

Glass Transition Temperature and Value of the Relaxation Time at T_g in Vitreous Polymers

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Summary: Many works focused on glassy polymers determine values of glass transition temperature (T_g) and an overview of the literature shows that depending on the method used, values of T_g are found different for the same material. In this paper, a review of data collected on different materials are used and interpreted in term of molecular mobility characterized by relaxation time functions. By using three independent experimental procedures (dielectric, thermally depolarized current and calorimetric), we show that the value of the glass transition and the value of the relaxation time at T_g can be correctly determined. It is also shown that the assumption: $\tau(T_g) = 100$ s is constant, is not correct. The protocol proposed also allows the determination of the value of the fragility index “m” of the glass forming liquid with a great accuracy.

Keywords: fragility index; glass transition; molecular dynamic; relaxation

Introduction

It is known that liquids can be transformed into glassy state by cooling, when the cooling rate is sufficiently high to avoid crystallization of the material. Below the crystallization point, the liquid state is transformed into a metastable state known as super cooled liquid (like liquid-state), in which the viscosity increases strongly as the temperature decreases. For a viscosity value, typically between 10^{11} – 10^{12} Pa s, the super-cooled liquid vitrifies, a glass is obtained (Figure 1 line A-B-C). A glass is thermodynamically a non-equilibrium state. The glassy nature is revealed by a transition occurring at a temperature (T_g) called the glass transition temperature. Due to the excess of free energy (or free volume, or entropy), structural relaxation phenomena will occur when the glass is maintained at a temperature $T < T_g$ (Figure 1 line C-D-E). This is the most easy way to define the glass

and the glass transition. Nevertheless, one needs to keep in mind that the origin of the glass transition is one of the unsolved problems of condensed matter physics, and up to day no predicting model exists to connect thermodynamic, kinetic and structural considerations with a value of T_g .

This is because all the properties of the glass will depend on its thermal history. The glass transition is not a thermodynamic transition. The thermal history includes, for example, the annealing time, the cooling and heating rates, the pressure and other characteristics of a specific history. The second important problem is to know what happens to the matter for temperatures above and below T_g . Do all the like liquid states freeze in at T_g during the cooling period? The model proposed by J. Hutchinson et al.^[1] supposed that only a fraction of the liquid is frozen in (Figure 2).

This model is also supported by the concept of the random walk model proposed by Arkhipov,^[2] a model successfully used by two independent research groups^[3–5] to analyze the sub- T_g molecular relaxation of unsaturated polyester resins. On the other hand, after infinite ageing, does the glass reach the equilibrium curve given as

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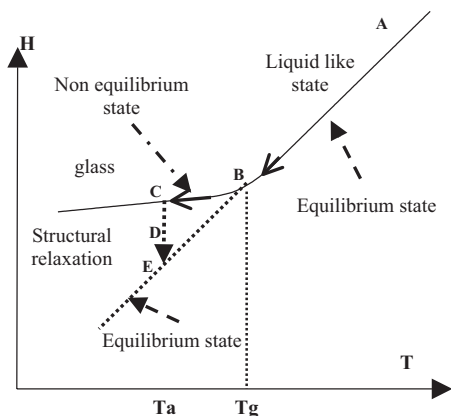


Figure 1.

Standard way to define the glass transition temperature T_g and to define the glassy state. $T_a < T_g$ is an annealing temperature. Keeping the glass at T_a during an infinite duration (ageing) will lead to molecular relaxations called physical ageing. During ageing the glass must lose its excess of energy and must reach the thermodynamic equilibrium given by the index E.

expected on Figure 1. In other words, does the following relationship valid?

$$\Delta H_{(\text{infinity})} = \Delta C_p [T_g - T_a] \quad (1)$$

Where $\Delta H_{(\text{infinity})}$ is the energy lost after an infinite ageing performed at the temperature T_a and ΔC_p is the difference of heat

