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Glass transition investigated by a combined protocol using thermostimulated depolarization currents and differential scanning calorimetry

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Abstract Relaxation times of bisphenol A polycarbonate around the glass transition temperature are estimated using the combination of differential scanning calorimetry (DSC) and thermostimulated depolarization currents (TSDC). These measurements are performed using samples with different thermal histories below and above the vitrification transformation. This protocol enables the extension of the range of equilibrium relaxation times measured by dielectric spectroscopy. By this mean we may recalculate the values of the Kauzmann temperature and fragility index.

Keywords Glass transition · Differential scanning calorimetry · Thermostimulated currents

Introduction

By cooling a liquid with a rate high enough to avoid the crystallisation, it is possible to obtain at low temperatures a quasi solid state called glass. This state appears below a characteristic temperature called the glass transition temperature, T_g, which is the border between the like-liquid state ($T > T_g$) and the glassy state ($T < T_g$) for which the molecular dynamics associated to the molecular relaxation processes are fundamentally different. The liquid-like state is an equilibrium state for which the molecular relaxation engages movements relatively short distances while for the glassy state the molecular relaxation engages cooperative movements at relatively large scales. This implies non exponential and non linear evolution of the properties with time. The evaluation of the equilibrium relaxation time of a glass-forming liquid above the glass transition can be experimentally done by dielectric (Dielectric Spectroscopy, DS) or mechanical (Dynamic Mechanical Analysis, DMA) relaxation spectroscopic methods. This leads to the analysis of the so called α relaxation mode. Close to the glass transition temperature, this evaluation becomes more problematic due to the inherent behaviour of glass forming liquids. Close to the glass transition temperature, the values of the relaxation time increase drastically and so their determination requires an experimental protocol difficult to bring into play. In order to be able to measure τ, it is often proposed to increase the temperature in such a way that the value of τ can be estimated during an experimentally accessible time. Moreover, as it is well known that below the glass transition temperature the glass-forming liquid is in a non-equilibrium state, the values of the physical properties for a glassy material are time-dependent. This is referred to the physical ageing phenomenon [1, 2]. The effect of physical ageing has been recently studied by means of DS experiments by Lunkenheimer and co-workers [3, 4], who have shown that physical ageing has a substantial effect on relaxation data when the temperature domain analysed is in the vicinity of T_g.

The glass transition temperature of glass-forming liquids and its associated relaxation time can be estimated using

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the combination of three techniques: DSC, TSDC and DS [5–9]. Thermal experiments conducted for samples having undergone the same thermal history (same cooling and heating conditions $q_c = q_h = 10$ °C min^{-1}) enable to combine the temperature dependence of the relaxation time. In the glassy state (Thermo Stimulated Depolarisation Currents, TSDC experiments); at the glass transition temperature (Differential Scanning Calorimetry, DSC experiments) and in the liquid-like state (DS experiments). This protocol has been validated on different samples including amorphous and semi-crystalline polymers and some nanocomposite materials [5–9].

In addition, the complete characterization of relaxation mechanisms occurring in a glass-forming liquid requires the generation of a relaxation map which gives the values of the characteristic relaxation time (τ) as a function of the temperature (T) or the inverse of T. Figure 1 gives an example of such a relaxation map on which the data are presented for an α process from a liquid to a glassy state. As previously explained, for many materials, it is very problematic to have a direct access to the value of the experimental relaxation time in the vicinity of T_g. This lack of data leads to an estimation of $\tau_{(T \approx T_g)}$ instead of a direct experimental measurement. This estimation is often done either by assuming $\tau_{(T_g)} = 100\mathrm{s}$, although it is now established that this value is not universal, or by the extrapolation of experimental data obtained at lower relaxation times, higher temperature, using the Vogel Tamman Fulcher (VTF) equation:

$$\tau = \tau_o \exp\left(\frac{B}{T - T_k}\right) \tag{1}$$

where T_k is the Kauzmann temperature.

