Fragility of a thermoplastic polymer. Influence of main chain rigidity in polycarbonate

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Abstract

We present new data on a vitreous polycarbonate (PC) and its fragility index. Measurements have been performed by means of differential scanning calorimetry (DSC). A comparison with other data already published in this field and concerning other linear polymers is made. We show that when experiments are performed by means of DSC, the use of the glass-forming liquid fragility concept does not lead to large enough variations of the fragility index values. Thus, any correlation with structural characteristics of linear polymers, is not possible, except in the case of main chain rigidity.

Keywords: Fragility; Calorimetry; Glass; Polymer; Polycarbonate

1. Introduction

Ever since the works carried out in XXth century by Tamman, it has been known that liquids can be transformed into glassy or vitreous states by cooling. This occurs when the cooling rate is sufficiently high to avoid the crystallisation of the material. Below the crystallisation (or melting) point the liquid state is transformed into a metastable state known as supercooled liquid. Continuing the cooling, the viscosity increases strongly with decreasing temperatures. For a viscosity typically between 10^{11}–10^{12} P, the supercooled liquid solidifies into a glass. Then, thermodynamically, the glass is in a metastable equilibrium.

The glassy nature is then revealed by a transition found at a temperature T_g (depending on the experimental method of observation) and called the glass transition. Due to this thermodynamic gap, some structural relaxation phenomena could occur when the glass is maintained at a temperature $T < T_g$. This phenomenon leads to the well-known physical ageing process [1], [2], [3] and [4]. The existences of a glass transition and of relaxation phenomena are the two main characteristic features of a glass.

A priori, all liquids could be vitrified, but this ability or easiness of vitrification mainly depends on the nature of the bonds present between the atoms [5] and [6]. A glassy structure is more easily reached when covalent bonds are involved. As an example, selenium is known to be the only periodic table element able to give a monoatomic glass. The resulting structure is made of two Se atom coordinated folds forming long polymeric chains. Covalent bonds are present between the Se atoms, while van der Waals bonds govern the interchain cohesion. Following this idea, organic polymers including thermoplastics are very interesting candidates (carbon, hydrogen, oxygen atoms are covalently bonded) for achieving understanding of the glassy state. Many of them exhibit glass transition temperatures in the range between 0 and 150 °C (experimentally easy to scan) and a large variety of different structures is available.

To characterize the glassy state of these materials, we may determine the value of the glass transition temperature T_g, the value of the heat capacity step at the glass transition, $\Delta C_p(T_g)$. $\Delta C_p = C_{pl} - C_{pg}$, where C_{Pl} is the heat capacity in the liquid state and C_{pg} in the glassy state. Since Angell's works [7], [8], [9] and [10] introducing the "strong–fragile" glass-forming liquid concept, it is also possible to characterize the associated glass-forming liquid. This last approach was formalized when it was observed that a large number of glass-forming liquid viscosities, plotted as a function of a T_g normalized Arrhenius scale, could be included between two extreme behaviours. An Arrhenius law can describe the first behaviour, leading to the definition of a strong glass-forming behaviour. At the opposite extreme, a fragile glass-forming liquid is defined when a Vogel–Tamman–Fulcher law must be used to represent variation of the viscosity. As the viscosity η is linked to the molecule mobility, a more appropriate scale is given by the shear relaxation time τ. The latter can be obtained from $\tau = v / G_\infty$, where G_∞ is the shear modulus measured at a high frequency. It is convenient to estimate the slope of log (τ) versus T_g / T at T_g, which allows to define the fragility index value, m [11]:

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

(1)

The two borderline limits are reached for $m = 16$ and $m \geq 250$ for strong and fragile glass-forming liquids respectively [12] and [13]. Even if this is not a general law [14] and [15] many glass-former liquids are also found to exhibit a value of $\tau = 100$ s at T_g, implying that a unique and general law governs the glass transition phenomenon.

Even if the variation range expected for the values of m seems large, does it allow a behaviour classification with regard to the molecular structures of thermoplastic polymers?