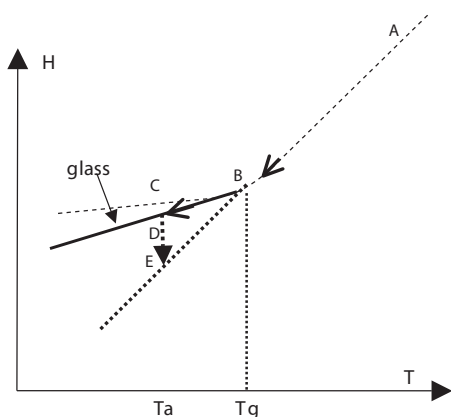


Figure 2.

J.M. Hutchinson model.^[1] $T_a < T_g$ is an annealing temperature. All the like liquid state is non-frozen in at T_g and we may distinguish two kinetics of relaxation, one fast and a second slow. During ageing the glass must reach the thermodynamic equilibrium given by the index E.

capacity $\Delta C_p = C_{p\text{liquid}} - C_{p\text{glass}}$ measured at T_g . The results obtained by different research groups^[6–8] show the need to introduce an intermediate equilibrium position defined the quantity δ as shown on Figure 3. Thus, with this model an infinite duration will lead the glass to the energy level given by:

$$\Delta H_{(\text{infinity})} = \Delta C_p [T_g - T_a] - \delta \quad (2)$$

Whatever the model proposed, for temperatures below the glass transition the relaxation phenomena (or the physical ageing) engage molecular movements of cooperative natures.

In the glassy state, one structural unit is allowed to move only if a certain number of neighboring structural units are engaged in the same process.^[9] This is one of the most important properties of the glass. The second important characteristic is: the relaxation phenomenon can be described by a relaxation function which is non exponential function of time. It is often used the so called Kohlrausch-Williams-Watt (KWW) relation:^[10]

$$\Phi(T, t) = \Phi_0 \left[\exp \left(- \frac{t}{\tau} \right)^\beta \right] \quad (3)$$

Where β is the non-linear parameter ($0 < \beta < 1$) and τ is the relaxation time function. This relaxation time function

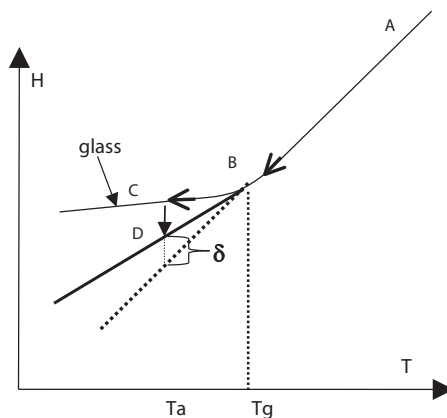


Figure 3.

J.L. Gomez Ribelles Model.^[6] T_a is an annealing temperature $< T_g$. All the like liquid state is frozen in at T_g . During ageing the glass must reach the pseudo thermodynamic equilibrium given by the index D.

must take into account the cooperative nature of the molecular relaxation. That means that τ is a function of the temperature, ($F(T)$) and of the instantaneous structure ($G(\zeta)$) or which is equivalent to of the time ($G(t)$); (ζ is a physical parameter which characterizes the structure of the glass at the time t), so:

$$\tau = \tau_0 \cdot F(T) \cdot G(\zeta) = \tau_0 \cdot F(T) \cdot G(t) \quad (4)$$