The accuracy of the VTF fitting parameters is obviously quite dependent on the number of experimental data available. Moreover, the accurate determination of T_k is very important because this parameter is included in almost all of the predictive models describing the physical ageing of a glass [2, 10]. In other words, with more accurate values of T_k, forecasts concerning the evolution of the physical properties of the glass will be better. To achieve this goal the number of data in the vicinity of T_g must be increased.

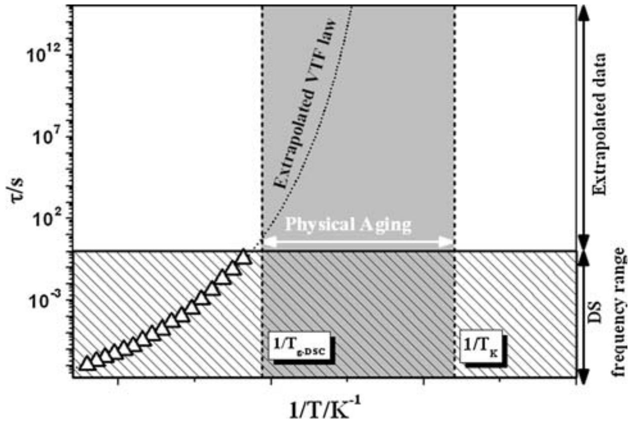

Fig. 1 Relaxation map in the vicinity of T_g for a glass-forming liquid

In this work we propose a new experimental protocol, focussed on the utilisation of thermal analysis techniques to drastically increase the accuracy on the determination of T_k. At the same time, by increasing the number of equilibrium relaxation times available to build the relaxation map in the T_g domain we propose to have a better estimation of the value $\tau(T_g)$. For these purposes, thermal analysis methods such as Differential Scanning Calorimetry (DSC) and Thermo Stimulated Depolarisation Currents (TSDC) have been used.

Experimental

Bisphenol A Polycarbonate (PC) supplied by General Electric (LEXAN 141) was used for this study. All the samples were heated to 180 °C prior to the experiments and held at this temperature to erase previous thermal history, such as ageing. Samples for TSDC and DSC studies with different thermal histories were then prepared by cooling at different cooling rates, as described below.

The determination of the relaxation time evolution in the glassy state was done using TSDC. In this method a sample is placed between two electrodes and heated to a polarization temperature $T_p = 155$ °C just above the glass transition. The sample is then subjected to an electrical field ($E = 10^6$ V/m) for 2 min. The temperature is then lowered to a temperature $T_o = 60$ °C at a constant controlled cooling rate q_c. T_o is chosen well below T_g in order to freeze the molecular motions. The electrodes are then shorted and the depolarization current "I" is measured during heating to a temperature T_f at constant heating rate of 10 °C min^{-1}, during which the complex relaxation spectrum is measured.

To study the effects of thermal history, different cooling rates were used between T_p and T_o ($q_c = 30, 20, 10, 5, 2, 1, 0.5, 0.2$ °C min^{-1}). In each case the same pre-treatment before cooling was used to avoid problems with reproducibility, and after cooling at the selected rate, the same heating rate of 10 °C min^{-1} was used during TSDC measurement.

A similar thermal history was applied to samples studied by DSC. After preconditioning, each sample was cooled down through the glass transition at one of the cooling rates ($q_c = 30, 20, 10, 5, 2, 1, 0.5, 0.2$ °C min^{-1}). The heat flow was measured during a heating ramp from 60 to 180 °C with a heating rate of $q_h = 10$ °C min^{-1}. DSC experiments were conducted on a Thermal Analysis Instruments heat flow calorimeter (DSC 2920 CE), coupled with a liquid Nitrogen cooling system. The DSC was calibrated using Indium and Zinc reference materials, by matching the temperature of fusion and the associated enthalpy of Indium and the melting temperature of Zinc. All the experiments were conducted under an inert Nitrogen atmosphere.

The α relaxation process of PC in the liquid state was studied 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. As for TSDC and DSC measurements, the sample was heated up to 180 °C and for held 2 min in order to erase any previous thermal history in the sample.

Results

Figure 2 shows the TSDC results obtained according to the protocol described previously for the PC samples. The TSDC spectra recorded during the heating ramp are presented for the different cooling rates from $q_c = 30$ to 0.2 °C min^{-1}.

