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THERMALLY STIMULATED CURRENT SPECTROSCOPY FOR THE STUDY OF THERMOPLASTICS

A. Bernes, J. J. Martinez, D. Chatain and C. Lacabanne

SOLID STATE PHYSICS LABORATORY, PAUL SABATIER UNIVERSITY, TOULOUSE, FRANCE

Relaxation phenomena in polycarbonate have been explored by Thermally Stimulated Current (TSC) spectroscopy. A comparative study of transitions by differential scanning calorimetry has also been undertaken. In the sub-T_g region, the observed relaxations have been associated with the diffusion of local defects along the chains. In the glass transition region, the annealing induces the segregation of two relaxation modes: the lower temperature component associated with the unstressed amorphous phase, the higher temperature component attributed to stressed amorphous phase responsible for the modules observed in electron microscopy and X-ray diffraction.

Introduction

The purpose of this work is to improve the molecular understanding of the specific relaxation phenomenon observed in thermoplastics around the glass transition temperature : bisphenol A polycarbonate Lexan (General Electric) [1] has been chosen for this work. So a comparative study of dielectric relaxations and transitions has been performed by TSC spectroscopy and Differential Scanning Calorimetry (DSC). For facilitating the interpretation of experimental results, reference data obtained on polystyrene have been used.

Materials and methods

We have investigated samples of bisphenol A polycarbonate Lexan with different thermal history:

– a quenched sample in its initial state as the reference material

– an annealed sample (250° for 20 minutes).

Thermally Stimulated Current experiments have been performed on a Solomat TSC/RMA Spectrometer. Differential Scanning Calorimetry DSC

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Thermograms have been recorded at the same heating rate than TSC spectra, on a Perkin-Elmer DSC 2.

The principle of the TSC technique is as followed: the sample is polarized by a static electrical field E at the temperature T_p. When the polarization P has reached its equilibrium value, the temperature is decreased till $T_0 << T_p$ in order to freeze this configuration. Then, the field is cut off. The polarization recovery is induced by increasing the temperature in a controlled manner. The depolarization current j flowing through the external circuit is measured by an electrometer and it gives the 'dynamic conductivity' $\sigma = j/E$. If the isothermal polarization is varying exponentially with time, then its relaxation time τ is deduced from:

$$\tau = \frac{P}{\sigma E}$$

In polymers, the polarization P is associated with a distribution of relaxation times so that P can be written as:

$$p = \sum_i P_i$$

With

$$\frac{\mathrm{d}P_i}{\mathrm{d}t} = -\frac{P_i}{\tau_i}$$

where τ_i is the relaxation time and t is the time. The advantage of the TSC spectroscopy is to give the distribution function of the relaxation time from and experimental resolution of complex spectra [2].

Experimental results

Differential Scanning Calorimetry (DSC)

A comparative study of reference and annealed polycarbonate has been performed. Figure 1 shows the time derivative of the enthalpy $\mathrm{d}H/\mathrm{d}t$ *vs.* temperature T of reference (solid line) and of annealed (dashed line) polycarbonate. In both samples, the classical step of the glass transition is observed around 153°. For the reference sample of polycarbonate we note at the glass transition onset a shoulder that disappears after annealing: this thermal event has been associated with the sub-T_g mode. Moreover the an-

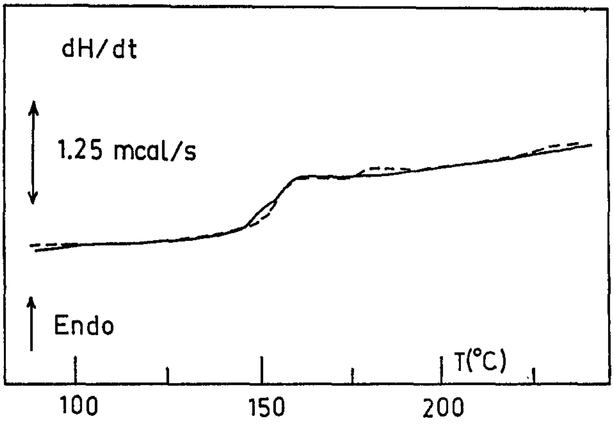

Fig. 1 DSC curves of reference (solid line) and annealed (dashed line) polycarbonate

nealing reveals an endothermic phenomenon around 32° above the glass transition, namely for 185°. These results are in good agreement with data previously published by Enns and Boyer [3].

