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Study of poly(bisphenol A carbonate) relaxation kinetics at the glass transition temperature

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Abstract

In this work, the variations of the relaxation times are investigated above and below the glass transition temperature of a model amorphous polymer, the polycarbonate. Three different techniques (calorimetric, dielectric and thermostimulated currents) are used to achieve this goal. The relaxation time at the glass transition temperature was determined at the temperature dependence convergence of the relaxation times calculated with dynamic dielectric spectroscopy (DDS) for the liquid state and thermostimulated depolarisation currents (TSDC) for the vitreous state. We find a value of $\tau(T_g) = 110$ s for PC samples. The knowledge of the temperature dependence, $\tau(T)$, and the value $\tau(T_g)$ enables to determine the glass-forming liquid fragility index, m. We find $m = 178 \pm 5$.

Keywords: Polycarbonate; Glass transition; Fragility; Thermostimulated currents; Dynamic dielectric spectroscopy; Differential scanning calorimetry

1. Introduction

An important question concerning the understanding of the amorphous polymer properties is linked to a correct description of the structural relaxation mechanisms occurring in the vicinity of the glass transition.

The glass transition characterized by its temperature T_g is up to day impossible to predict in regard with the structures engaged in the liquid phase. One of the problems is the influence of the sample thermal history. Indeed it is established that T_g depends on the cooling rate used during the vitrification process [1], on the heating rate [2,3], on the glass "age" [4] and of course on the glass-forming liquid structural characteristics [5].

The glass transition appears as a mobile border separating a thermodynamic stable liquid phase

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from a disordered and thus unstable glassy phase. The existence of this structural disorder contributes to a lower material density, which means that the volume occupied by the molecules is greater than the one expected under equilibrium conditions. As a consequence, maintaining a glass at a temperature $T_a < T_g$ will lead to structural evolutions involving volume entropy and enthalpy decrease. After an infinite duration annealing performed at $T_a < T_g$ the glassy system must reach the thermodynamic equilibrium given by the liquid curve extrapolated at T_a. This phenomena which does not modify the sample chemistry is called "physical ageing".

For $T > T_g$ the liquid state properties govern the molecular dynamics. The characterization of the liquid state appears as the first fundamental step to be done to understand the glassy state properties. To achieve this purpose, the "strong–fragile" glass-forming liquid concept proposed by Angell can be used [6].

This author proposed to analyse and compare the viscosity variations for several glass-forming liquids for temperatures close to T_g. So, these liquids can be defined using the "strong–fragile" concept, with two limit behaviours. 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. To quantify the "strong–fragile" behaviour of a glass-forming liquid a fragility index m has been defined [7] depending on the shear relaxation time variation versus T_g/T for $T = T_g$:

$$m = \left.\frac{\mathrm{d}(\log(\tau))}{\mathrm{d}\left(\frac{T_g}{T}\right)}\right|_{T=T_g} \tag{1}$$

The fragility indexes presented in the literature exhibit values ranging from $m = 16$ for a very strong glass-forming liquid to $m \geqslant 250$ for very fragile glass-forming liquids [8,9].

The calculation of m requires a correct knowledge of T_g and thus of $\tau(T_g)$. In many already published works a value of 100 s is considered to be acceptable for $\tau(T_g)$. Nevertheless, this value of relaxation time is not universal and as recently reported by Dargent et al. [10] depends on the structure engaged. A value of $\tau(T_g) = 16$ s has been found 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). For these authors, a correct determination of $\tau(T_g)$ requires measurements performed with at least three different experimental ways as calorimetry – thermally depolarisation currents – dielectric spectroscopy.

Our goal is to apply this analysis protocol so as to determine the fragility value for a model amorphous polymer, the polycarbonate. This material allows us to study the main parameters of the relaxation process associated to the glass transition.

2. Experimental

Bisphenol A polycarbonate (PC) supplied by General Electrics has been used for this study. 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.

The PC molecular unit is presented on Fig. 1.

Before carrying out the experiments, each sample was heated up to an annealing temperature (T_a) above the glass transition temperature (T_g): $T_a = 160$ °C. This allows to erase the effects of previous thermal treatment.