The depolarisation peak observed on the measurement is labelled as the α process. This peak is the dielectric manifestation of the glass transition. It can be noted that the depolarisation peak is obviously influenced by the variation of the cooling rate during the vitrification process. The main modifications of the α process are the shift of the peak to higher temperatures and the increase of its maximum intensity. This evolution is in good agreement with the influence of thermal treatment, the cooling rate or physical ageing, on the α relaxation observed in TSDC [10, 11] or Thermostimulated Creep (TSCr) [12, 13]. The maximum current I_{max} and the temperature of the maximum current T_{max} are reported in Table 1 versus the cooling rate.

The same experiments performed by means of DSC are presented in Fig. 3. In this figure, the variations of normalized heat flow versus T for q_c ranging from 30 to 0.2 °C min are superimposed. As expected, the classical behaviour of PC at the glass transition is observed, i.e. an endothermic heat flow step and a superimposed endothermic peak.

On these curves, the heat flow step at the glass transition temperature is shown to be independent of the cooling rate. The value of the heat flow step at T_g is $\Delta C_p(T_g) = 0.24$ J $(\text{g K})^{-1}$, where $\Delta C_p(T_g) = C_{p,L} - C_{p,g}$ at the glass transition temperature $T_g = 145$ °C. $\Delta C_p(T_g)$ is in good agreement with the values reported in literature for amorphous PC [14].

The magnitude of the relaxation peak and the temperature of its maximum greatly depend on the value of q_c/q_h. According to the standard theories of glass-forming liquids [15, 16], decreases in the ratio q_c/q_h result in increases in the magnitude of the relaxation peak and the temperature of its maximum as can be seen in Fig. 3. The values of the peak maximums are reported in Table 2.

Table 1 TSDC α depolarisation peak parameters, maximum current I_{max} and temperature of the maximum current T_{max}, versus cooling rate

q_c (°C min^{-1})	30	20	10	5	2	1	0.5	0.2
I_{max} (pA)	1.2	1.4	1.5	1.8	2	2.4	2.7	3.1
T_{max} (°C)	146.7	147.1	147.9	148.3	148.7	149.5	150.1	151.9

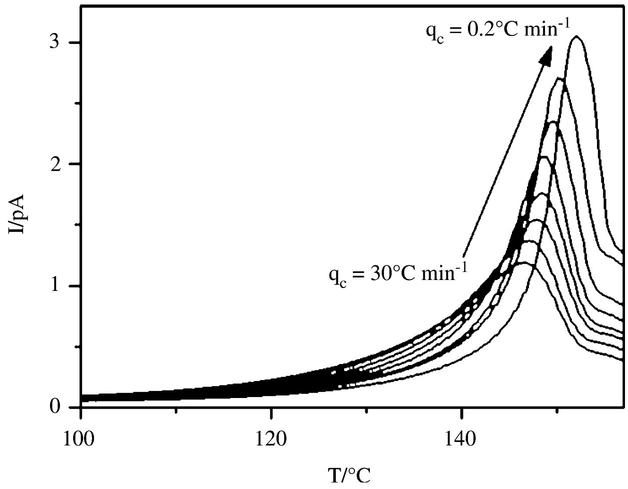

Fig. 2 TSDC complex spectrum of PC sample recorded after a polarization at $T_p = 155$ °C for 2 min with $E = 0.4$ MV m^{-1}, followed by cooling rates ranging from $q_c = 30$ to 0.2 °C min^{-1}