For temperatures above T_g , a classification of the glass forming liquids from the variations of the viscosity with the temperature (Figure 4), and more exactly with the normalized reduced T_g/T quantity has been proposed by Angell.^[11] For the extremes, glass-forming liquids with an approximately Arrhenius-type temperature dependence of the viscosity (or the relaxation time) are referred to as “strong”, while the other extreme a non-Arrhenius-type temperature dependence of the viscosity (or the relaxation time) is termed “fragile”. For the later

a Vogel- Tammann-Fulcher relationship (called VTF) can be used to fit the data:^[12–14]

$$\tau = \tau_0 \exp \left[\frac{B}{T - T_0} \right] \quad (5)$$

Where B is a constant and T_0 the Kauzmann temperature.^[15] For $T_a < T_0$ the time needs for the glass to reach the equilibrium is infinity. From the variations of the relaxation time (τ) with the temperature, a fragility index m can be calculated according to the following relationship:^[16]

$$m = \left. \frac{d \log(\tau)}{d \left(\frac{T_g}{T} \right)} \right|_{T=T_g} \quad (6)$$

The value of the fragility index varies from $m=16$ ^[17] for very strong glass-forming liquids like those formed by high directional bond molecules, to $m=250$ ^[18] for very fragile glass-forming liquids for which the inter atomic or intermolecular

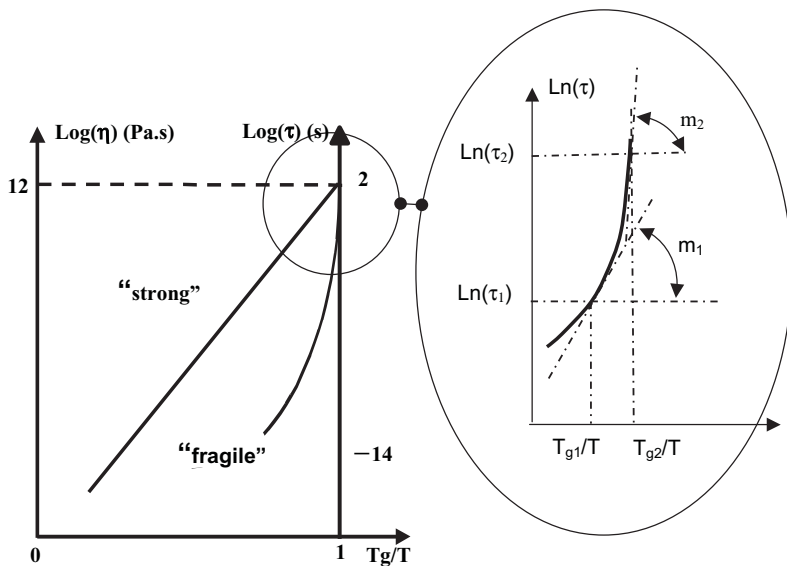


Figure 4.

Classification of the glass forming liquids from the variations of the viscosity with the normalized reduced T_g/T quantity as proposed by Angell.^[11] For the extremes of the behavior, glass forming liquids which exhibit an approximately Arrhenius temperature dependence of viscosity (or relaxation time) are defined as strong glass formers; and on contrary those which exhibit a non-Arrhenius behavior are declared as fragile glass formers. The value of the fragility index i.e. the slope of $\ln(\tau)$ at T_g depends on the chosen values of T_g . This is particularly true for fragile glass forming liquid.

bonds are non-directional.^[19] As the viscosity of a glass-forming liquid depends on the nature of intra- and intermolecular interactions, the fragility index m allows to characterize the nature of bond interactions in the liquid state at the glass transition.^[20] The determination of the value of m requires the knowledge of the value of T_g which is often made with the assumption that the value of the relaxation time at T_g is $\tau(T_g) = 100$ s.^[11] But as T_g depends on the thermal history, the value of m also will depend on the thermal history. This is exemplified on Figure 4, in which it is shown how an error on the value of T_g or/and $\tau(T_g)$ is able to modify drastically the value of m . Thus it is clear that the use of Equation 1, 2 and 6 requires a correct and an accurate measurement of the glass transition temperature.

In this paper, a protocol is presented to estimate the correct value of $\tau(T_g)$, and the correct measurement of the glass transition temperature. The basic idea of the method we propose here is to determine the complete relaxation map covering a wide temperature range above and below the glass transition.