TSC spectroscopy

Complex spectra

For the purpose of comparison, we reported experimental findings of the dipolar conductivity (σ). Figure 2 shows the TSC spectra of the reference

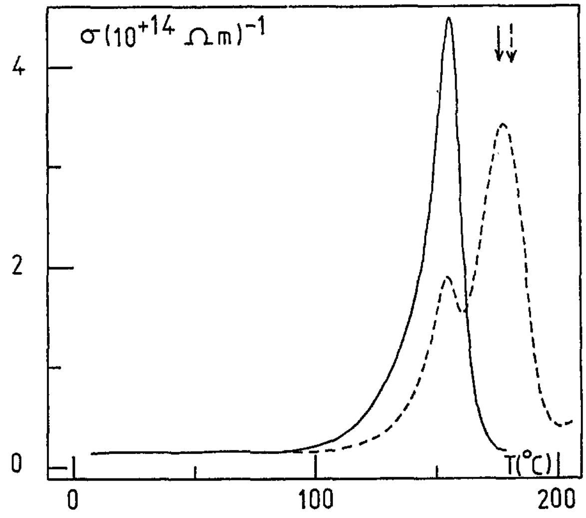

Fig. 2 TSC spectra of reference (solid line) and annealed (dashed line) polycarbonate

sample of polycarbonate (solid line) and of annealed polycarbonate (dashed line). The polarization ($E = 10^5$ V/m) is applied during 2 minutes at temperatures indicated by an arrow on the figure. It is important to note the TSC spectrum of reference polycarbonate is perfectly reproducible if the temperature in a TSC experiment is lower than 175°. The peak at 155° being situated in the vicinity of the glass transition temperature (T_g), it has been associated to the dielectric manifestation of the glass transition. After annealing an additional upper temperature component is observed at 177° while the sub-T_g mode decreases in intensity.

Fine structure of complex spectra

The TSC spectrum of polycarbonate is in reality rather complex in the vicinity of the glass transition. It has been resolved by the technique of fractional polarizations [2]. The polarizing field is the same than for the complex TSC spectrum, however a temperature window of 10° has been shifted by 5°. In those conditions, the elementary TSC peaks are uniformly shifted along the temperature axis. Figure 3 shows as example the elementary peaks for the reference sample of polycarbonate around the glass transition indicating a wide distribution of relaxation times. Each elementary peak has been analysed and the relaxation times have been deduced from Eq. (1). In addition, the experimental points have been plotted as an Arrhenius diagram:

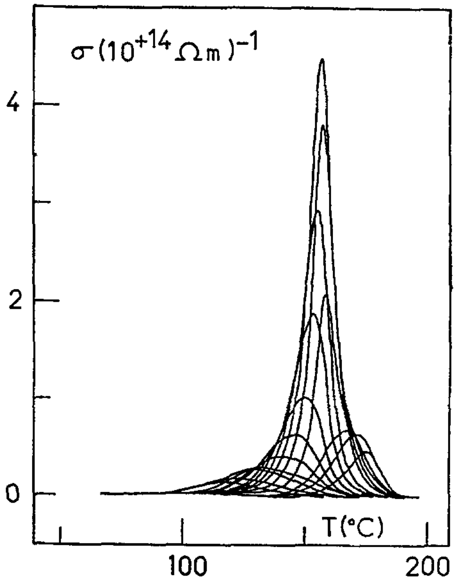

Fig. 3 Elementary peaks isolated for the reference sample of polycarbonate

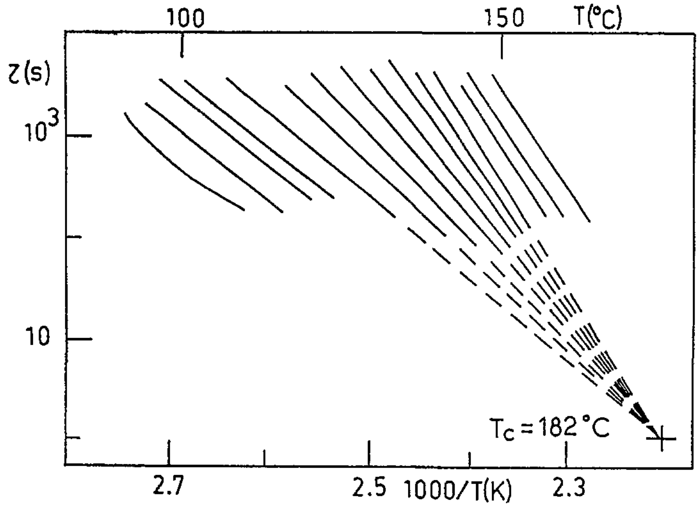

Fig. 4 Arrhenius diagram of the dielectric relaxation times isolated for the reference sample of polycarbonate

Figs 4 and 5 correspond respectively to the reference and annealed polycarbonate. These diagrams show an ensemble of straight lines converging at a point T_c, τ_c) called compensation temperature (T_c) and compensation time (σ_c). The values T_c and τ_c are characteristics of the material.