In this work, we propose to present new data obtained on a polycarbonate (PC). The comparison of these results with those already found on other polymers such as poly(ethylene terephthalate) (PET), poly(ethylene naphthalene 2,6-dicarboxylate) (PEN) and poly(cyclohexane 1,4-dimethyl terephthalate) (PCT), will be performed.

2. Experimental

The studied material is the bisphenol A polycarbonate (PC) supplied by General Electrics. The polymer grade used is LEXAN 141. Before moulding, PC pellets were dried for 5 h or more at 110 °C. PC samples were moulded at 250 °C to obtain 0.5 mm thick sheets. The PC molecular unit used for this study is presented in Fig. 1.

Fig. 1. Repeat unit of polycarbonate.
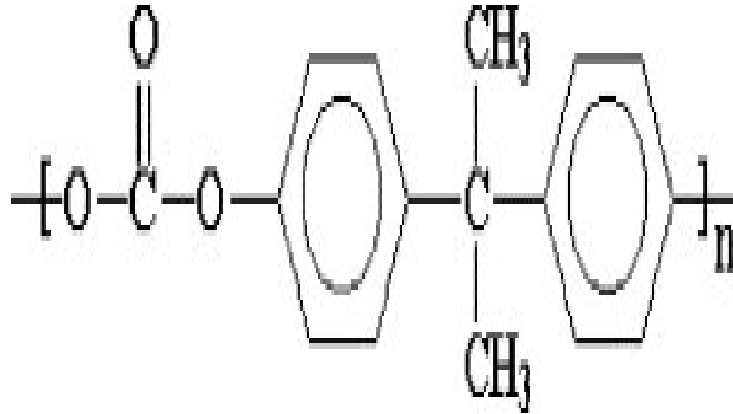
DSC measurements were performed on a TA Instruments TMDSC 2920. Typically samples were heated up to 180 °C (30 °C above T_g) and cooled down to 60 °C (90 °C below T_g) at rates q_c varying from 30 to 0.1 °C/min. Then measurements were performed at the constant heating rate q_h = 10 °C/min. The glass transition value was determined at the mid-point of a non-aged sample for $|q_c| = |q_h|$ = 10 °C/min. The DSC apparatus was calibrated in temperature and energy using the melting of an indium sample. Sample masses put in aluminium pans were around 10 mg. Finally, experiments were carried out under a nitrogen atmosphere.

According to Eq. (1), the fragility index determination requires the definition of a time constant $\tau(T, T_f)$ associated with molecular relaxation. This thermally activated relaxation also depends on the glass structure. In this work, we will use the well-known Tool–Naraynaswamy–Moynihan (TNM) equation for $\tau(T, T_f)$ [16], [17] and [18]. For a constant glass structure, the variation of τ with the temperature is associated with the apparent activation energy Δh^*. As demonstrated in numerous precedent papers [19], [20] and [21], we may determine Δh^* from the variation of the limiting fictive temperature T'_f (as defined by Tool [16]) with the cooling rate q_c according to Ref. [18]:

$$\frac{d\ln|q_c|}{d\left(\frac{1}{T'_f}\right)} = -\frac{\Delta h^*}{R} \tag{2}$$

The fictive temperature T_f can be obtained from calorimetric measurements using the Moynihan's method [15] namely:

$$\int_{T_f}^{T_0} \left(C_{p,l} - C_{p,g}\right)dT' = \int_{T}^{T_0} \left(C_p - C_{p,g}\right)dT' \tag{3}$$

Then, the limiting fictive temperature T'_f is the constant value of T_f for glassy structure for $T \ll T_g$. From the knowledge of the apparent activation energy, the fragility index m can be calculated according to Bohmer [22] as:

$$m = \frac{\Delta h^*}{\ln(10)RT_g} \tag{4}$$

3. Results

Fig. 2 presents a typical DSC curve obtained for a polycarbonate (PC). The endothermic step characterizing the glass transition is well observed. In a first approximation, using the mid-point of this endothermic step to define the glass transition temperature, we find T_g = 145 °C. This value agrees with the ones given in the literature. For instance, Bauwens-Crowet and Bauwens gives T_g = 145 °C [23] and Orreindy and Rincon 146 °C [24].