DSC measurements were performed on a TA Instruments TMDSC 2920. For this study, samples were heated up to 180 °C (30 °C above T_g) and cooled down to 60 °C (90 °C below T_g) at a rate $q_c = 10$ °C/min. Then, measurements were performed with a constant heating rate $q_h = 10$ °C/min. The DSC apparatus was calibrated in temperature and energy using the melting of an Indium sample. Sample masses were around 10 mg and were put in aluminium pans. The experiments were carried out under nitrogen ambiance.

TSDC measurements were performed on an apparatus developed in our laboratory [11]. For these measurements the protocol presented on Fig. 2 was applied on the sample.

For TSDC measurements, an electric field (0.4 MV m^{-1}) was applied to the sample at a polarisation temperature $T_p = 155$ °C for 2 min. Then,

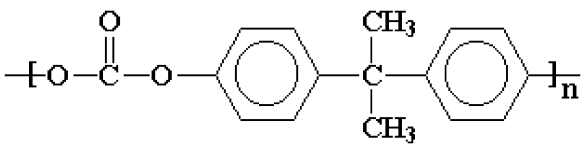

Fig. 1. Repeat unit of polycarbonate.

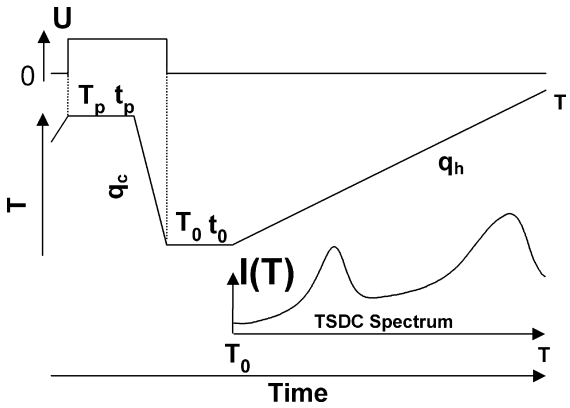

Fig. 2. TSDC complex measurement protocol.

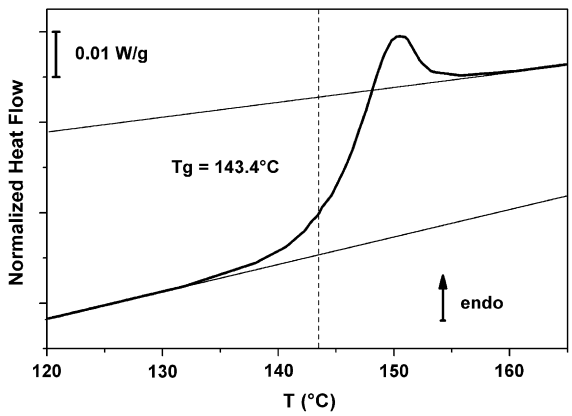

Fig. 3. DSC measurements of PC sample after a cooling from 180 °C to 60 °C with cooling rates $q_c = 10$ °C/min and $q_h = 10$ °C/min.

the sample was cooled down to $T_0 = 60$ °C and the electric field was removed. After a 2 min annealing at T_0, the TSDC measurement was realized from T_0 to T_p with a heating rate of 7 °C/min. During this measurement, the depolarisation current versus the temperature is called complex relaxation spectrum. As it is monitored in the temperature range associated with the glass transition of the polycarbonate, it is labelled α relaxation mode.

DDS experiments were performed with a Novocontrol BDS4000 broadband dielectric spectrometer. The frequency range for measurements was from 0.1 up to 3.10^6 Hz in a temperature range from 130 to 190 °C by steps of 2.5 °C.

3. Results

Fig. 3 shows the DSC measurements obtained on a rejuvenated PC. In the temperature domain scanned, a classical endothermic step of heat capacity is observed traducing the glass transition phenomenon. Superposed to this heat capacity step, a small relaxation endothermic peak appears. From this measurement we may determine the value of the glass transition temperature T_g according to the equivalent area procedure proposed by Moynihan [1,2]. Then, we may calculate the value at T_g of $\Delta C_p(T_g) = C_{pl} - C_{pg}$ where C_{pl} is the liquid heat capacity and C_{pg} is the vitreous heat capacity. We find $\Delta C_p(T_g) = 0.24$ J/(g K) and $T_g = 143.4$ °C, values in good agreement with those given in the literature by Orreindy and Bauwens [12,13].

