JOURNAL OF MATERIALS SCIENCE 14 (1979) 1817–1826

The relationship between the effect of thermal pre-treatment and the viscoelastic behaviour of polycarbonate in the glassy state

C. BAUWENS-CROWET, J-C. BAUWENS
Physique des Matériaux de synthèse, Université Libre de Bruxelles, 1050 Bruxelles, Belgium

The viscoelastic behaviour of three different samples of polycarbonate, with differing pre-treatment, is described here by a generalized non-linear Maxwell system, proposed previously. This model gives the variation of the tensile yield stress related to each sample as a function of temperature and strain rate. The response is checked over a large range of strain rates, at temperatures from 20 to 80° C. The model allows the determination of the damping peak arising from the molecular movements which it expresses. A correspondence is found with the intermediate loss peak location, which occurs for each sample just below the α transition. Results obtained from dynamic mechanical tests and differential scanning calorimetry show that the structure of the samples changes in the range of temperatures where the intermediate loss peak arises at 1 Hz.

1. Introduction

This paper is a contribution to the study of the mechanical behaviour of polycarbonate (PC) in the range of temperatures between 20° C and T_g

Previously [1], one of us proposed a rheological model where a spectrum of non-linear Maxwell elements is converted to another spectrum during the course of the deformation of a glassy polymer. The spectra represent the initial and the deformed structure of the sample, respectively.

Assuming that the initial spectrum depends on the thermal history of the polymer, we attempt here to check some consequences of the model on the mechanical behaviour of 3 samples of PC differing by their thermal pre-treatment. The PC samples are referred to as: "original", "annealed" (below T_g) and "quenched".

We give results obtained in tensile tests, dynamic mechanical measurements and differential scanning calorimetry (DSC) on these 3 samples. Between 20 and 80° C, it is found that the yield stress σ_y, measured as a function of absolute temperature T and strain rate $\dot{\epsilon}$, may be expressed by an Eyring-type equation:

$$\frac{\sigma_y}{T} = A\left(\ln 2C\dot{\epsilon} + \frac{Q}{RT}\right) \qquad (1)$$

where R is the universal gas constant, and A, C and Q are constants. Therefore, this formula, previously used empirically for the "original" PC [2, 3], remains valid for the two other samples.

It is shown here that this equation can be derived from the generalized non-linear Maxwell model.

As a first approximation, it is assumed that the spectra characterizing each sample depend on a single parameter of the Eyring dashpot of the Maxwell elements, the others being kept constant for each element in any sample.

The lower limit of the initial spectrum for each sample is determined from the tensile curve; all the constants of the related Maxwell element are given. The relaxation time of each sample is calculated, and the temperature T_m at which it relaxes in a damping test conducted at 1 Hz is noted. This allows the location of the beginning of the damping peak which corresponds with the molecular move-

0022–2461/79/081817–10 $03.00/0

ments expressed by the formula of the proposed model.

This peak is identified here with the so called "intermediate peak" appearing just below the α transition in the damping curves [4–6]. Damping measurements performed while the temperature is cycled allow us to demonstrate that the observed maxima of these peaks are an artefact, as the structure of the sample is affected by heating during the test. Differences in the DSC curves obtained on various forms well-known in the literature [6–9], are related here to the loss curves and the spectra used in the model.

2. Experimental details

2.1. Specimens

Makrolon (Bayer) is used throughout. Test pieces are machined from extruded sheets 0.2 cm thick. It is called "original" when no thermal pre-treatment has been performed. It has a viscosity average molecular weight of $\bar{M}_v = 26\,000$.

2.2. Thermal pre-treatments

Specimens of "original" PC are converted into the "annealed below T_g" sample by annealing 45 h at 120° C, and into the "quenched" sample by annealing 1 h at 165° C and ice-quenching. These thermally pre-treated PC samples, have the same average molecular weight as the original one.

Examination of original and annealed test pieces in polarized light does not reveal any frozen-in stresses or orientation.

2.3. Tensile and creep tests

Specimens and equipment used in tension and creep tests at various strain rates and temperatures in order to determine the yield stress, as well as the method of choosing the yield point in a creep test, are described elsewhere [2, 3].

In addition, for tensile stress–strain curves obtained at room temperature, the extension is recorded using a strain gauge extensometer of the Baldwin type. The imposed strain rate in this case equals 4.16×10^{-4} sec^{-1}. Engineering stresses are used throughout.

2.4. Dynamic mechanical measurements

The damping tests are performed using a free oscillation torsional pendulum, with specimens having dimensions of 11 cm × 1.5 cm × 0.2 cm, at frequencies of about 1 Hz in the range of temperatures from -80 to 140° C. The heating and the cooling rates are constant and equal to 1° C min^{-1}. Measurements are made every 5° at intervals of 15 min, the temperature remaining the same for 10 min.

2.5. Differential scanning calorimetry

DSC measurements are carried out with a du Pont DSC900 at a heating rate of 20° C min^{-1}. The specimens weigh about 60 mg.