Fig. 2. Polycarbonate sample DSC measurements after cooling from 180 to 60 °C with cooling rates (q_c) equal to heating rates (q_h) = 10 °C/min.
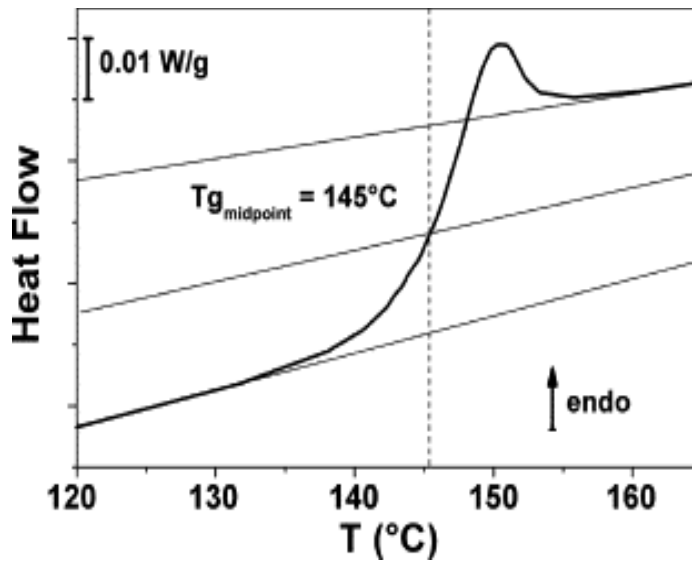
Neither crystallisation nor melting could be observed on the DSC trace indicating that PC is a totally amorphous polymer. On the other hand, the maximum temperature reached during the DSC experiments (180 °C) allows the erasing of the thermal history and could be used to rejuvenate the material. Finally, a very good reproducibility of the successive scans performed on the same sample has been observed. $\Delta C_p(T_g)$ measurement gives the value of 0.24 J/g K, in agreement with that reported by Orreindy [24], namely 0.21 J/g K. It is important to notice that the value of ΔC_p remained constant for all samples. This shows that only molecular relaxations are present in the material. Clearly irreversible chemical modifications do not occur during the experiments.

As shown in Fig. 3, an endothermic peak is observed in addition to the traditional ΔC_p step when experiments are performed at different cooling rates and the same heating rate. For each cooling rate used, we have calculated the fictive temperature T_f according to Eq. (3) and determined its variations with the temperature (Fig. 4). These variations permit the observation of the glass evolution for different thermal histories during the glass-forming process. Three variation domains can be evidenced depending on the temperature range. Above the glass transition temperature, we should have $T_f(T) = T$ since the polymer is in thermodynamic equilibrium. In the glass transition region, $T_f(T)$ continuously evolves to reach a constant value associated with vitreous non-equilibrium state. Finally, for $T < T_g$, a constant value is obtained for each cooling rate. The resulting limiting fictive temperature T_f' may be associated with the calorimetric glass transition temperature. As expected, we immediately observe a representative decrease of T_f'

value with a decrease of the cooling rate q_c.

