Relaxation Time at Glass Transition Temperature Measured by Simplex Thermo Stimulated Depolarisation Current

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Summary: The aim of this work is to propose a reliable approach to estimate values of the relaxation time constant of polymers at the glass transition temperature. This approach consists of using a new thermo stimulated depolarisation current TSDC protocol which analyzes the relaxation current kinetics obtained after submitting the sample to an electrical field shock at constant temperature. The measurements have been performed on a series of polyethylene terephthalate (PET), polycarbonate (PC) and polyethylene terephthalate glycol (PETg) samples. Different temperatures were needed to explore the range of the glass transition domain of each polymer. The results compared to calorimetric and dielectric data show a good agreement. So we confirm that the value $\tau_{ms} = 100$ s often used for characterizing the molecular dynamic of the liquid glass former at T_g is not universal.

Keywords: glass transition temperature; relaxation times; thermo stimulated depolarisation current

Introduction

The description of the different mechanisms of structural relaxation occurring in the field of glass transition in polymer materials is one of the major challenges for the understanding of the amorphous state and its properties.

The glass transition domain is often defined as the temperature range where the material changes from the liquid state to the glassy one. This field is characterised by the notion of glass transition temperature "T_g" which remains to this day a very difficult parameter to define. Indeed, there is no clear theory today, whether based on thermodynamics or otherwise, which can fully explain all macroscopic phenomena occurring close to this temperature T_g. In fact, the glass transition temperature depends on many factors, particularly the thermal history of the sample: the cooling rate during vitrification process[1] (T_g increases when the cooling rate increases), on the heating rate,[2,3] on the glass "age"[4] and on the structural characteristics of glass-forming liquid.[5]

Below T_g the vitreous state is reached. It is a non-equilibrium thermodynamic system; in fact, the volume occupied by the molecules is larger than expected under conditions of equilibrium. Thus, this system will seek to move towards equilibrium as accessible through a structural relaxation which does not affect the chemical characteristics; this phenomenon is known as physical aging.[6] The study of this molecular relaxation is based on the determination of an important parameter: the characteristic relaxation time.

Being dependent on this set of parameters, the glass transition temperature (T_g) can not characterize a glass-forming liquid near its glass transition. A phenomenological approach based on the variations of viscosity (or relaxation time) as a function of T_g/T has been proposed by C. A. Angell

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et al.[6] thus highlighting the existence of two classes of liquid-forming glasses which can be defined by the "strong-fragile" concept. Strong glass-forming liquids have an Arrhenius behaviour for the viscosity variations versus T_g/T while fragile glass-forming liquids present a Vogel–Tamman–Fulcher behaviour in this temperature range.

The relaxation time is based on the study of this molecular relaxation. A value of 100 seconds is usually assigned in the simulation programs.[7] However, several studies have shown that this value was not universal. A value of $\tau(T_g) = 16$ s has been found by Dargent et al.[8] for a wholly amorphous PET and this value rises up to $\tau(T_g) = 600$ s for the same PET drawn with a rate $\lambda = 5$ ($\lambda = l/l_0$ where l_0 is the initial sample length and l is the length after the elongation).

We propose in this work a new reliable approach to determine the characteristic relaxation time τ measured near the glass transition temperature for some polymer materials like PET, PETg and PC. The PET, PETg couple is chosen to show the resolution of the method for two similar characteristics materials and the PC, for it higher value of relaxation time. The estimated values of τ will be compared with those obtained by using various experimental techniques which include the dynamic dielectric spectroscopy "DDS" and thermo stimulated depolarisation current spectroscopy "TSDC".[9–11]

Experimental Part

The measurements have been performed on a series of polyethylene terephthalate (PET), polycarbonate (PC) and polyethylene terephthalate glycol (PETg) illustrated in Figure 1.

We study firstly an amorphous polyethylene terephthalate PET provided as a film (E.K. 7352) with a thickness of 0.625 mm. Samples of polycarbonate PC were supplied by General Electrics. The polymer grade used was LEXAN 141. Before moulding, PC pellets were dried at 110 °C for 5 to 10 h. Samples of PC were moulded at 250 °C to obtain 1 mm thick sheets.[12] Samples of amorphous PETg were obtained from Eastman Chemical Company. The reported glass transition temperatures of these polymers are, respectively, 74 °C, 75 °C and 143 °C.[13]

The experiments were performed on an apparatus developed in our laboratory.[14] Figure 2 shows the new experimental protocol used in this study.