3. Results

3.1. Tensile stress–strain curves

Examples of stress–strain curves obtained on the

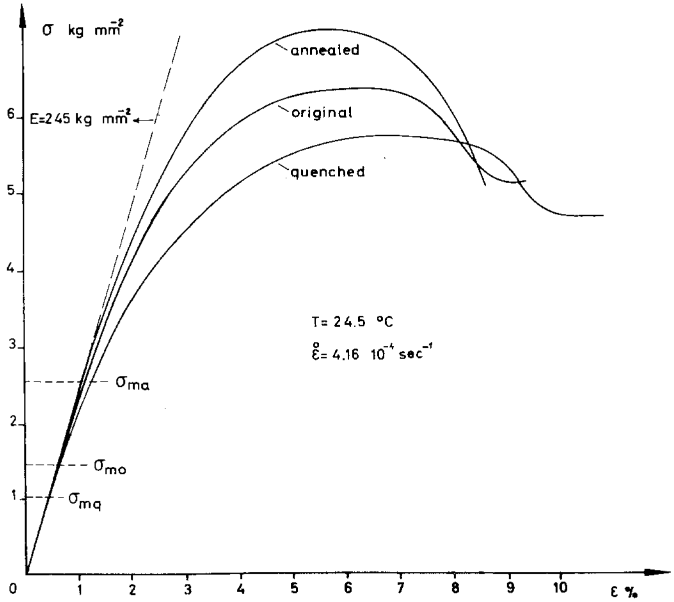

Figure 1 Examples of tensile stress–strain curves of the 3 different samples of PC.

TABLE I Constants determined from the stress–strain curve reduced to 20° C ($\dot{\epsilon} = 4.16 \times 10^{-4}$ sec^{-1}).

	E (kg mm^{-2})	σ_{mo} (kg mm^{-2})	σ_{ma} (kg mm^{-2})	σ_{mq} (kg mm^{-2})
Specimen 1	245 ± 10 (same value	1.96	2.46	1.0
Specimen 2	for the 3 samples)	1.46	2.52	0.97

three PC samples are given in Fig. 1. It can be seen that the shape of the curves differs from one PC to the other, which we attribute to differences in the assumed initial spectrum.

Within the sensitivity of the technique used, Young's modulus E, calculated from the Hookean part of the tensile curve, seems to be the same for the three samples of PC studied, while σ_m the stress related to the end of this Hookean part, differs perceptibly. Let subscripts o, a and q denote the original, annealed and quenched PC respectively; therefore it is found that:

$$\sigma_{ma} > \sigma_{mo} > \sigma_{mq}. \quad (2)$$

Estimated values of these stresses and of Young's modulus are given in Table I.

3.2. Yield stress measurements

A plot of σ_y/T against the logarithm of strain rate for temperatures of 20 to 80° C is given in Fig. 2 for the "original" and in Fig. 3 for the "annealed" and "quenched" PC. A set of parallel straight lines is drawn throughout the data for each PC. It is calculated from Equation 1 and the values of the constants given in Table II. These constants are adjusted to give a good fit to the data, assuming, for a first approximation, that Q remains unchanged for the three PC. This assumption implies that differences between the yield stresses from one to the other arise from differences in the values of C. Therefore we cannot claim that the obtained fit, although good, is the best one. Of course a refined treatment requires the adjustment of both C and Q for each PC, but the accuracy of the data does not justify such a treatment. However, the choice of the same value for A (the slope of the parallel straight lines) for the 3 PC samples is fully consistent with a least-squares linear regression.

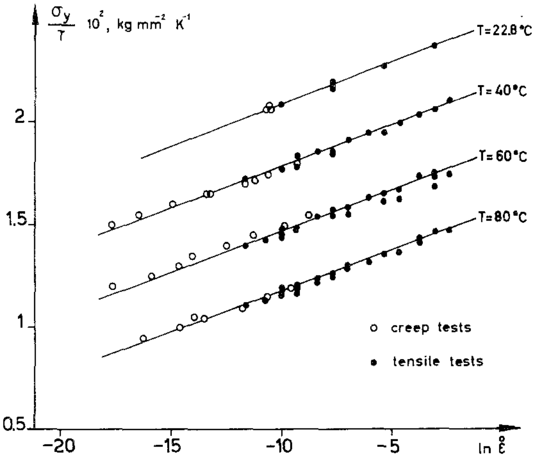

Figure 2 A plot of the ratio of the engineering yield stress to temperature, against the logarithm of the strain rate at yield ($\dot{\epsilon}$ in sec^{-1}) for tension and creep test performed on the original PC. The set of parallel straight lines is calculated from Equation 1 and Table II.

