Interpretation of the mechanical damping behaviour of glassy polycarbonate strained in the non-linear range of deformation below the yield point

J. Othmezouri-Decerf
Physique des Matériaux de Synthèse, 194/8, Université Libre de Bruxelles, 1050 Bruxelles, Belgium

(Received 6 November 1986; revised 30 July 1987; accepted 5 November 1987)

Mechanical damping measurements were made by torsion at 1 Hz on strained polycarbonate (PC) samples at ambient temperature. A marked thermal and mechanical history dependence of the damping during straining was observed. Adopting a simple rheological system to simulate the mechanical behaviour of PC, it appeared that the evolution of the damping during straining may be ascribed to a change in the viscosity. A model is proposed linking the creep strain and the damping to the same viscous process, governed by a linear time dependence of the viscosity, in agreement with a configurational evolution similar to that produced by physical ageing. Creep and tensile damping data obtained on quenched samples are used to test the validity of the model. Satisfactory agreement is obtained between the theoretical curves derived from the model and the data.

(Keywords: polycarbonate; mechanical damping; thermal history; physical ageing)

INTRODUCTION

Mechanical damping measurements on strained polycarbonate (PC) samples have been carried out by Parisot *et al.*[1,2] to investigate transient effects during differential strain-rate tensile tests and stress-relaxation tests, and by Kolman *et al.*[3] to study the behaviour of specimens submitted to incremental increases in loadings followed by periods of creep. In these works, the damping behaviour was correlated either to the density of mobile defects from a metallurgical point of view[1,2], or to the mobility of molecular chains[3]. The purpose of the present paper is to propose in a first approach a simple model ascribing the damping variation during straining to the same viscous process as that involved in transient creep. The viscosity η is expressed through an Eyring-type relation, as a function of temperature, stress and configurational entropy. The simple linear time dependence of η proposed is consistent with an improved treatment used previously by Bauwens-Crowet and Bauwens[4] to describe the enthalpy relaxation of glassy PC. Mechanical damping data derived from traction and creep experiments performed on quenched samples were used to check the validity of the model.

EXPERIMENTAL

Samples

Test pieces were machined from extruded sheets of Makrolon (Bayer), 0.2 cm thick. The samples had gauge dimensions of 4 cm × 0.8 cm × 0.2 cm. The specimen was called 'original' when no thermal pretreatment had been done.

Thermal treatments

Specimens of 'original' PC were 'quenched' from above T_g (1 h at 165°C followed by ice quenching) or 'annealed' below T_g (45 h at 120°C and cooled in the environmental chamber). Some quenched specimens were tested after ageing or stress-ageing at ambient temperature.

The quenched specimens were aged for 3 or 4 days at ambient temperature after quenching before being tested, a delay after which the damping remained constant during a lapse of time equal to the duration of the mechanical test.

Mechanical measurements

The tensile tests were performed at ambient temperature on an Instron tensile machine at imposed strain rates ranging from $2.1 \times 10^{-5}\,s^{-1}$ to $8.3 \times 10^{-4}\,s^{-1}$. Creep tests were made at ambient temperature at engineering stresses varying between 20 and 44 MPa. During recovery tests a stress of 5 MPa remained due to the weights of the lower jaw and the lever arm left after removal of the load to avoid any handling of the sample. The elongation was measured using an extensometer with 26 mm gauge length, set on the specimen.

In order to measure the mechanical damping $\tan \delta$ during straining by tensile or creep testing, a pendulum was set along the tensile axis following the set-up used by Parisot *et al.*[1]. Mechanical damping measurements were made using the free decay method at a frequency of about 1 Hz in the unstressed state. The maximum vibrational shear strain was equal to 2.3×10^{-3}.

Mechanical damping variation and tensile curve were registered simultaneously on the same specimen; two

0032-3861/88/040641-05$03.00

specimens submitted to the same engineering stress were needed to measure the elongation and $\tan\delta$ during creep, as the elongation was registered through an extensometer.

The values of $\tan\delta$ given in this paper are the measured ones, and no correction was made to account for the frequency increase (from 1 Hz to 1.25 Hz maximum) with the applied stress.