Experimental Part

To reach our objectives we have to measure the relaxation time for temperatures below and above T_g in two independent ways. For $T > T_g$ we may use dynamic spectroscopy (DMA) or/and dielectric spectroscopy (DS). In this work dielectric spectroscopy was used. DS experiments were carried out on a Thermal Analysis Instruments apparatus (DEA 2970 Dielectric Analyser). The sample was put between 2 gold electrodes sputtered on alumina substrates. The distance between electrodes is about 0.3–0.4 mm. A voltage (1 V) is applied with a frequency sweep between $3 \cdot 10^{-3}$ and $3 \cdot 10^5$ Hz. The samples sustained a thermal treatment between the electrodes in order to improve the material/electrodes contact and to erase thermal history. This treatment consisted of annealing at $T_g + 10^\circ\text{C}$ during

10 min, followed by a cooling at $10^\circ\text{C}/\text{min}$ to ambient temperature. The measurements were conducted at different temperatures with 2.5°C steps, after a thermal equilibrium plateau of 10 min period.

The second step consists of measuring the relaxation time in the glassy state as a function of the temperature. We propose to use thermally stimulated depolarization current technique (TSDC). This technique presented in Figure 5 has been described in details in ref.^[21] To summarize, the sample is placed between two electrodes, and the sample head is installed into positioned in a heating/cooling chamber. At a polarization temperature T_p just above the glass transition, samples were subjected to a constant electrical field ($E = 106$ V/m) for 2 min. Then, the temperature was lowered to T_{00} , samples were short circuited and the depolarization current “ I ” was measured during heating up to T_p at 10 K/min to obtain a complex relaxation spectrum.

As the glass transition temperature depends on the history, it is clear that the samples studied must have exactly the same history whatever the measurement performed. This is possible by using the rejuvenation procedure which consists to heat-up the sample to a temperature $T_r > T_g$ ($T_r = T_g + 10^\circ\text{C}$) and then to chose a cooling rate (for all the experiments performed here the value of the cooling rate is 10 K/min). For all the samples studied, the ageing is nil, and when it was required, the heating rate was 10 K/min. We have to note that this rejuvenation procedure is only possible if no crystallization occurs or irreversible processes such as post curing etc. In this work, results obtained on different poly(ethylene terephthalate) films, on polycarbonate and on PET_g/Montmorillonite vitreous nano-composites (PET_g is a copolymer of PET and PCT).

Finally, a third experimental experiment can be done by using calorimetry. Indeed the glass transition of many glasses are very well observed by means of differential scanning calorimetry (DSC). The glass transition signal is observed as an endothermic ΔC_p step when the values of the cooling

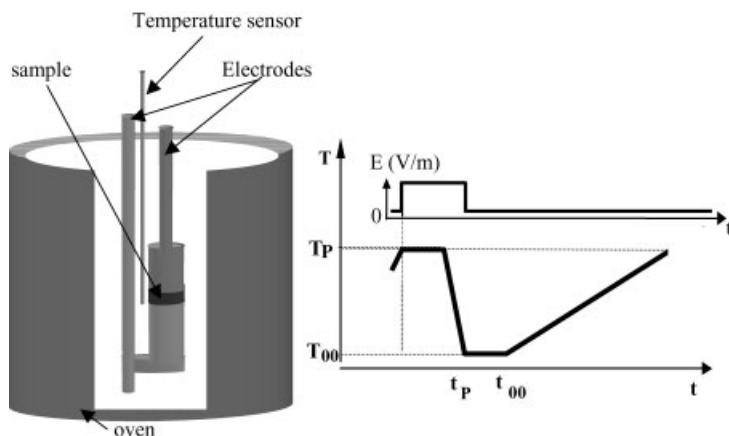


Figure 5.