Arrhenius relaxation time

At the highest temperatures nearly all variations $\tau(T)$ (14 on the Fig. 4 and 13 on the Fig. 5) follow an Arrhenius equation:

$$\tau(T) = \tau_{oa} \exp(\Delta H / kT)$$

where τ_{oa} is the pre-exponential factor, ΔH is the activation enthalpy and k is Boltzmann constant.

Compensation law

For the lower temperature component of reference and annealed polycarbonate, the elementary processes isolated have the same relaxation time τ_c = 0.7 s and τ_c = 8.2 s respectively at a specific temperature T_c = 182° and T_c = 167°. They obey a compensation law:

$$\tau(T) = \tau_c \exp((\Delta H / k)(T^{-1} - T_c^{-1}))$$

In this particular case, the variation $\tau(T)$ are well described by only one parameter: the activation enthalpy ΔH. The upper temperature component of annealed polycarbonate is also constituted of relaxation times following another compensation law with $T_c = 212^0$ and $\tau_c = 0.94$ s.

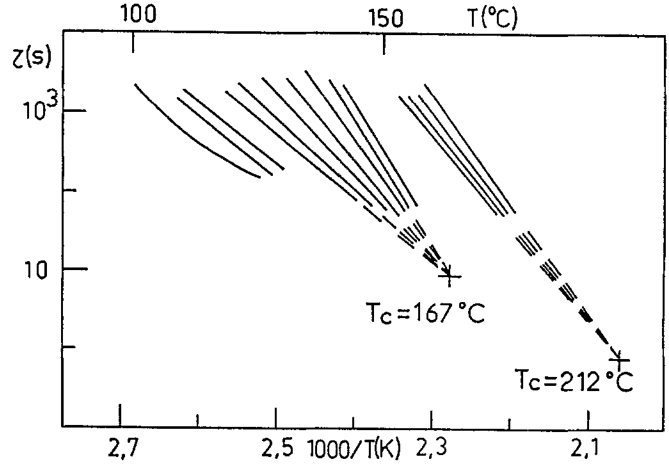

Fig. 5 Arrhenius diagram of the dielectric relaxation times isolated for the annealed polycarbonate

Vogel relaxation time

For reference and annealed polycarbonate the first variations $\tau(T)$ at low temperature (on Figs 4 and 5) are well fitted by a Fulcher-Vogel equation:

$$\tau(T) = \tau_{ov} \exp(\alpha f(T - T_\infty))^{-1}$$

where τ_{ov} is the pre-exponential coefficient. According to the Cohen and Turnbull free volume theory below T_∞ any molecular motion is frozen, and above T_∞ the fractional free volume f expands with a thermal expansion coefficient αf so that:

$$T < T_\infty \quad f = 0$$

$$T > = T_\infty \quad f = \alpha f(T - T_\infty)$$

The corresponding parameters have been plotted in Table 1.

Table 1 Parameters of Vogelian relaxation times

	$T\infty$, °C	αf, k^{-1}	τ_{ov}, s
Reference PC	44	$2.37 \cdot 10^{-3}$	0.23
Annealed PC	34	$1.45 \cdot 10^{-3}$	$7.43 \cdot 10^{-2}$

Discussion

The study of Polycarbonate by Differential Scanning Calorimetry and TSC spectroscopy has allowed us to show the evolution of its transition and dielectric relaxation spectrum *vs.* the thermal history.

Sub-T_g transition/relaxation

Figure 6 shows the sub-T_g region of TSC spectra on reference (solid line) and annealed (dashed line) polycarbonate. For the purpose of comparison, the magnitude of both spectra has been normalized at 155°. The sub-T_g relaxation is clearly observed for the reference polycarbonate between 90 and 140°. The magnitude of this sub-T_g mode is strongly decreased upon annealing. It is important to point to the fact that the sub-T_g transition observed on DSC thermograms has exactly the same behaviour. This sub-T_g transition/relaxation phenomenon has also been observed in dielectric [4, 5]

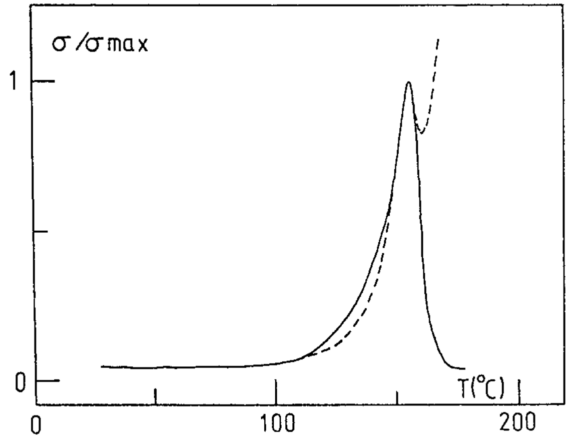

Fig. 6 Normalized complex TSC spectra of reference (solid line) and annealed (dashed line) samples of polycarbonate

and mechanical [6] relaxation. The phenomena has been associated to the existence of a microscopical order.