The sample is placed at a temperature corresponding simultaneously to the temperature of polarisation (T_p) and experimentation ageing temperature (T_a). Each

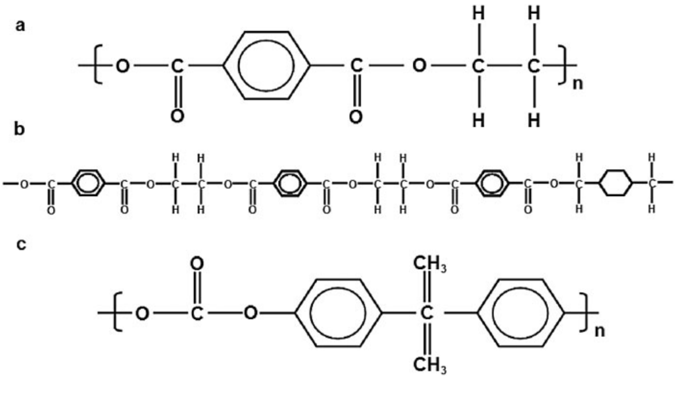

Figure 1.
Unit structure of: a. polyethylene terephthalate (PET), b. polyethylene terephthalate glycol (PETg), c. polycarbonate (PC).

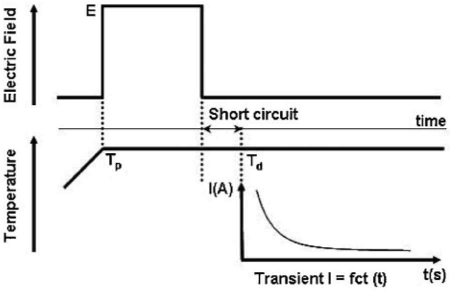

Figure 2.
New TSDC experimental protocol.

sample is previously cooled down from about 10 °C above its glass transition temperature domain (85 °C for PET and PETg and 155 °C for PC) to the temperature of polarisation at a rate of 10 K min^{-1}. When this temperature is reached, each sample is subjected to the action of an electric field ($E_p = 450\,\text{V mm}^{-1}$ for 2 min). $t_p = 2\,\text{min}$ is enough time to reach the equilibrium polarisation showed by Teyssedre et al.[15] The electric field is then switched and the sample short-circuited during 30 s and then connected to a picoelectrometer (Keithley System Electrometer 6514). The sample is short-circuited to create an equipotent on its two surfaces to eliminate the fast charges of the interface. We performed several tests in terms of short-circuit's time; we find that for 30 s we have a good compromise between the intensity of the electric current and the possible electric shock of the measuring device. By this way, a transient isothermal depolarisation current curve I(t,T) is registered as a function of time. Then the experiment is performed for another isothermal temperature.

The temporal analysis of the isotherm transient current I(t,T) leads us to consider the measured signal as sum of exponentials:

$$I(t,T) = I_0 + \sum_{i=1}^{n} I_i \exp\left(-\frac{t}{\tau_i}\right) \tag{1}$$

I_0 is an eventual constant and [I_i, τ_i] are related to a i elementary Debye process. The Simplex method[16] is used to fit our data with relationship (1). It has been used for optimising data of nonlinear functions of several variables.

Results and Discussion

The experiments were conducted in the glass transition range of each material tested. Transients were obtained from 70–80 °C for PET and PETg samples and 140–150 °C for polycarbonate PC sample with an increase of one degree between each isotherm as shown in Figure 3.These transients show a clear decrease in the depolarization current as a function of time