Schematic view of a TSDC head. The sample is included between two electrodes and put into a heating/cooling chamber. The graph on the right side shows the thermal cycle used to obtain a TSDC spectrum.

and heating rates are equal and when the glass is without any ageing. DSC experiments were conducted on a Thermal Analysis Instruments heat flow calorimeter (DSC 2920 CE), coupled with a liquid nitrogen cooling system or a Perkin Elmer DSC series 7 with the same cooling equipment. The apparatus were calibrated by the Indium fusion temperature and enthalpy. All the experiments were conducted under inert nitrogen atmosphere and after a step to avoid thermal history.

Construction of the Relaxation Map

To build the relaxation map, we have to determine the values of the relaxation time for temperatures above and below T_g . The dielectric spectra show a peak maximum (the α -relaxation peak) for each temperature above T_g . Examples obtained with polycarbonate are presented in Figure 6.

The peaks observed are the dielectric manifestation of the glass transition and

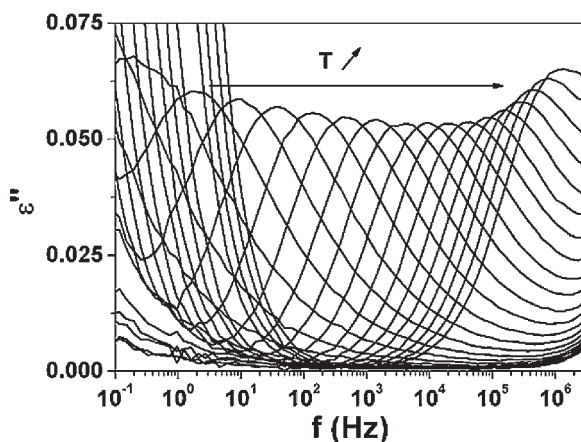


Figure 6.

Example of dielectric spectra obtained on vitreous polycarbonate film. From the maximum of each signal obtained for each temperature, the value of the relaxation time is obtained according relationship (8).

represents the α mode or the main relaxation mode. We notice a shift of the peak maximum toward high temperatures with increasing frequency. This is the expected behavior. For samples with montmorillonite (Figure 7), we also observe a conductivity phenomenon at low frequency, which is usual when such polymers are studied common in these types of systems.^[22]

The frequency dependences of the complex permittivity provided by dielectric spectroscopy are fitted using the Cole-Davidson equation to take into account the peak asymmetry:

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1 + i\omega\tau)^{\beta_{CD}}} \quad (7)$$

With ε^* the complex permittivity, $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$, ε_s the permittivity at high frequencies (or short times), ε_∞ the permittivity at low frequencies f (or long times), ω the angular frequency, τ the relaxation time, and β_{CD} a characteristic parameter from the peak asymmetry. When no peak asymmetry is observed the calculation of τ can be performed according to

$$\tau(T) = \frac{1}{2\pi f} \Big|_{T_{\max i}} \quad (8)$$

The dielectric spectra allows us to plot the Arrhenius diagrams presented in Figure 8 which give the variations of $\ln(\tau)$ versus $1/T$ in the like liquid state.

For temperature below T_g , the variations of the relaxation time with the temperature are obtained by TSDC. Figure 9 A shows some complex spectra obtained for the different samples studied in this work. A peak of current is observed attributed to the α transition (i.e. the dielectric manifestation of the glass transition) when the temperature reaches the glass transition.

The relaxation time τ (T) of the dielectric manifestation of the glass transition can be obtained by different formalisms. Alegria et al.^[21] had shown that the α relaxation can be analyzed with the Kohlrausch-Williams-Watts (KWW) equation:

$$Q(t) = Q_0 \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] \dots \text{where} \quad (9)$$

$$\dots Q(t) = \int_t^\infty Idt$$

Q_0 is the value of the initially stored charge, and β is a parameter accounting for the non-Debye character of the α relaxation. As shown by Alegria et al.,^[23] the time