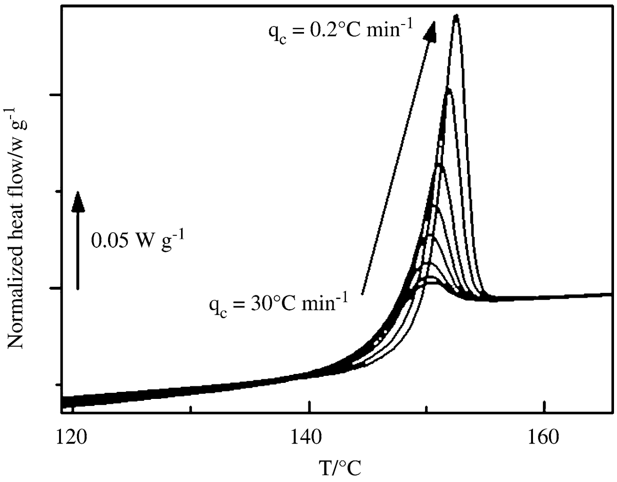

Fig. 3 DSC measurements of PC after a cooling ramp from 180 to 60 °C at cooling rates ranging from $q_c = 30$ to 0.2 °C min^{-1}. The heating rate is $q_h = 10$ °C min^{-1}

Table 2 DSC glass transition values, endothermic peak maximum temperature $T_{\max}$ and equilibrium fictive temperature T_f' shown versus cooling rate

q_c (°C min^{-1})	30	20	10	5	2	1	0.5	0.2
$T_{\max}$ (°C)	150.1	150.1	150.1	150.2	150.5	151.1	151.9	152.5
T_f' (°C)	143.3	142.7	141.8	140.9	139.8	139.6	138.3	137.8

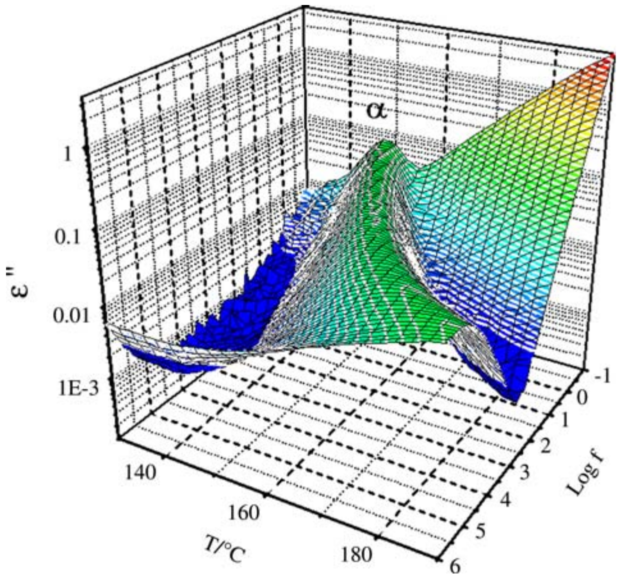

Fig. 4 DS measurements of ε'' versus frequency from 0.1 to 3.10^6 Hz and versus temperature from 130 to 190 °C obtained by using steps of 2.5 °C

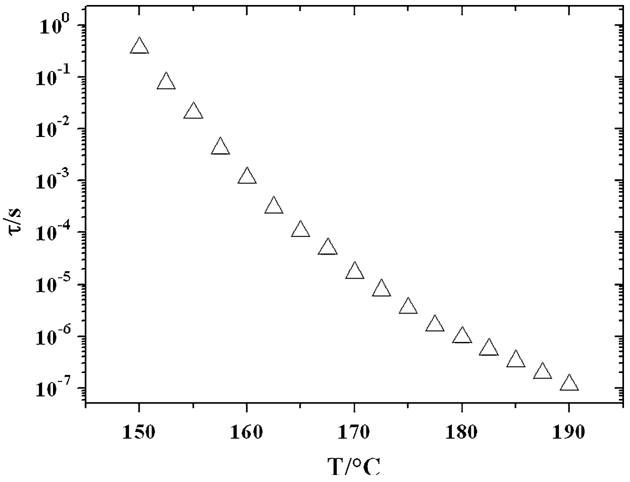

Fig. 5 Relaxation times in the liquid state versus temperature calculated from DS relaxation data

DS results are shown in Fig. 4.

The variation of the dissipative part of the electrical permittivity (ε'') versus frequency is plotted for each isothermal measurement. On this map one can identify the α relaxation process as a peak shifting to high frequency with the increase of the measurement temperature. As expected, on the low frequency/high temperature side of the map there is an exponential rise of the signal associated to a conductivity effect in liquid amorphous phase.