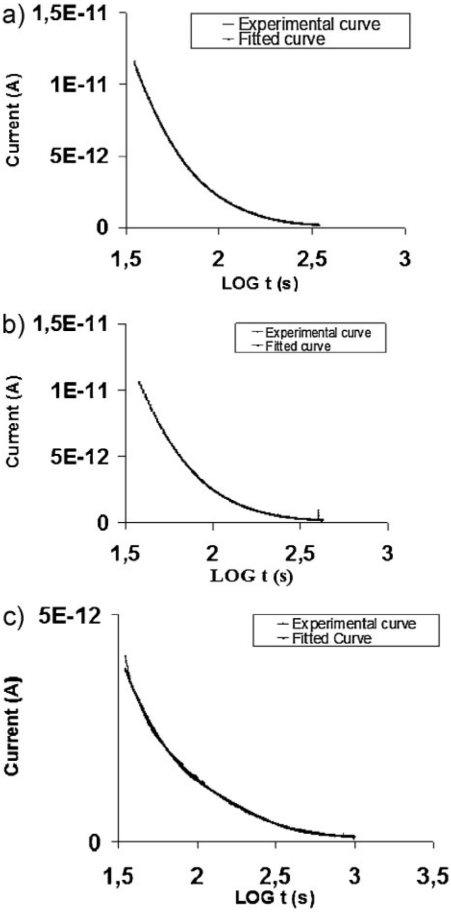

Figure 3.
Experimental and fitting curves obtained by using two exponential of: a. PET sample at 78 °C, b. PETg sample at 76 °C and c. PC sample at 146 °C.

which finally tends to zero after a certain period.

In a previous article,[17] we demonstrated that the model with two relaxation times was the one which best fitted the data. Thus the relaxation spectra will be described according to

$$I(t,T) = Y_0[T] + A_1[T]\exp(-t/\tau_1[T]) + A_2[T]\exp(-t/\tau_2[T]) \quad (2)$$

We have therefore applied it to all transients obtained. As expected, the application of the model with two exponentials shows the existence of two relaxation times τ_1[T] and τ_2[T] clearly distinct which are displayed in Figure 4. For each sample, we do not observe a drastic variation of time constants with temperature.

The variations of the different parameters Y_0[T], A_1[T] and A_2[T] for each polymer is displayed on Figure 5. These parameters show a peak at the temperature corresponding to the glass transition temperature of the corresponding polymer. They have relatively the same shape to the complex spectra of α transition obtained by classical spectroscopy.

For the PET sample, the variations of the pre-exponential parameters A_1[T] and A_2[T] with the temperature are shown in Fig. 5. a. A_1[T] exhibits a maximum at T = 76 °C which corresponds to the

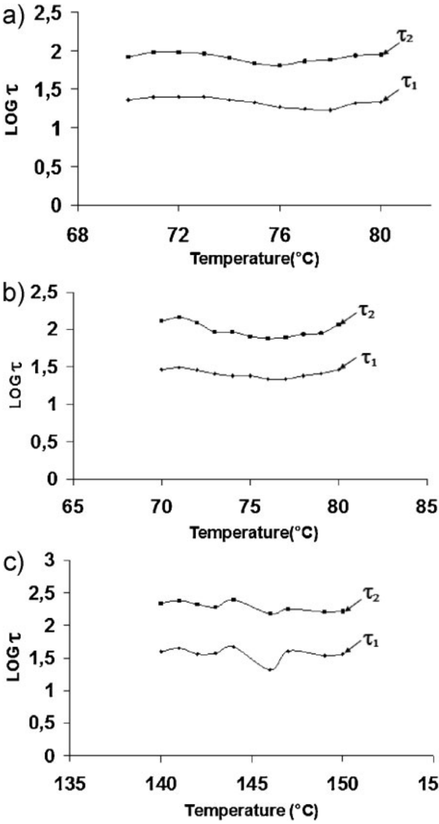

Figure 4.
Temperature dependence of the relaxation times τ_1 and τ_2 determined from isothermal depolarisation current experiment after using simplex method fitting with two exponentials in glassy domain of: a. PET, b. PETg, c. PC.