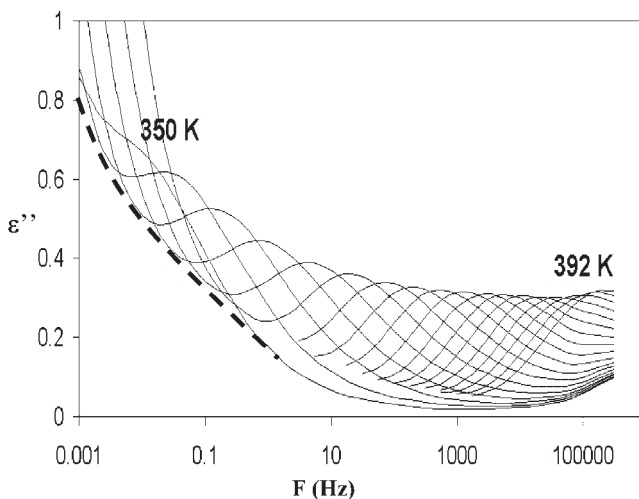


Figure 7.

Example of dielectric spectra obtained on PETg/Montmorillonite nano composites. A conductivity phenomenon is observed at low frequency (dashed line). This is usual when such polymers are studied.

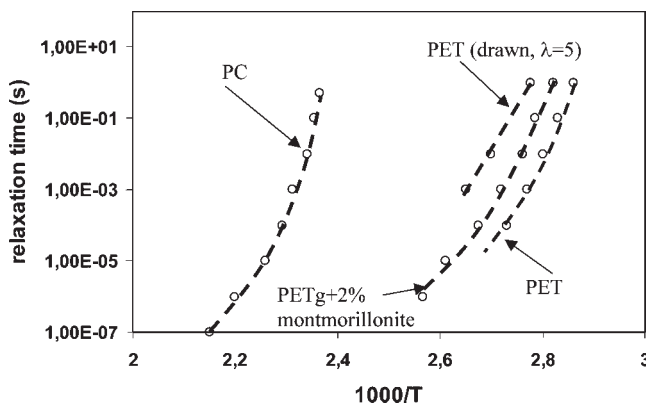


Figure 8.

Relaxation times in the like liquid state obtained from DS measurements performed on a polycarbonate film, a PETg/montmorillonite (2% W/W) nano composite, on a vitreous PET film and a drawn PET film (drawn ratio = 5).

derivative of Equation 9 gives:

$$\tau = \beta \frac{Q}{I} \left[\ln \frac{Q_0}{Q} \right]^{[1-1/\beta]} \quad (10)$$

Doing the calculation of τ according to relationship 10 leads to the values of relaxation time reported on Figure 9 B.

Estimation of T_g , $\tau(T_g)$ and m

The different results obtained previously and reported in the same Figure 10 leads to the relaxation map which characterizes the molecular dynamic of each material in the like liquid and in the glassy temperature domains. The glass transition is at the intercept of the two functions $\tau = F(T)$ obtained for each domain. When the intercept is not experimentally observed, we may extrapolate the two curves by adjusting with Equation 5 for the liquid state, and with the law proposed in one of our works for the glassy domain.^[24] From this method we obtain the data presented in Table 1 which gives the value of T_g and the value of the relaxation time at T_g for each material. The first conclusion concerns the value of the relaxation time at T_g which is not found constant. So the assumption of $\tau(T_g) = 100$ s as an universal value is not true.

To determine the value of the glass transition temperature we may also use

results obtained with DSC. To measure T_g the fictive temperature concept proposed by Tool^[25,26] to describe the thermodynamic state of glasses will be used. The fictive temperature T_f is calculated according to the equivalent area method proposed by Moynihan^[27] and obtained according to the following relationship (Figure 11):

$$\int_{T_f}^{T_2} (C_{p,g} - C_{p,v}) dT = \int_{T_1}^{T_2} (C_p - C_{p,v}) dT \quad (11)$$

with C_{pg} and C_{pl} the respectively glass and liquid mass heat capacities; C_p the material mass heat capacity at the temperature T , T_2 an arbitrary temperature upper than the glass transition domain for which $C_p = C_{pl}$ in the equilibrium; and T_1 , an arbitrary temperature lower than the glass transition domain for which $C_p = C_{pg}$ in the frozen state. As shown in Figure 11, in the liquid state T_f equals T , while in the vitreous state, T_f is equal to T_f' , the equilibrium fictive temperature.