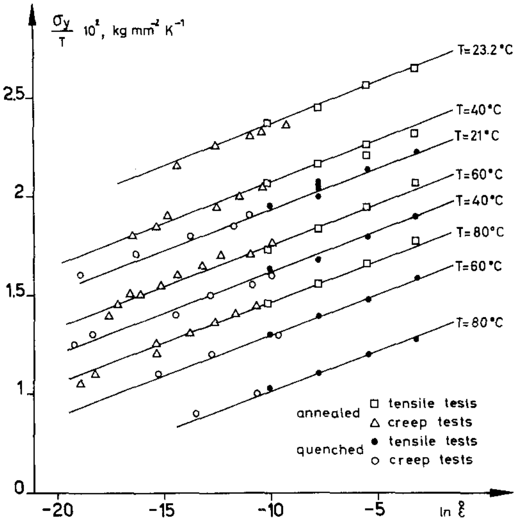

Figure 3 Same plot as in Fig. 2 but related to the annealed and the quenched PC samples respectively.

It can be seen from Figs. 2 and 3 that, for given conditions of temperature and strain rate:

TABLE II Parameters of the Eyring-type Equation 1.

	A (kg mm^{-2} K^{-1})	Q (kcal mol^{-1})	C (sec)
Original	4×10^{-4}	81	1.4×10^{-33}
Annealed	4×10^{-4}	81	1.5×10^{-30}
Quenched	4×10^{-4}	81	1.7×10^{-35}

$$\sigma_{ya} > \sigma_{yo} > \sigma_{yq} \tag{3}$$

We have observed moreover that a similar relation is still valid for the "yield drop", which confirms the results of Adam *et al.* [10].

3.3. Dynamic mechanical measurements

The loss curves (tan δ against temperature) obtained on the 3 PC samples are given in Fig. 4. Results agree with the data of the literature [4–6]. Admitting a one to one correspondence between the dielectric and dynamic mechanical loss peaks, they are similar to the observations of Watts and Perry [11].

At low temperatures, the high temperature side of a broad loss peak can be discerned on the graph. This reflects the β process as classified by Sauer [12]. Only minor differences are observed between the three samples.

Just below the α peak associated with the glass–rubber transition, the loss curve exhibits an intermediate peak, easily observable in the original and quenched PC. This peak is located in a lower range of temperatures in the quenched than in the original PC. At first sight, it is not present in the annealed PC, but we think, like Watts and Perry [11], that it is in this case, almost completely merged with the α peak. Although the molecular origin is unknown, this intermediate peak has been previously attributed to stresses frozen into the material during manufacture or quenching [13].

The loss curve related to the annealed PC is found to be quite reversible from −80 to 120° C. Starting from room temperature and heating to 120° C, then cooling to −80° C and re-heating to 140° C, the obtained curve remains unchanged. An example in the range of temperatures from 20 to 140° C is given in Fig. 5a. Such cycles of measurements performed on both other PC samples, show that the intermediate peak disappears when the specimen is cooled and then re-heated. Fig. 5b gives results obtained on a specimen of the original PC. Measurements are made while it is heated to 100° C, then cooled to room temperature and re-heated to 140° C. The same procedure is used on a quenched specimen: heating to 80° C, then cooling to room temperature and re-heating to 140° C; results are given in Fig. 5c. Cooling and re-heating data superpose.

The loss curves of a quenched specimen and of a quenched specimen annealed 3 h at 80° C, are compared in Fig. 6. The additional peak at about 50° C has disappeared by annealing at 80° C which confirms that the effect shown in Fig. 5c occurs by simple heating. Damping is also measured as a function of time at constant temperature (90° C) on the original PC; it can be seen in Fig. 7 that tan δ decreases continuously.

3.4. DSC measurements

Fig. 8 shows the DSC curves obtained for the three samples. The annealed PC exhibits a high endothermal peak at T_g as a consequence of annealing at 120° C; the area of this peak is a measure of the energy associated with the free volume of the sample [14]. Such a peak is not observable in the two other PC samples. In the quenched PC, the slope of the DSC curve is less steep between 80 and 140° C, indicating an exothermal tendency. This tendency is reduced in the DSC curve (not

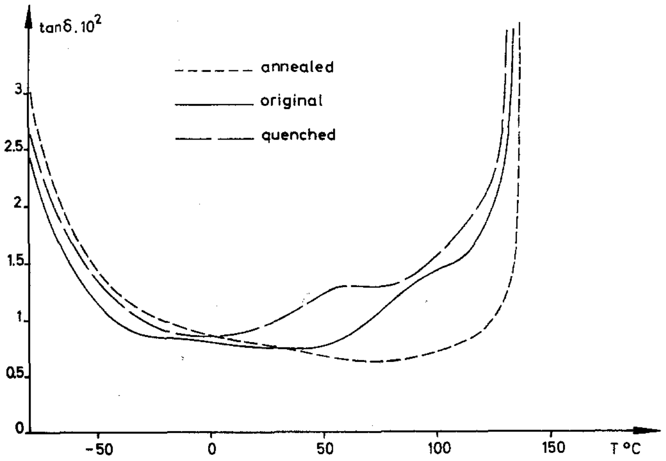

Figure 4 Loss tangent as a function of temperature for the 3 samples of PC studied (frequency ~ 1 Hz).