For many wholly amorphous linear polymers, $\Delta C_p(T_g)$ is ranging from 0.1 J/(g K) to 0.4 J/(g K). Our PC samples do not differ from the other linear thermoplastics with a value comparable to the $\Delta C_p(T_g) = 0.24$ J/(g K) obtained for a PCT [14] or $\Delta C_p(T_g) = 0.31$ J/(g K) obtained for a PET [14].

According to Angell's works [9], low values for ΔC_p (for instance $\Delta C_p(T_g) = 0.1$ J/(g K)) can be associated with a "strong" behaviour and at the extreme opposite a high value ($\Delta C_p(T_g) = 0.4$ J/(g K)) to a "fragile" behaviour. The value obtained for PC is in the middle of the range concerning a "strong/fragile" scale classification. As we have shown [15], the use of ΔC_p value to characterize the fragility of a glass forming liquid when applied to linear polymers must be done carefully. Indeed, the variation range of ΔC_p is not wide enough to permit a good resolution on the fragility behaviour variations. However, according to relation (1), we may expect a non-Arrhenius dependence for the variation of the relaxation time.

Fig. 4 shows the frequency dependence of the dielectric loss factor ε'' obtained for different temperatures on the same sample. We observe the classical behaviour, i.e., the dielectric loss peak shifts to higher frequencies with increasing temperatures. The variations of $\varepsilon''(f)$ present at low frequencies and high temperatures an important rising associated with a conductivity process occurring in the liquid amorphous phase. This is a common phenomenon widely described in the literature. This appears in addition to the dielectric relaxation peak [16,17].

The TSDC signal obtained is presented on Fig. 5.

Several authors observed this TSDC depolarisation peak on polycarbonate in the same temperature range [18,19]. It is attributed to the dielectric manifestation of the glass transition as observed by

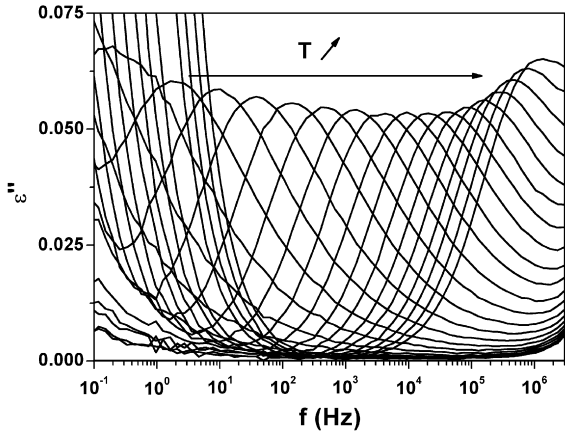

Fig. 4. Isothermal dielectric spectra ε'' versus log(f) for PC sample recorded for temperature ranging from 130 °C to 190 °C with an incremental step of 2.5 °C.

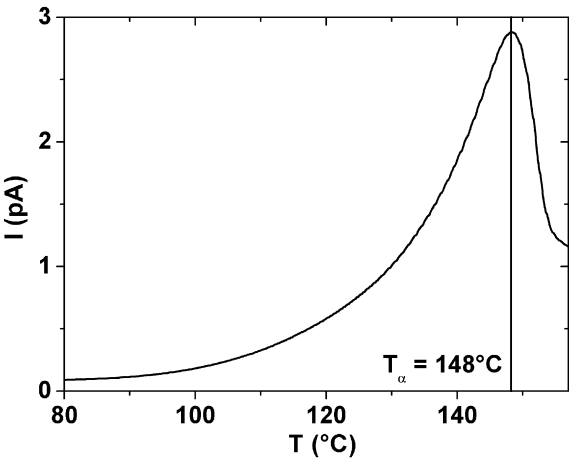

Fig. 5. TSDC complex spectrum of PC sample recorded after a polarisation at $T_p = 155$ °C for 2 min with $E = 0.4$ MV m^{-1}.

DSC and is labelled α relaxation process. The magnitude of this peak is related to the number of dipoles implied in the cooperative motions associated to the molecular mobility enhancement at T_g. The characteristic temperature associated to the depolarisation peak is chosen at the maximum of the peak and it gives for our sample a value of $T_\alpha = 148$ °C.