The fictive temperature is equivalent the glass transition temperature when the values of the cooling rate is the same as the value of the heating rate and if the glass does not undergo any ageing (Figure 11). The value of T_g obtained using this protocol are also reported in Table 1 and also reported on the relaxation map presented

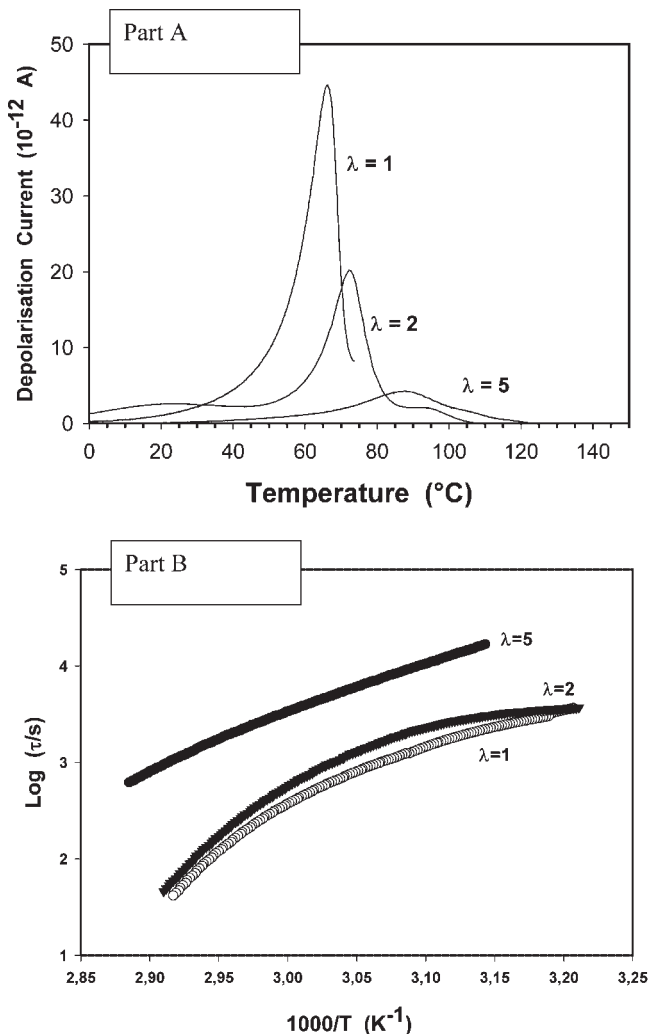


Figure 9.

Part A: TSDC spectra obtained on a PET films with different drawn ratio (λ). The relaxation time is obtained according relationship (10) and its dependence with the temperature is shown on the part B.

in Figure 10. The first immediate conclusion is the very good data correspondence observed on the value of T_g . At this stage of the data presentation, we have to keep in mind that the thermal history of the samples was identical whatever the experimental method used. This is a very important point. From the knowledge of the T_g value, it is now possible to calculate the fragility indices m and the value of $\tau(T_g)$. For DSC experiments, it is necessary to choose an expression for the relaxation

time. Different expressions are proposed in the literature and we will use the well known Tool–Narayanawamy–Moynihan relationship:

$$\tau = \tau_0 \left\{ \exp\left(\frac{x\Delta E}{RT}\right) \exp\left[\frac{(1-x)\Delta E}{RT_f}\right] \right\} \quad (12)$$

Where x is the Narayanawamy parameter ($0 < x < 1$) and ΔE an activation energy. Combining Equation (12) and (6), the