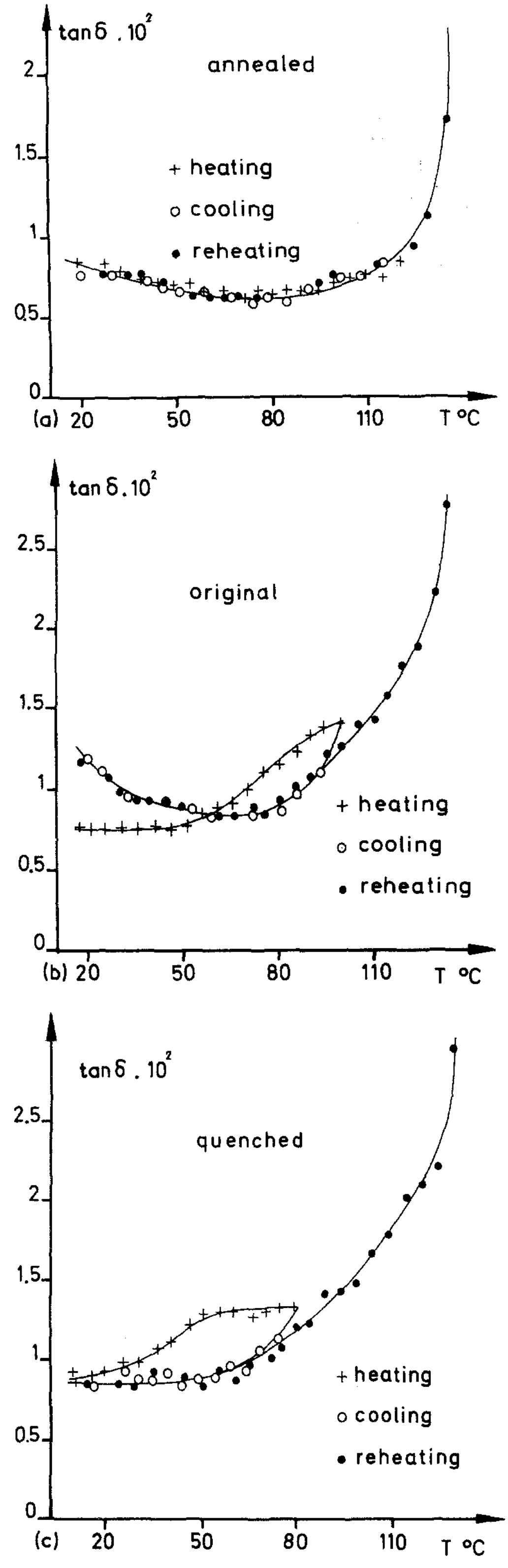

Figure 5 Temperature dependence of loss tangent during a heating, cooling and re-heating cycle, on annealed PC (a), original PC (b) and quenched PC (c) (frequency ~ 1 Hz).

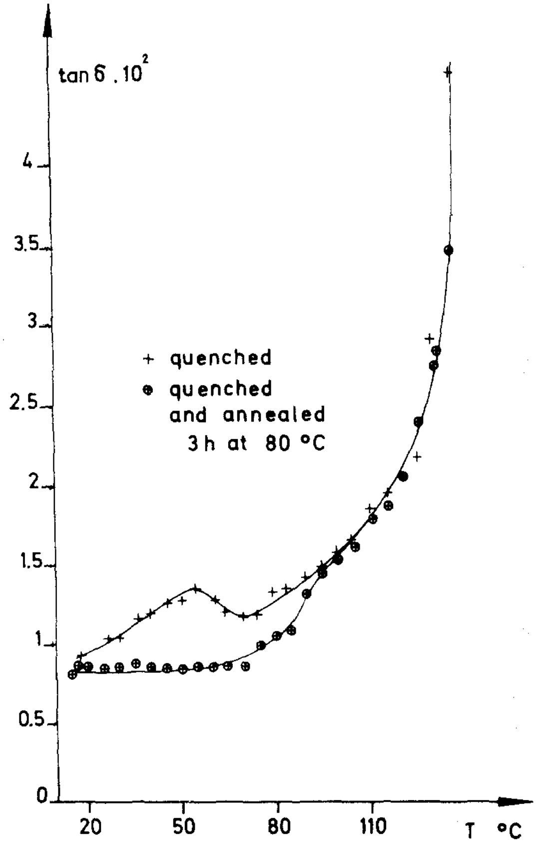

Figure 6 Temperature dependence of loss tangent of a quenched specimen which has been annealed 3 h at 80° C. The loss curve of the quenched PC is given for comparison (frequency ~ 1 Hz).