Fig. 3. DSC measurements of PC sample after cooling from 180 to 60 °C with cooling rates (q_c) ranging from 30 to 0.1 °C/min and q_h = 10 °C/min.
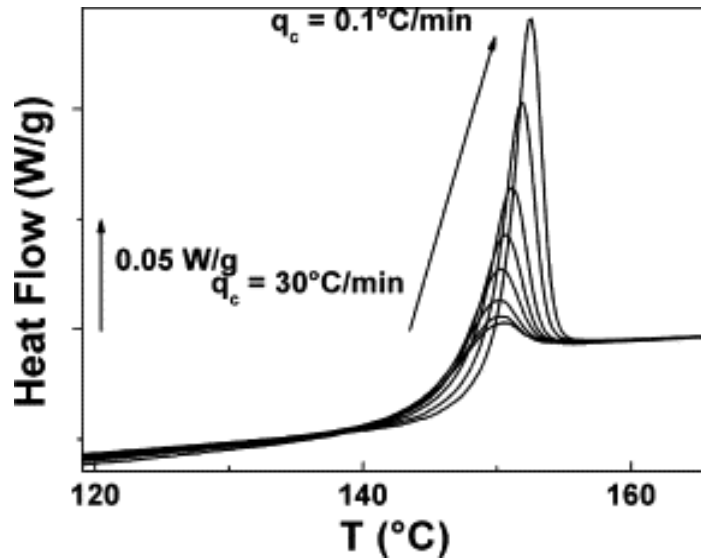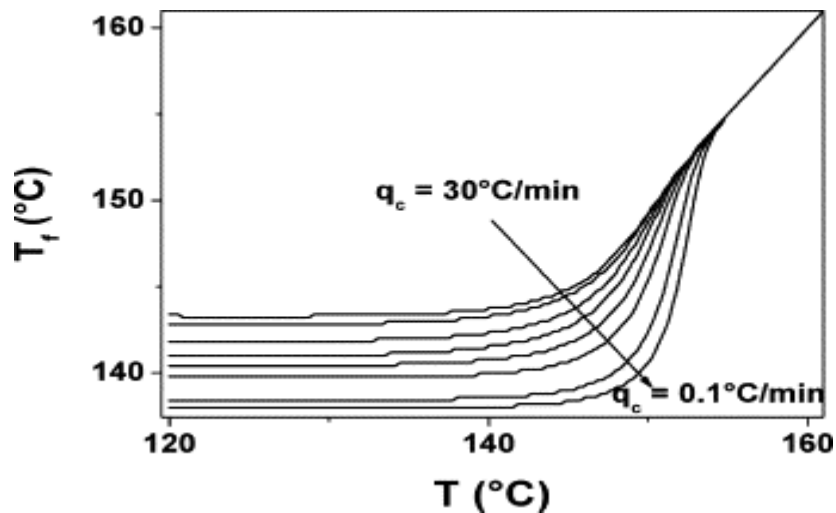

Fig. 4. T_f temperature dependence in the glass transition temperature range for polycarbonate and for different cooling rates ranging from 30 to 0.1 °C/min.

The variations of T_f' versus Ln q_c as reported in Fig. 5 and according to the Eq. (2) lead to an apparent activation energy $\Delta h^* / R$ = 163 kK. The use of the T_g value obtained for $|q_c| = |q_h|$ = 10 °C/min, finally leads to the fragility index m equal to 170.

Fig. 5. Limit fictive temperature as defined by Tool for different cooling rates q_c (30–0.1 °C/min).
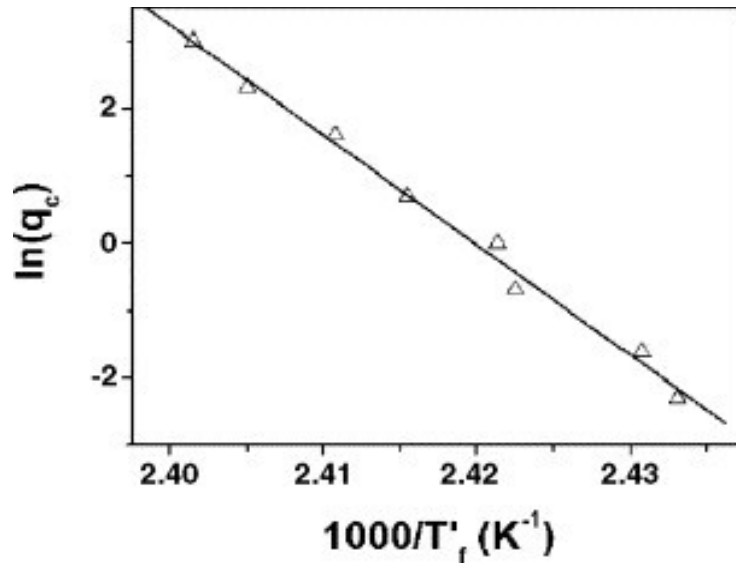
4. Discussion

As reported in Table 1, the glass transition temperature of PC is relatively high, compared to those of other thermoplastic polymers [22], [23] and [24]. Chemical formulae of the polymer considered are displayed in Fig. 6.