For each isothermal measurement the relaxation time of the α process is calculated with the frequency of the peak maximum using the relation:

$$\tau = \frac{1}{2\pi f_{\max}}. \qquad (2)$$

The variations of the relaxation time with temperature obtained using this method are plotted in Fig. 5.

Discussion

One way to get the thermodynamical equilibrium temperature of a glass-forming liquid is to use the concept of the fictive temperature. As indicated by the Tool–Naraynaswamy–Moynihan (TNM) model, the relaxation time depends on both the temperature and on the fictive temperature. The TNM model defines a relaxation function $\tau(T, T_f)$ [17–19] given by:

$$\tau = \tau_0 \exp\left(\frac{x\,\Delta E}{RT} + \frac{(1-x)\Delta E}{RT_f}\right) \qquad (3)$$

where τ_0 is the reference relaxation time, T is the temperature, T_f is the fictive temperature, ΔE is the activation energy, x is the nonlinearity parameter ($0 \leq x \leq 1$), and R is the ideal gas constant.

The fictive temperature is representative of the instantaneous thermodynamic state of the glass. It can be calculated from calorimetric measurements using Moynihan's method (also called equal areas method) [19] given by solving the relation:

$$\int_{T_f}^{T_0} \left(C_{p,l} - C_{p,g}\right) dT' = \int_{T}^{T_0} \left(C_p - C_{p,g}\right) dT'. \qquad (4)$$

The evolutions of $T_f(T)$ for the different cooling rates, calculated using relationship (4) and the DSC data are presented in Fig. 6.

The fictive temperature is a function of the vitrification conditions and in the case of this work, it is characterized by the cooling rate. The limiting fictive temperature T_f' is the constant value of $T_f(T)$ of the glassy structure for $T \ll T_g$ obtained for a specific cooling rate and for a non-aged glass. It represents the temperature at which the glass could reach the liquid state equilibrium under all conditions. In fact, when $q_h = q_c$ for a non-aged glass, $T_f' = T_g$. This parameter can be used to characterize the evolution of the glass structure during physical ageing. The limiting

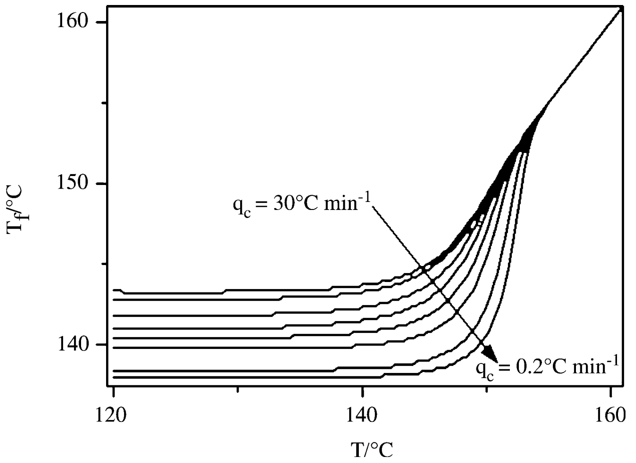

Fig. 6 Fictive temperature variation with temperature around T_g for cooling rates ranging from $q_c = 30$ to 0.2 °C min^{-1}. The low temperature constant values of $T_f(T)$ are limiting fictive temperature T_f'

fictive temperatures determined for each cooling rate are reported in Table 2.

The relaxation behaviour of a glass has been shown to depend on several factors including ageing [20] and the cooling rate [18]. For the glass structure the variations of τ with the temperature are associated with the apparent activation energy Δh^*. Assuming that

$$q_c \cdot \tau(T_g) = \text{cst.} \tag{5}$$

Δh^* can be determined from the variations of the limiting fictive temperature T_f' as a function of the cooling rate q_c according to

$$\frac{\mathrm{d}\ln|q_c|}{\mathrm{d}\left(\frac{1}{T_f'}\right)} = -\frac{\Delta h^*}{R}. \tag{6}$$

Figure 7 shows how the equilibrium fictive temperature depends on the variation of the cooling rate during the vitrification process. As shown in the figure, the thermal history (in this case represented by the cooling rate) affects the thermodynamic equilibrium temperature and moreover the dynamic response of the glassy state.