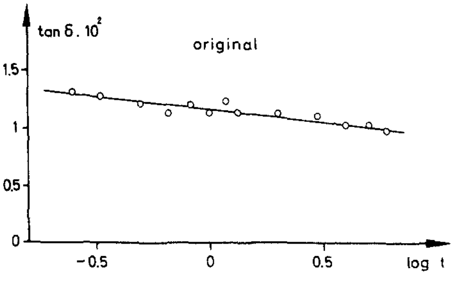

Figure 7 Time dependence of loss tangent at constant temperature (90° C) on the original PC sample (t in hours).

shown on the graph) of a quenched specimen annealed 3 h at 80° C prior to testing. But this DSC curve still differs from that of the original material. Therefore DSC measurements as well as damping tests show that a thermal treatment at 80° C does not eliminate the effect of quenching in all respects.

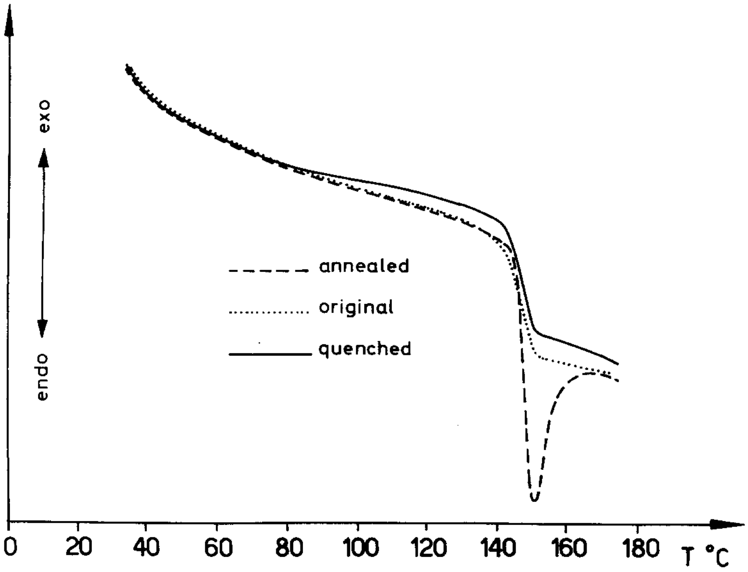

Figure 8 DSC curves for the 3 samples of PC studied.

4. Characteristics of the model

Let us now attempt to characterize each sample in its initial state, before any mechanical test, by a generalized non-linear Maxwell model [1]. The quite classical system is represented in Fig. 9. We have neglected here, for the sake of simplicity, the rubber elasticity contribution, previously considered [1].

All the Maxwell elements have the same Hookean spring E value, as this does not depend on the sample considered. This is supported by the observation that the Hookean part of the tensile stress–strain curve has the same slope for the 3 PC samples, as already outlined above. An Eyring dashpot is related to each element. Based on our results obtained for the yield stress (see Figs. 2 and 3), we assume, for a first approximation, that each element in any sample has the same value of A and Q respectively. The viscous deformation of a given Maxwell element may be neglected as long as the stress it bears remains smaller than a definite value expressed by:

$$\sigma_j = AT\left(\ln 2\dot{\epsilon} + \frac{Q}{RT} + \ln c_j\right). \tag{4}$$

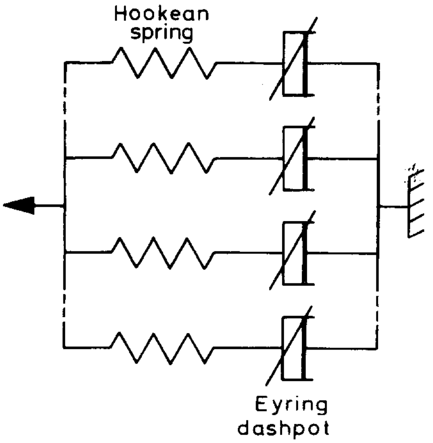

Figure 9 Proposed rheological system valid for the three samples of PC with the related value of the parameters given in Tables I and II.

c is used when Maxwell elements are considered individually. This viscous deformation starts when the following condition is fulfilled:

$$E\epsilon = \sigma_j \tag{5}$$

where ϵ denotes the strain of the specimen. As all the elements have the same value of A, Q and E, the previous treatment [1] reduces, here, to considering a distribution function or spectrum $P_\mathrm{i}(\ln c)$ related to the initial state of a given PC. Let $\ln c_m$ be its lower limit. This spectrum is converted to another spectrum $P_\mathrm{d}(\ln c)$, during the course of the tensile deformation. The tensile stress σ related to the value of the strain for which Equation 5 is satisfied may be expressed as a function of both spectra:

$$\sigma = \int_{\ln c_m}^{\ln c_j} AT\left(\ln 2\dot{\epsilon} + \frac{Q}{RT} + \ln c\right) P_\mathrm{d}(\ln c)\,\mathrm{d}\ln c + E\epsilon\int_{\ln c_j}^{\infty} P_\mathrm{i}(\ln c)\,\mathrm{d}\ln c \tag{6}$$

TABLE III Lower limit of the initial spectrum

	c_{mo} (sec)	c_{ma} (sec)	c_{mq} (sec)
Specimen 1	3.8×10^{-50}	2.4×10^{-48}	$4.5\ 10^{-53}$
Specimen 2	2.1×10^{-51}	2.2×10^{-47}	$1.5\ 10^{-53}$