Table 1.

Glass transition characteristic parameters of linear thermoplastic polymers

	T_g (°C)	ΔC_P (J/(g K))	$\Delta h^* / R$ (kK)	m	Ref
PC	145.2	0.27	163	170	Our sample
PET	70	0.31	133	169	[25]
PEN	116.85	0.35	131	146	[25]
PCT	90	0.24	107	128	[25]
PETP	77	0.39	126	156	[26] and [27]
PPTP	95	0.3	106	125	[26] and [27]
PPIP	77	0.32	78	97	[26] and [27]
PDPT	25	0.4	132	192	[26] and [27]

All these materials are vitreous and the measurements of T_g have been made with the

same experimental protocol.

Fig. 6. Repeat units of: (a) poly(ethylene terephthalate) also called PETP, (b) poly(ethylene naphthalene 2,6-dicarboxylate), (c) poly(cyclohexane 1,4-dimethyl terephthalate), (d) poly(ethylene terephthalate glycol), (e) poly(Propylene isophthalate glycol), (f) poly(dipropylene terephthalate glycol).
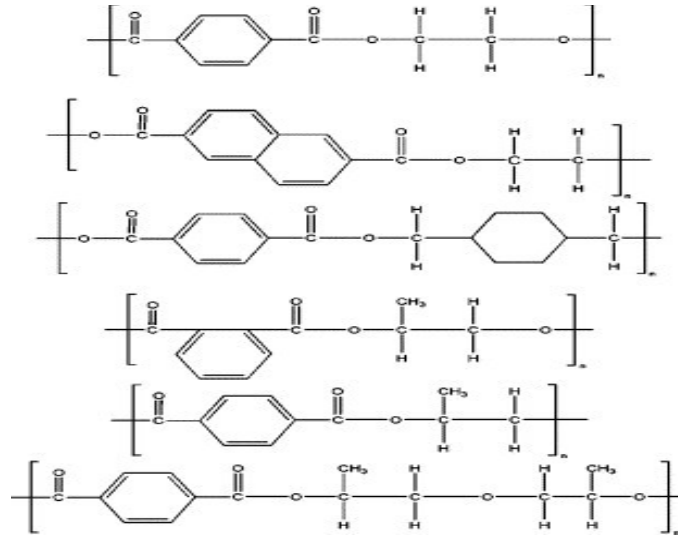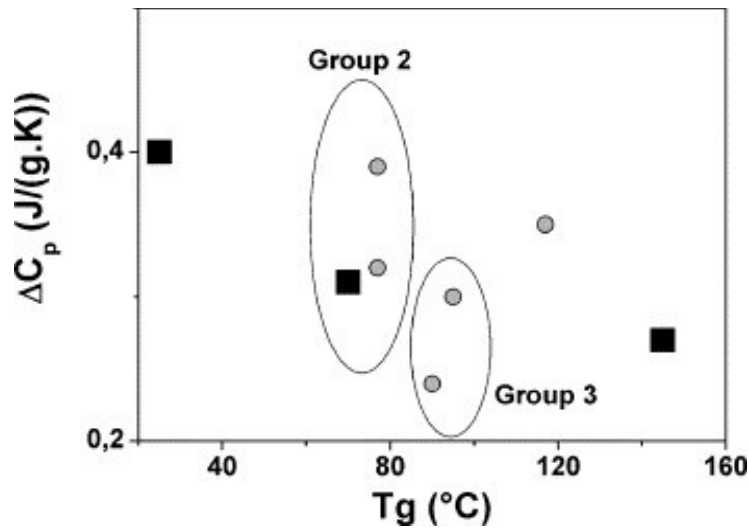

In a broad sense, one can assume the value of T_g is linked to the connectivity (the higher the connectivity, the higher the value of T_g) or to the rigidity of the overall structure (the higher the rigidity, the higher the value of T_g).

Further, PC can be expected to exhibit large differences of behaviour with PET which has a glass transition temperature at $T_g = 70$ °C and a larger difference with respect to PDPT for which a value of $T_g = 25$ °C has been obtained. Moreover, PET, PETP and PPIP, which all exhibit roughly the same T_g, should behave similarly.