As shown by Alegria et al. [21] and Saiter et al. [22], the α relaxation is well described by the Kohlrausch–Williams–Watts (KWW) law given by

$$Q(t) = Q_0 \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{7}$$

where $Q(t) = \int_t^{\infty} I\mathrm{d}t$, I is the depolarization current, Q_0 is the initially stored charge and β characterizes the non-Debye behaviour of the α relaxation mode. The relaxation time associated with the α relaxation mode, $\tau_\alpha(T)$, can be calculated with the relation

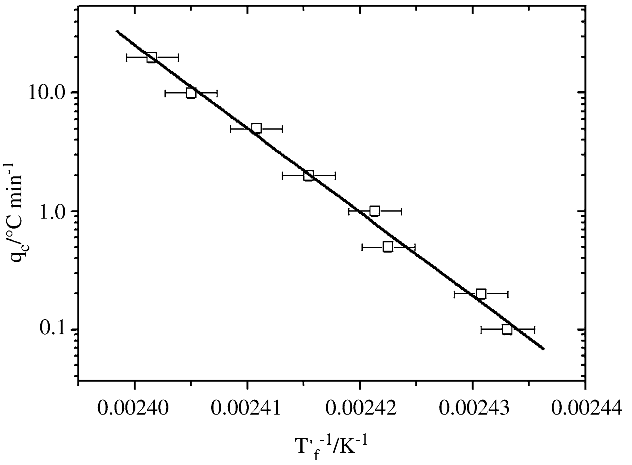

Fig. 7 Evolution of the limiting fictive temperature for samples that have undergone different cooling rates from q_c = 30 to 0.2 °C min^{-1}

$$\tau_\alpha(T) = \beta\frac{Q(T)}{I(T)}\left[\ln\frac{Q_0}{Q(T)}\right]^{[1-1/\beta]}. \tag{8}$$

The β parameter value taken as an input in this relation, has been found in previous works to be nearly unaffected by thermal history for $T < T_g$ [23]. For this work $\beta = 0.46$ [6]. Using relationship (8), the evolution of the relaxation time with temperature has been calculated from the TSDC spectra presented in Fig. 2. Thus, for each cooling rate, the $\tau_\alpha(T)$ curves are shown in Fig. 8.

The combination of the relaxation times and limiting fictive temperatures enables the determination of the relaxation time variation in the vicinity of T_g, $\tau(T_g)$ vs. T_f'. These relaxation data are superimposed on the relaxation map in Fig. 9 with the DS relaxation times.

Using the points obtained by the TSDC/DSC method, one may re-evaluate the VTF parameters in Eq. 1 by including these new data into the fitting procedure. This introduces the effects of longer relaxation times into the determination of the VTF model. Table 3 shows the VTF parameters both with and without the TSDC/DSC data.

As can be seen, the influence of including the new data has a substantial effect on the parameters. The results of the fitting procedure using only DS data lead to $T_k = 379$ K. Including the data obtained by the TSDC/DSC method to the DS data, the same fitting procedure leads to a value $T_k = 374$ K. This is a large difference assuming the fact that, as defined by Hutchinson et al. [24], for glass-forming liquids the cooperative relaxation movements in the glassy state can occur in a temperature domain between T_g and T_k. The value $T_g - T_k$ is found to be 37 K for the fitting procedure with only DS data and 42 K for DS + TSDC/DSC data which represents a relative difference of 13%.

For the glass-forming liquid domain ($T > T_g$), Angell [25] has introduced a classification that uses the variation