TABLE IV Determination of T_m for $\nu = 1$ Hz

	T_{mo} (° C)	T_{ma} (° C)	T_{mq} (° C)
	Calculated from Equation 12 and Tables II and III		
Specimen 1	66	78	48
Specimen 2	58	85	45
	Determined from the loss curve		
	57	85	27

From Equation 6, an expression of σ_y analogous to Equation 1 may be obtained (see Appendix). This equation, previously used empirically, can thus be derived from the proposed generalized Maxwell model. Moreover, the relationship (Equation 6) points out the dependence on P_i ($\ln c$). This spectrum must evidently be affected by thermal history. For example, in the case of the quenched PC and to a lesser degree the original PC, rapid cooling increases the amount of both frozen-in stresses and free volume present in the sample and eases viscoelastic deformation. On the contrary, the annealed PC, which exhibits an endothermal DSC peak at T_g, has a comparatively low amount of free volume. This opposes viscoelastic deformation and must raise the lower limit of the spectrum.

We do not intend here to determine the shape of $P_i(\ln c)$; we will restrict our study to the influence of thermal history on c_m, the lower limit of this spectrum. This quantity may be calculated for each sample using Equation 4 with $j = m$ and the values of σ_m, A and Q summarized in Tables I and II. Results are given in Table III, where it can be seen that:

$$c_{mq} < c_{mo} < c_{ma} \tag{7}$$

5. Response of the model submitted to damping tests

In the case of damping tests, the stresses are low and the viscosity of the Maxwell elements may be considered as Newtonian [15]. The model reduces to a linear generalized Maxwell system, from which the loss shear modulus G'' is given for a first approximation by:

$$G'' = \frac{\pi}{2} H(\ln \tau) \tag{8}$$

where $H(\ln \tau)$ denotes the relaxation spectrum. It is related to P_i by:

$$H(\ln \tau) = G P_i(\ln \tau) \tag{9}$$

G being the shear modulus corresponding to Young's modulus E of the Maxwell elements. Let τ_m be the lowest relaxation time of the spectrum. It is therefore related to the Maxwell element for which $c_j = c_m$ and the viscosity equals η_m.

Taking into account that, in the linear range [16]:

$$\eta_m = \frac{A c_m T}{\sqrt{3} \exp\left(-\dfrac{Q}{RT}\right)} \tag{10}$$

then the lowest temperature T_m at which tan δ begins to increase is determined by:

$$2\pi\nu = \frac{1}{\tau_m} = \frac{G}{\eta_m} \tag{11}$$

where ν denotes the frequency of the damping test.

By substituting the value of η_m given by Equation 10, it comes from Equation 11 that:

$$2\pi\nu = \frac{\sqrt{3} G \exp\left(-\dfrac{Q}{RT_m}\right)}{A c_m T_m} \approx \frac{E \exp\left(-\dfrac{Q}{RT_m}\right)}{A c_m T_m} \tag{12}$$

from which T_m may be calculated for each sample. Results are given in Table IV.

6. Discussion

Clearly, it appears from the damping measurements that the annealed PC is the more stable one, while the structure of the other samples still changes in the glassy state. Results obtained in DSC lead to the same conclusion.

We think that the observed maximum of the intermediate peak of the loss curve relating to the original and quenched PC (see Figs. 4 to 6) is an artefact resulting from a thermal treatment which occurs during the measurements. This involuntary thermal treatment attempts to bring the sample to a stabler structure and therefore affects its initial spectrum. This effect starts at about 50 and 80° C