PCT and PPTP represent a third group with similar T_g values but higher than those for the groups previously quoted. Finally PEN is intermediate between PC and the second group. The first point we may control concerns the decrease of ΔC_p with the increase of T_g. For instance, this is observed during the curing of thermosetting resins. For our sample set, such correlations between T_g and ΔC_p are globally obtained, as shown in Fig. 7. The full squares represent the values for PC, PET and PDPT and for them the expected trend is well visible; when samples of group 2 and group 3 are added, the data dispersion increases but this general behaviour remains valid.

Fig. 7. Values of the ΔC_p step at T_g as a function of the glass transition temperature for a set of glassy thermoplastics.

Fig. 8. Values of ΔC_P (T_g) as a function of the fragility index for 8 thermoplastic polymers. The error bars are estimated on the basis of the methods used in this work.

Secondly, a direct correlation between the engaged structures and the fragility index seems more difficult to observe [25], [26] and [27]. Indeed, although PC, PET and PDPT are the most different materials in term of local structure, they practically exhibit the same value for m. On the contrary, PET and PPIP, which have practically the same values of T_g and ΔC_P, show large differences for their m values. This lack of correlation indicates the physical origin of the phenomena characterized by the value of m cannot be linked to such basic considerations. This implies that either accuracy of the measurements is not sufficient or such structural modifications are not large enough to allow any correlation. Concerning the first point, the T_g and ΔC_P measurement accuracy is relatively good for this kind of samples and can be estimated as amounting to around 1%. This is more important for the determination of Δh^* and m values for which an accuracy lower than 10% is unreasonable. This is mainly due to the difficulties in calculation of the limiting fictive temperature. Indeed, it was observed that small variations of this parameter have a great influence on the determination of Δh^*. As a consequence, if we plot on the same figure the values of ΔC_P and m with the ad hoc error bars, we get the data reported in Fig. 8.

With regard to the full scale of variations expected for m (16–250) and the associated scale for ΔC_P (0.1–0.5 J/g K), it is clear that the domain scanned for these thermoplastics is not large enough to provide a correlation. With regard to the fragility behaviour, all these materials appear as nearly equivalent.

Fig. 8. Values of ΔC_P (T_g) as a function of the fragility index for 8 thermoplastic polymers. The error bars are estimated on the basis of the methods used in this work.
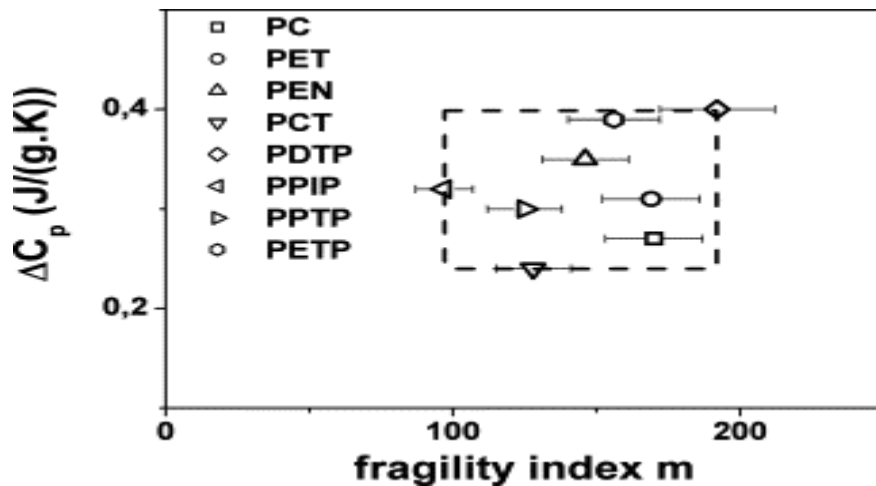
Thus, the fragility index *m* does not seem sufficiently sensitive to allow such a discrimination between the presented series of linear polymeric material differentiated only by their repetitive unit. *m* is more representative of motions occurring in the liquid state at temperature close to T_g on a larger scale than the one generated by such local modifications.

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