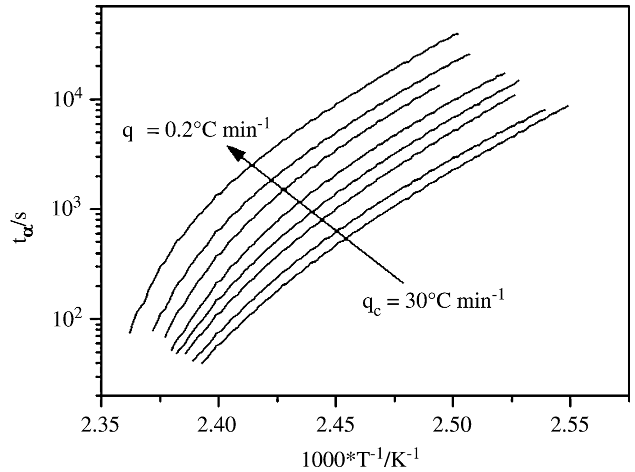

Fig. 8 $\tau_\alpha(T)$ calculated from TSDC measurements for cooling rates ranging from $q_c = 30$ to 0.2 °C min^{-1}

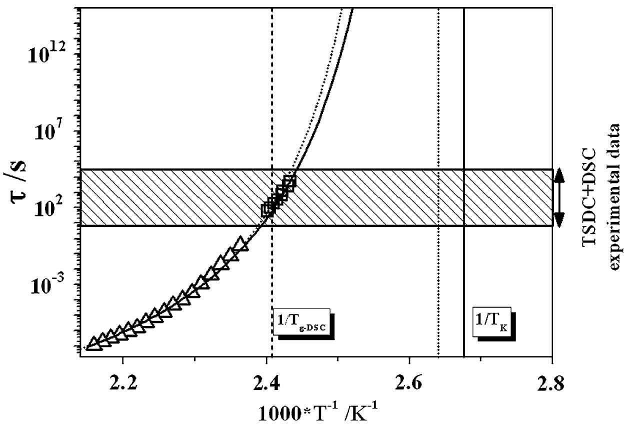

Fig. 9 Relaxation map around T_g with relaxation times calculated at $T = T_f'$ for each TSDC measurement (*open square*) and DS relaxation time (*open triangle*). The VTF fit is plotted taking into account only the DS data (*dotted line*) and also using all the relaxation times (*solid line*)

Table 3 VTF parameters of PC with DS data and DS + TSDC/DSC data

	τ_0 (s)	B (K)	T_k (K)
DS data	2×10^{-14}	1,330	379
DS + TSDC/DSC data	4.2×10^{-15}	1,541	374

of the viscosity or of the relaxation time with the temperature as a characteristic parameter. It has been proposed [26] that one may quantify the polymer's behaviour by the so-called fragility index m defined by

$$m = \left. \frac{d(\log(\tau))}{d\left(\frac{T_g}{T}\right)} \right|_{T=T_g}. \tag{9}$$

Values of m are observed to vary from $m = 16$ for a very strong glass-forming liquid to $m \geq 250$ for very fragile glass-forming liquids [27, 28]. According to Eq. 9, the determination of the fragility index requires the evaluation of $\tau_\alpha(T)$ and a correct value of T_g.

According to Eq. 9 and the VTF law we can calculate the variation of the fragility index with the evolution of the glass structure using the relation:

$$m = \frac{BT_g}{2.3 \times \left(T_g - T_k\right)^2}. \tag{10}$$

In the case of only using the DS relaxation data $m = 178 \pm 5$. When one adds the new relaxation data obtained using TSDC/DSC $m = 165 \pm 5$. Thus, as noted in a previous work [29], the main difficulty in the calculation of the fragility index, is the experimental determination of the relaxation time at the glass transition temperature, $\tau(T_g)$. This fact implies that the calculation of the fragility index is made by using the extrapolated data, using VTF model, at T_g and the use of the hypothesis $\tau(T_g) = 100$s. This alternative protocol enables the evaluation of the fragility index with calculated relaxation times in the glass transition temperature domain.

Conclusions

We have shown that by combining DSC and TSDC experiments one can evaluate the equilibrium relaxation time evolution in the glass transition temperature range. This protocol applied on polycarbonate samples that have undergone different cooling rates during their vitrification process enable an increase of the temperature range of the experimentally accessible relaxation map by the addition of new data. These new data, added to the DS relaxation data, introduce an obvious modification in the parameters of the VTF fitting procedure of the α process relaxation times. This modification is quantified on T_k where an increase of 13% is observed on the value $T_g - T_k$. Moreover the fragility index calculated at the glass transition is shown to decrease from $m = 178$ to 165.

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