ageing and stocked at temperatures between 15° and 20°C. Because of the structural relaxation during this ageing time, the final forming process (which generally implies heating above T_g) will be different (due to the T_g changes). So it is quite important to be able to estimate the thermal past and the future of these preforms. Figure 6 shows the variations of T_{gi} and of T_{ge} for the ageing temperature range considered. Using these values and the relaxation constants of PET, we could draw the Time–Temperature ageing diagram of this batch (Fig. 7). In this diagram, the glass transition temperature of a preform must fall in the shaded area which represents the ageing zone.

Now, it is sufficient to make a statistical study of the glass transition temperature of this batch. Results reported in Fig. 8 do not show significative differences between the three regions of preforms studied (with respect to the different cooling conditions in the matrix after injection, we have arbitrarily distinguished three regions of analysis: the external sides and the middle). Then the mean value of T_g (74°C) reported in Fig. 7 indicates a stockage duration of 1000 h. In the same way, for these ageing conditions, Fig. 7 does not show no-

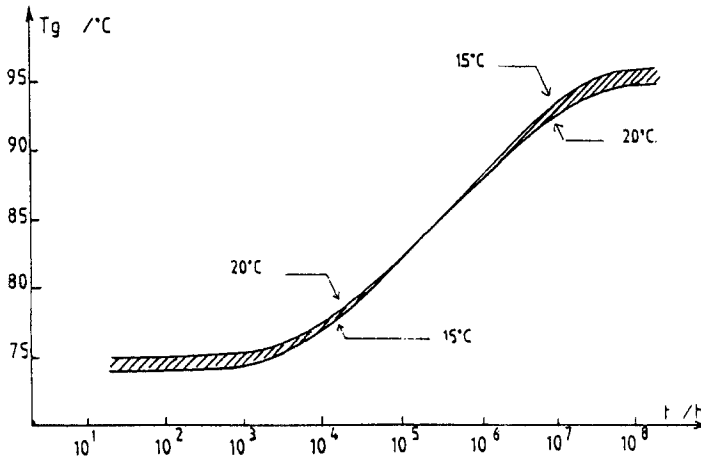


Fig. 7 Time- T_g diagram: the shaded area indicates the ageing zone of the material for the considered stockage temperature range (15° – 20°C)

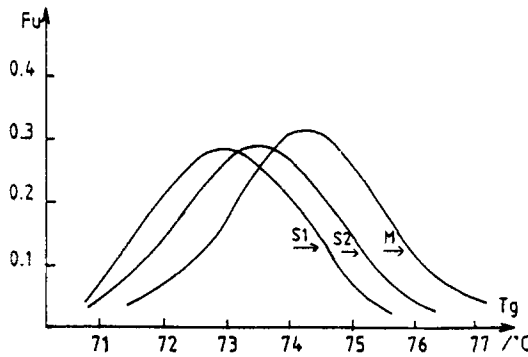


Fig. 8 Distribution function of the T_g measured of a batch of unknown PET preforms (S1, S2 and M indicates the sides and the middle of the analyzed samples, respectively)

ticeable changes of the glass transition temperature before 5000 hours (≈ 6 months) of ageing. Then, for the youngest preforms, the forming process could be the same whereas for the oldest ones the temperature of the processes must be increased up to twenty degrees.

References

- 1 A. J. Kovacs, *J. Polymer Sci.*, 30 (1958) 131.
- 2 A. J. Kovacs, *Fortschr. Hochpolym.Forsch.*, 3 (1963) 394.

- 3 N. Clavaguera, M. T. Clavaguera-Mora, S. Surinach, M. D. Baro, *J. Non-Crystalline Solids*, 104 (1988) 283.
- 4 J. P. Lamagnac, J. Grenet and P. Michon *J. Non-Crystalline Solids*, 45 (1981) 157.
- 5 J. M. Saiter, A. Assou, J. Grenet and C. Vautier, *Phil. Mag. B*, 64 (1991) 33.
- 7 C. T. Moynihan, A. J. Easteal, J. Wilder and J. Tucker, *J. Phys. Chem.*, 78 (1974) 2673.
- 8 A. J. Kovacs, J. M. Hutchinson and J. J. Alkonis, *Structure of Non-Crystalline Materials*, edited by P.H. Gaskell, Taylor & Francis, London 1977, p. 153.
- 9 A. Q. Tool, *J. Am. Ceram. Soc.*, 29 (1946) 240.

Zusammenfassung — Mittels DSC wurde der Einfluß der Alterungstemperatur (unterhalb T_g) auf das physikalische Altern von glasartigen PET untersucht. Die Lage der Glasumwandlungsendothermen hängt stark von den Temperungsbedingungen (Dauer, Temperatur) ab. Es wird ein Relaxationszeitmodell für die Analyse physikalischen Alterns vorgeschlagen.

Die Parameter dieses Modelles können aus der Änderung der Gleichgewichtsrelaxationszeit $\tau_{i,30}$ mit der Temperungstemperatur ermittelt werden. Unter Benutzung dieser Konstanten kann die thermische Vergangenheit unbekannter Proben bestimmt und die thermische Zukunft derselben vorhergesagt werden, was für Vorgänge bei Temperaturen um den Glasumwandlungspunkt von primärer Wichtigkeit ist.