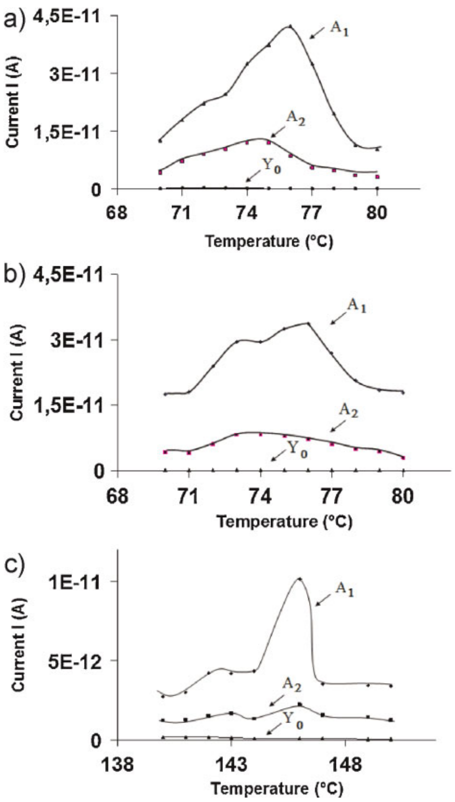

Figure 5.
Temperature dependence of A_1, A_2 and Y_0 parameters determined from isothermal depolarisation current experiment and using simplex method fitting with two exponentials in glassy domain of: a. PET, b. PETg, c. PC.

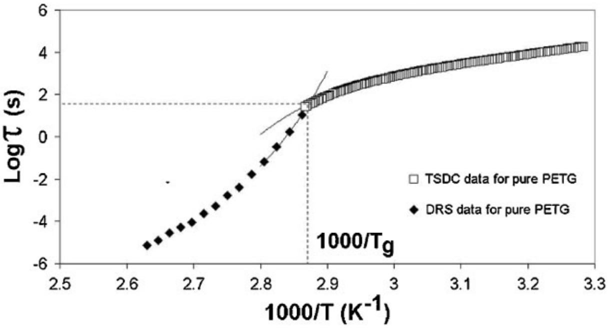

Figure 6.
Superposition of relaxations times calculated from TSDC and DRS measurements, the glass transition plotted is calculated from DSC data of PETg sample.

expected glass transition temperature. The value of $A_2[T]$ is always less than $A_1[T]$ and the variations of $A_2[T]$ exhibits also a maximum at $T = 74\,°C$. Thus it appears that at the glass transition two mechanisms with different magnitude and time constant exist. This comment is true for the two others materials PETg and PC close respectively to 76 °C and 146 °C. The very low values of parameter $Y_o[T]$ seems to have no influence and will be an inconsiderable parameter.

By combining three different analytical techniques which are the thermo-stimulated depolarization current (TSDC), dielectric spectroscopy (DRS) and differential scanning calorimetric (DSC) spectroscopy, Delbreilh et al.[18] have determined this time constant for some semi-crystalline polymers at the glass transition temperature (T_g). From these two spectroscopies (DRS and TSDC), the plot of temperature dependence of the relaxation time above and below the glass transition domain is showed on the same scale in Figure 6. The value of T_g estimated by DSC is added at the end on this figure.

In Table 1 we compare our values of the relaxation time obtained by applying the Simplex–CDTS with those obtained by Delbreilh et al.[18] at glassy transition temperature of each material. We remark that the values are very close.

Conclusion

We have shown in this work that it is possible to have a good estimate of the relaxation time characteristic close to the glass transition temperature for different parts of polymer materials. Instead of three measurement techniques that are heavy to implement, we use only one method of measurement based on both the transient response to an excitation current of an electric field using a conventional CDTS protocol and the nonlinear analysis by Nealder Mead Lagarias Simplex. The method showed that the results we get

Table 1.
Relaxation times and glass transition temperature obtained with TSDC-DRS-DSC methods and the new TSDC protocol.

Methods	TSDC + DRS + DSC[8,13]		Our results[18]	
Materials	T_g (°C)	τ(s)	T_g (°C)	τ (s)
PET	74	16	76	18,4
PETg	75	21	76	21,8
PC	143	110	146	151,7

are similar to those obtained by other techniques, both thermal and dielectric, but the method has a clear advantage: it is not subject to the use of a parameter whose value depends on the material studied like β of the Kohlrausch-Williams-Watts CDTS spectroscopy. This technique can be easily applied to other available polymer materials. The generalization of our method is thus confirmed and we almost can therefore propose it as a complementary method for the characterization of polymer materials, especially with a reliable estimate of the relaxation time at the glass transition temperature with a single method that is the Simplex-CDTS. So we confirm that the value $\tau_{ms} = 100$ s often used for characterizing the molecular dynamic of the liquid glass former at T_g is not universal.

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