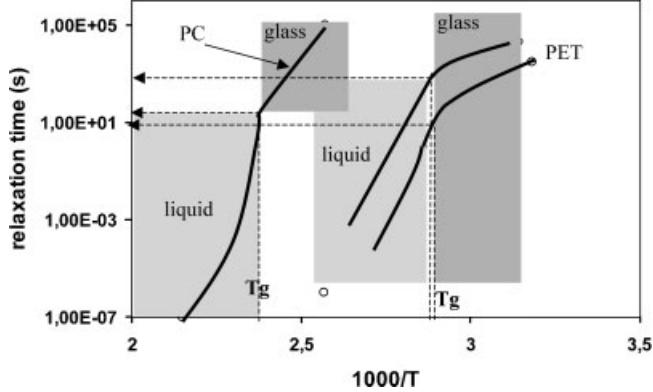


Figure 10. Relaxation map of the different materials, the vertical lines correspond to the value of T_g measured by DSC.

Table 1. Values of the glass transition temperature, of the relaxation time and values of the fragility index obtained according to the proposed protocol.

Material	T_g ($^{\circ}\text{C}$)	$\tau_{(T_g)}(\text{s})$	m	$q-$ ($^{\circ}\text{C}/\text{min}$)
PC	143	110	170	10
PET drawn $\lambda = 5$	75	250	66	10
PET	74	6	142	10
PET drawn $\lambda = 2$	73	40	160	10
PETg	348	34	144	10
PETg/MMT 1%	345	163	173	10
PETg/MMT 2%	349	24	147	10
PETg/MMT 3%	343	105	132	10

calculation of m leads to:

$$m = \frac{\Delta E}{2.3RT_g} \tag{13}$$

The values of ΔE can be obtained by using the Moynihan method^[27] which

consists to analyze the dependence of T_g on the cooling rate ($q-$) according to:

$$\frac{d(\ln q-)}{d\left(\frac{1}{T_g}\right)} = \frac{\Delta E}{R} \tag{14}$$

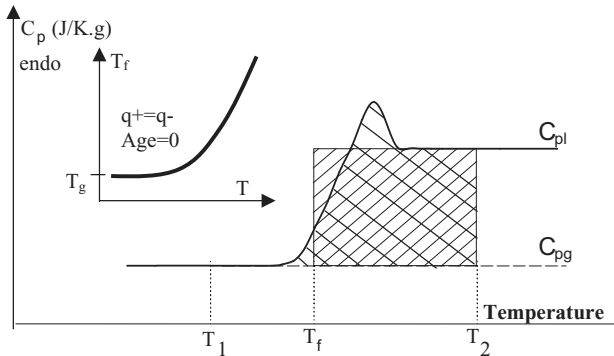


Figure 11. Equal area method to calculate the fictive temperature from DSC measurements. On the left side, the expected variation of T_f with T when the heating rate $q+$ and the cooling rate $q-$ absolute values are identical and for a non aged glass.

The calculation of m using Equation (13) and (14) requires some precaution. Indeed the values of cooling rates q — used must surround the close to the one used for TSDC and DSC experiments and must scan a reasonable domain. For DSC that means that the value of cooling rate between 1 k/min to 50 K/min are reasonable. The calculation of m can also be performed from DS measurements by combining relationship (5) and (6) leading to:

$$m = \frac{BT_g}{2.3(T_g - Tk)^2} \quad (15)$$

The calculation of m performed from these two formula lead to identical data (reported in Table 1). Thus, when a well-defined value of T_g is used a reasonable value for m is obtained.

Conclusion

In this work, we have shown that it is possible to determine a well-defined value of the glass transition by coupling three independent ways of measuring the molecular mobility around the glass transition. From this method, the value obtained for T_g does not depends on the experimental method if the thermal history is maintained the same for all the experiments. We have also shown that the relaxation time at the glass transition is not a constant and finally with the correct knowledge of $\tau(T_g)$ and of T_g a reasonable estimation of the fragility index can be performed.

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