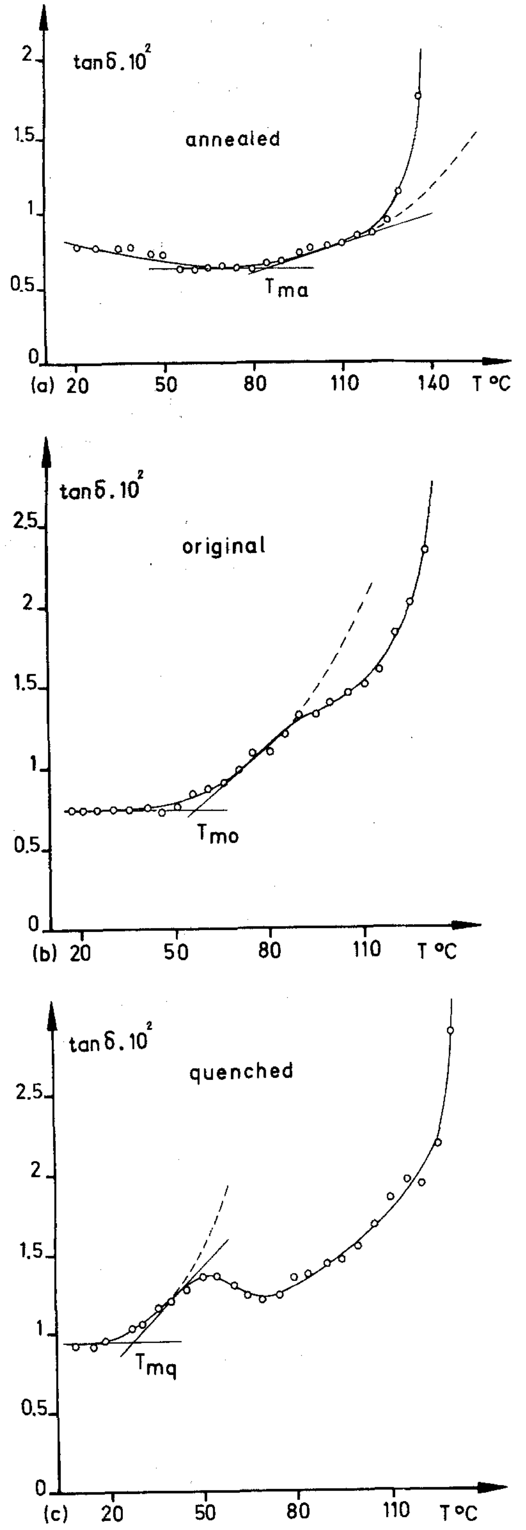

Figure 10 Graphical determination of the temperature T_m at which starts the intermediate loss peak on the loss curve of the annealed PC (a), the original PC (b) and the quenched PC (c). The assumed real shape of this peak is extrapolated from its left side (dashed line).

for the quenched and the original PC respectively. We assume that the real shape of this intermediate peak is analogous to that extrapolated from its left side as schematically represented on Fig. 10; the maximum being probably merged with the α peak. This assumption leads us to advance that the expression capable of accounting for the molecular movements which give rise to this peak, corresponds to our generalized Maxwell model. The basic idea, which was proposed a long time ago, [17], is that viscoelastic deformation may be expressed either by a formalism derived from Eyring's equation, or by the WLF equation, the latter case occurring exclusively above T_g and corresponding to the α loss peak.

In our view, the intermediate peak is therefore associated with the spectrum which characterizes a given sample and the molecular movements related to a model in agreement with Eyring's equation. The intermediate process is perhaps "a proximated precursor of the α process" as suggested by Watts and Perry [11], but it is distinguished and governed by a quite different formalism. Our interpretation implies that calculated values of T_m must agree with experimental ones related to the intermediate peaks.

Such experimental values of T_m are not easy to determine. The treatment implies that an increase in the tan δ value will be reflected in the tensile curve as a deviation from the Hookean part of this curve, but the lower limit of the variation of tan δ which can be detected is unknown. We propose the following procedure as a first approximation: we take as T_m the point of intersection of the base line of the loss curve with a line tangent to the left side of the intermediate peak (see Fig. 10). Results are given in Table IV.

Of course our treatment implies that this peak is also present in the loss curve related to the annealed PC. We cannot prove this, but the results derived from this assumption are coherent. The greatest discrepancy ΔT_m between calculated and experimental values of T_m is obtained on the quenched PC. It reaches about 21 K, thus $\Delta T_m / T_m \sim 6.5\%$. We cannot expect greater accuracy owing to the approximations made and the versatile character of this sample. The fit obtained with the other PC is better (about 3%).

Our approach constitutes an attempt to link together the loss curve and the tensile behaviour and we think that the results obtained on three different samples of PC are promising. Let us recall that we have previously found a good correlation between the β peak and the tensile and compressive yield stresses for three different polymers including PC [2, 14, 18, 19]. DSC measurements support our assumption that the structure of the quenched PC is affected by heating during the experiment. As the heating rate is higher than in damping tests, this effect, which is detected as an exothermal tendency, occurs within a range of higher temperatures (80 to 140° C). The endothermal peak exhibited at T_g by the annealed PC agrees with the absence of a prominent intermediate peak distinguished from the α peak. The DSC curve related to the original PC is intermediate to the other two curves. The structure and the behaviour of this sample as revealed by other types of measurements is also of an intermediate nature.

7. Conclusions

The conclusions of this study are that in the investigated range of temperatures:

(1) The viscoelastic behaviour is governed by a similar expression related to an Eyring-type equation in the three different samples of PC considered.

(2) Although the nature of the molecular movements is not established, it appears from our measurements and the response of the proposed model, that this viscoelastic process gives rise to a loss peak intermediate between the β and α peaks (or almost entirely merged with the α peak).

(3) The annealed PC has a more stable structure than the original and quenched materials.

Acknowledgements

We wish to thank Professor J-P. Mercier and co-workers (Université Catholique de Louvain) for performing DSC measurements. We are also indebted to Professor G. Geuskens and co-workers (Université Libre de Bruxelles) for DSC and intrinsic viscosity measurements.