4. Discussion

For the dielectric relaxation peaks presented on Fig. 4, characterizing the α relaxation mode and for each temperature T, two parameters can easily be determined, the frequency sweep temperature

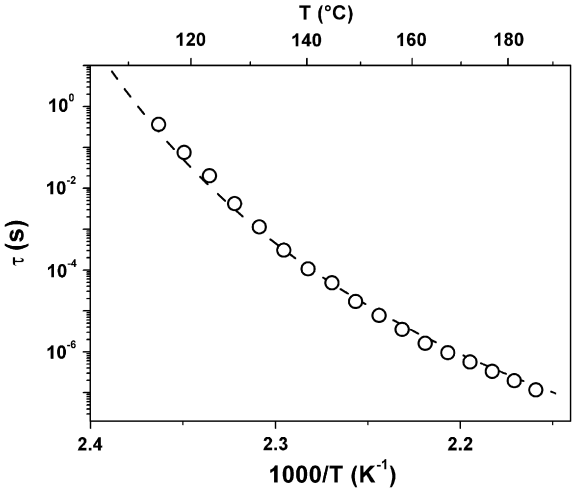

Fig. 6. Arrhenius plot of relaxation times associated with α relaxation process recorded with DDS measurements.

and a characteristic relaxation time τ calculated with the relationship:

$$\tau = \frac{1}{2\pi f_{\max}} \tag{2}$$

where $f_{\max}$ is the frequency taken at the peak maximum.

As expected with the value of $\Delta C_p(T_g)$, log(τ) variations versus $1/T$ plotted on Fig. 6 cannot be described with an Arrhenius model. We propose the use of a Vogel–Tamman–Fulcher relationship [20–22]:

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \tag{3}$$

The pre-exponential factor τ_0, the parameter B and the temperature $T_0 = T_k$, Kauzmann temperature, are determined by means of a fitting procedure and the results are reported in Table 1. These values are in the same range that ones reported in the literature: $T_k = 373$ K, $B = 1450$ [23] and $T_k = 372$ K [24]. We find a value $T_k = 379$ K. Depending on the glass-forming liquid fragility, the T_k value can be linked to the T_g value in such a way that the difference $T_g - T_k$ must be lower than 50 °C. This difference must be considered as a rough estimate, and we find for our sample $T_g - T_k = 38$ °C which is not out of the expected domain of variations.

Table 1
VTF parameters of PC

τ_0 (s)	B	T_0 (K)
2×10^{-14}	1330	379

From the knowledge of the B and T_k values, the fragility index can be calculated according to:

$$m = \frac{BT_g}{2.3 \times (T_g - T_k)^2} \tag{4}$$

This relationship (4) is easily obtained by coupling relationships (1) and (3). Nevertheless, the use of relationship (4) requires the knowledge of a value for T_g. The main question is: what is the value for T_g? Or the equivalent question: what is the value of $\tau(T_g)$?

This is not an easy problem because, as previously mentioned [9], the idea of $\tau(T_g) = 100$ s is not universal. To precise this value without specific assumption we have to provide another independent experimental protocol to suppress this unknown value.

The experimental way chosen to achieve this goal is the use of thermostimulated depolarisation currents (TSDC). It permits to calculate the evolution of the relaxation time associated with the α relaxation mode in vitreous state. There are different ways to analyse the relaxation time distribution. The simplest could be to consider a Debye-like polarisation decrease as used in many studies [25,26]. This first method does not take into account the complexity of the relaxation response by omitting a relaxation time distribution. Thus, the α relaxation mode is better described by means of a Kohlrausch–Williams–Watts (KWW) equation as shown by Alegria et al. [27]:

$$Q(t) = Q_0 \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{5}$$

where $Q(t) = \int_t^{\infty} I\,dt$, Q_0 is the initially stored charge, I the depolarisation current and the β parameter characterizes the non-Debye behaviour of the α relaxation mode. The relaxation time associated to the α relaxation mode, $\tau(T)$ can be calculated with the relation:

$$\tau = \beta \frac{Q}{I}\left[\ln\frac{Q_0}{Q}\right]^{[1-1/\beta]} \tag{6}$$

Fig. 7 presents the temperature dependence of relaxation time τ obtained with the relation (6). (For PC, β has been shown to be equal to 0.46 [28]). Such types of relaxation times dependence for others techniques, DSC for instance [29]. It can be observed that in the glassy state the same shape has been observed, with a linear variation,