The analysis of the fine structure of the sub-T_g dielectric relaxation mode has shown that it is constituted of elementary processes following a Fulcher-Vogel equation. From the corresponding parameters, the fractional free volume f has been calculated at the temperature of sub T_g TSC peak. The obtained values for reference and annealed polycarbonate have been listed in Table 2. It is interesting to compare those data with the ones of polystyrene: at the liquid-liquid transition (160°) $f = 8.3\ 10^{-2}$. So, the fractional free volume obtained 50° above T_g in polystyrene is lower than the one found at the sub-T_g mode in polycarbonate.

Table 2 Fractional free volume f at the temperature T for reference and annealed samples of polycarbonate

	f	T, °C
Reference PC	0.168	116
Annealed PC	0.139	130

This more liquid-like environment in polycarbonate relative to most glassy polymers provides high degree of motion. A relatively simple model on a molecular level, consistent with the previous data, has been proposed by Jones [7]. A correlated conformational interchange between two neighbouring carbonate units has been proposed. One carbonate unit starts with a trans-trans conformation and the adjacent is regarded as a *cis*-trans conformation. The interchange produced by a rotation about one of the CO bonds in each of the carbonate units. The *cis*-trans conformation diffuses down the chain composed of largely trans-trans units by the repeated action of this process. This diffusion process could initiate the rapid reduction of a macroscopic strain.

Glass transition/relaxation

Lower temperature component.

Figure 2 shows that the lower temperature component of the TSC peak is observed at 155° i.e. around the glass transition temperature independently from the thermal history of polycarbonate. It is important to note that the magnitude of this peak decreases upon annealing. The study of the fine structure of this peak shows that it is constituted of elementary processes characterized by relaxation times obeying a compensation law. This behaviour is phenomenologically analogous with the one of amorphous polymers where local order is mechanically [8] or chemically [9] induced. In polycarbonate the bulkyness of the bisphenol A groupment might be responsible for this local order.

It is interesting to compare the compensation temperature, T_c, with the glass transition temperature, T_g. In the reference sample of polycarbonate, T_c-T_g = 19°: similar relationships have been found in semi-crystalline polymers like polyolefins [10], polyamides [2]. Then, it has been postulated that the crystallites and the ordered regions have the same consequence on the cooperative movements liberated at the glass transition.

Upper temperature component

Upon annealing a new peak is observed at 177° corresponding to the upper temperature component of the TSC peak (cf. Fig. 2). The DSC trace exhibits a step in the corresponding temperature range; no trace of crystallization is found. This last observations is coherent with the very low crystallization rate previously published for polycarbonate [11, 12].

This upper temperature sub-mode is constituted of elementary processes characterized by relaxation times following a compensation law. This behaviour is characteristic of polycarbonate. Indeed, in semicrystalline polymers having a double glass transition like polyethylene [13] or polypropylene [14], the upper temperature component is associated with relaxation times that do not obey a compensation law. In this case, amorphous regions under stress from crystallites are responsible for that upper temperature component.

In polycarbonate, the upper temperature sub-mode has been assigned to a 'constrained amorphous phase' that would segregate under annealing. This assumption is coherent with the existence of ordered modules of some 40 Å postulated by Yeh [15] for explaining electron microscopy [16, 17] and X-ray diffraction data [18].

Conclusion

The DSC and TSC study of transition and relaxation phenomena in polycarbonate show that this thermoplastic material has a a specific behaviour. In the sub-T_g region, the observed relaxation mode has been assigned to conformational defects travelling all along the main chain. Diffusion of such a change in backbone shape could initiate a rapid reduction of a macroscopic strain. In the T_g region, a double glass transition/relaxation has been observed by DSC and TSC. Since both components are constituted of elementary processes following a compensation law, the hypothesis of two segregated amorphous phases has been proposed. The lower temperature component has been attributed to the 'true amorphous phase' while the upper temperature component has been assigned to the 'constrained amorphous phase'. This last component favoured by annealing might be responsible for the modules observed by Yeh in electron microscopy and X-ray diffraction patterns.

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Zusammenfassung — Relaxationsphänomene von abgeschrecktem und getempertem Polycarbonat (Lextan) wurden mit Thermisch Stimulierten Feldpolarisations Spektroskopie [Thermally Stimulated Current (TSC) Spectroscopy] untersucht. Unterhalb der Glasumwandlung wird eine Relaxation beobachtet, die mit einem molekularen Kettenmechanismus in Zusammenhang gebracht wird. Temperung verursacht eine Trennung in eine spannungsfreie und eine unter Belastung durch die Kristalle stehende amorphe Phase. Experimentelle Befunde werden diskutiert und Modellbetrachtungen zur dielektrischen Relaxation vorgestellt.