Appendix

Expression of the yield stress

By substituting in Equation 6 the value of $E\epsilon$ given in Equation 5, we obtain:

$$\sigma = AT\left(\ln 2\dot{\epsilon} + \frac{Q}{RT}\right)\int_{\ln c_m}^{\ln c_j} P_\mathrm{d}(\ln c)\,\mathrm{d}\ln c$$

$$+ AT\int_{\ln c_m}^{\ln c_j} \ln c \times P_\mathrm{d}(\ln c)\,\mathrm{d}\ln c$$

$$+ AT\left(\ln 2\dot{\epsilon} + \frac{Q}{RT}\right)\int_{\ln c_j}^{\infty} P_\mathrm{i}(\ln c)\,\mathrm{d}\ln c$$

$$+ AT\ln c_j\int_{\ln c_j}^{\infty} P_\mathrm{i}(\ln c)\,\mathrm{d}\ln c \qquad \text{(A1)}$$

or equivalently:

$$\sigma = AT\left(\ln 2\dot{\epsilon} + \frac{Q}{RT}\right)\left[\int_{\ln c_m}^{\ln c_j} P_\mathrm{d}(\ln c)\,\mathrm{d}\ln c\right.$$

$$\left. + \int_{\ln c_j}^{\infty} P_\mathrm{i}(\ln c)\,\mathrm{d}\ln c\right]$$

$$+ AT\left[\int_{\ln c_m}^{\ln c_j} \ln c \times P_\mathrm{d}(\ln c)\,\mathrm{d}\ln c\right.$$

$$\left. + \ln c_j\int_{\ln c_j}^{\infty} P_\mathrm{i}(\ln c)\,\mathrm{d}\ln c\right] \qquad \text{(A2)}$$

Taking into account that:

$$P_\mathrm{d}(\ln c)\,\mathrm{d}\ln c + \int_{\ln c_j}^{\infty} P_\mathrm{i}(\ln c)\,\mathrm{d}\ln c = 1 \qquad \text{(A3)}$$

Equation 6 may be expressed as:

$$\sigma = AT\left[\ln 2\dot{\epsilon} + \frac{Q}{RT} + f(c_m, c_j, P_\mathrm{i}(\ln c), P_\mathrm{d}(\ln c)\right] \qquad \text{(A4)}$$

Equation A4 gives the value of the yield stress σ_y when $f[c_m, c_j, P_\mathrm{c}(\ln c), P_\mathrm{d}(\ln c)]$ reaches its maximum. Let us call $\ln C$ this maximum value of f for $c_j = c_y$:

$$\ln C = f[c_m, c_y, P_\mathrm{i}(\ln c), P_\mathrm{d}(\ln c)] \qquad \text{(A5)}$$

From Equations A4 and A5, we obtain:

$$\sigma_y = AT\left(\ln 2\dot{\epsilon} + \frac{Q}{RT} + \ln C\right) \qquad \text{(A6)}$$

an expression of σ_y analogous to Equation 1.

References

1. J-C. BAUWENS, *J. Mater. Sci.* **13** (1978) 1443.
2. C. BAUWENS-CROWET, J-C. BAUWENS and G. HOMES, *J. Polymer Sci. A-2* 7 (1969) 735.

3. C. BAUWENS-CROWET, J-M. OTS and J-C. BAUWENS, *J. Mater. Sci* **9** (1974) 1197.
4. G. ALLEN, D. C. W. MORLEY and T. WILLIAMS, *ibid.* **8** (1973) 1449.
5. J. H. GOLDEN, B. L. HAMMANT and E. A. HAZELL, *J. Appl. Polymer Sci* **11** (1967) 1571.
6. K. NEKI and P. H. GEIL, *J. Macromol. Sci Phys.* **B-8** (1973) 295.
7. M. S. ALI and R. P. SHELDON, *J. Appl. Polymer Sci* **14** (1970) 2619.
8. *Idem. J. Polymer Sci part C* **38** (1972) 97.
9. R. J. MORGAN and J. E. O'NEAL, *J. Polymer Sci, Polymer Phys.* **14** (1976) 1053.
10. G. A. ADAM, A. CROSS and R. N. HAWARD, *J. Mater. Sci.* **10** (1975) 1582.
11. D. C. WATTS and E. P. PERRY, *Polymer* **19** (1978) 248.
12. J. A. SAUER, Polymer Science Symposium **32** (1971) 69.
13. R. P. KAMBOUR and R. E. ROBERTSON, "Polymer Science", Vol. 1, edited by A. D. Jenkins (North Holland, Amsterdam, London, 1972) p. 717.
14. K. H. ILLERS, *Makromol. Chem.* **127** (1969) 1.
15. T. REE and H. EYRING in "Rheology", Vol. 2, edited by F. R. Eirich (Academic Press, New York) p. 86.
16. J-C. BAUWENS, *J. Mater. Sci* **7** (1972) 577.
17. J-C. BAUWENS, C. BAUWENS-CROWET and G. HOMES, *J. Polymer Sci A-2,* **7** (1969) 1745.
18. J-C. BAUWENS, *J. Polymer Sci part C* **33** (1971) 123.
19. C. BAUWENS-CROWET, *J. Mater. Sci* **8** (1973) 968.

Received 31 July and accepted 16 November 1978.