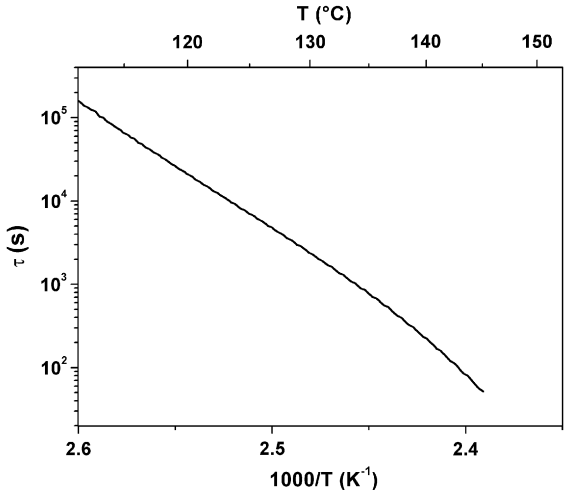

Fig. 7. Arrhenius plot of relaxation times associated with α relaxation process recorded with TSDC measurements.

in the Arrhenius diagram, at low temperatures and an important modification of this behaviour in the glass transition temperature range.

From the three experimental procedures, for two of them (DDS, CDTS) we plot the temperature dependences of the relaxation times above and below the glass transition. Plotting these relaxation times on the same scale leads to the data presented on Fig. 8. It is clear TSDC and DDS measurements permit a clear focus on a convergence point.

By adding the value of T_g estimated by DSC on this figure, it is found that the 3 measurement methods (DSC, DDS and TSDC) gives a behaviour

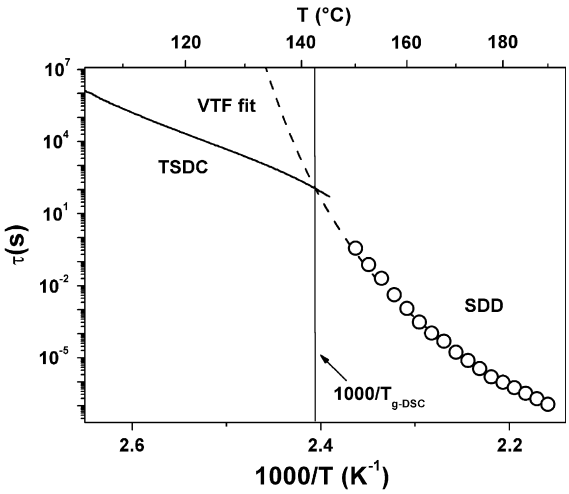

Fig. 8. Superposition of relaxations times calculated from TSDC and DDS measurements, the glass transition plotted is calculated from DSC data.

Table 2
Polycarbonate glass transition temperature, fragility index value m

	T_g (°C)	m	Ref.
DSC	143.4	170	[15]
DDS	–	178	Our sample

convergence for a relaxation time $\tau = 110\ \mathrm{s} \pm 10\ \mathrm{s}$. Thus for this polymer we find that TSDC, DDS and DSC data allow as firstly reported by Dargent et al. [10] an unique value for the relaxation time at the glass transition temperature. For this polymer, the generally reported value, $\tau(T_g) = 100\ \mathrm{s}$ is obtained. Thus we may estimate the value of $\tau(T_g)$ from three independent experimental protocols. From the knowledge of $\tau(T_g)$, we may now calculate the value of the fragility index according to the Eq. (4). We find $m = 178 \pm 5$ using the DDS results. This value is close to the one calculated using DSC results and already published [15]: $m = 170 \pm 5$. The values obtained are reported in Table 2.

5. Conclusion

In this work we have shown that a correct determination of the $\tau(T_g)$ value requires the use of more than one technique. We have proposed the use of TSDC, DDS and DSC as experimental independent methods. The correct determination of $\tau(T_g)$ enables an accurate calculation of the fragility index, we find respectively $\tau(T_g) = 110\ \mathrm{s} \pm 10$ and $m = 178 \pm 5$.

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