RESULTS

Tensile tests

Influence of the thermal treatment. The magnitudes and the shapes of $\tan\delta$ *versus* strain and the stress–strain curves depend on the thermal pretreatment of the sample (*Figure 1*). In *Figure 2a*, a comparison is made between a quenched sample (curves A) and a specimen aged for six months at ambient temperature after quenching (curves B). Ageing extends the linear part of the stress–strain curve, and reduces the damping value at low strain. Yield stress and mechanical damping at the yield point are unaffected by the ageing treatment. *Figure 2b* illustrates the influence of ageing under stress: when the tensile test is continued after stress-ageing (curve D), it may be noticed that the stress–strain curve first rises steeply, then merges with the curve related to the non-aged sample (curve C) at the yield point. Tan δ (curve D), which is very small after stress-ageing, rises steeply, reaching the level of the quenched sample at the yield point. It appears clearly from the examples given in *Figures 1* and *2* that the mechanical damping during deformation and the strain are affected in the same way by the thermal treatment.

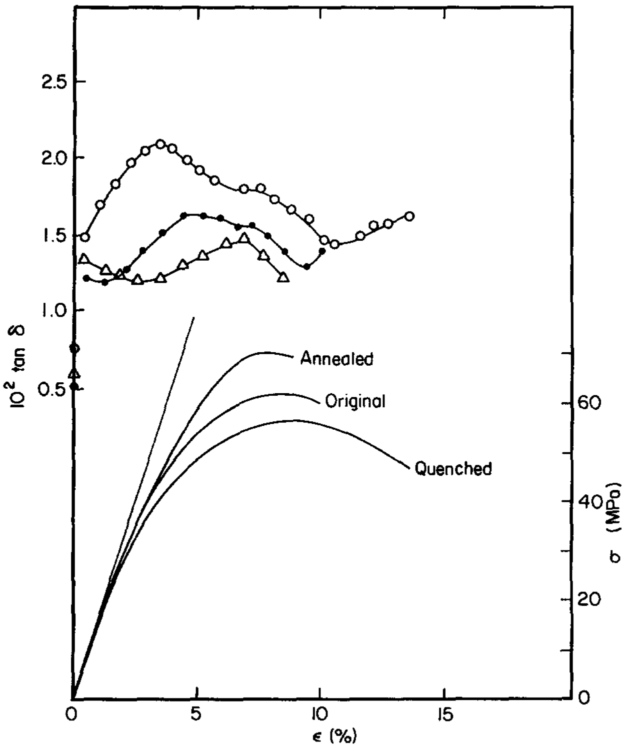

Figure 1 Stress–strain and damping–strain curves of three different samples of PC submitted to a tensile test at $T=23°C$ and $\dot{\varepsilon}=2\times10^{-4}\,s^{-1}$ (○, ● and △ refer respectively to the quenched, original and annealed PC)

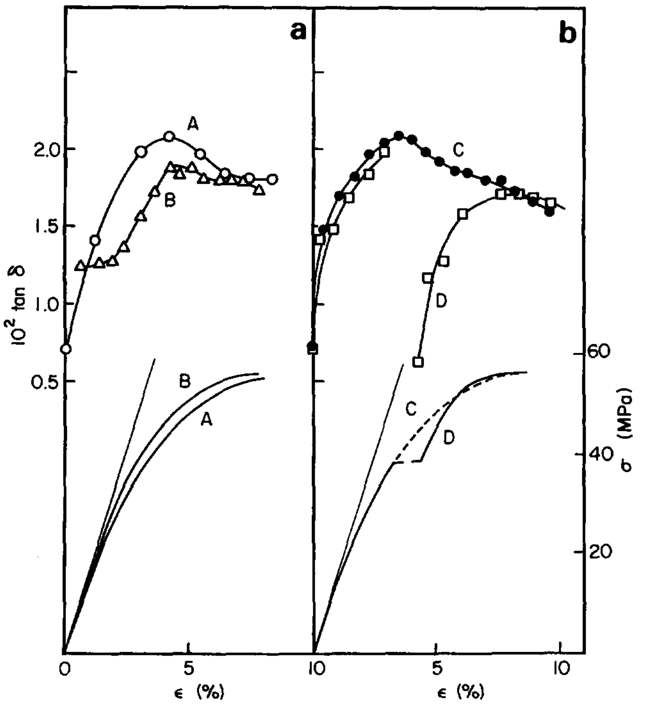

Figure 2 Influence of ageing after quenching on stress–strain and damping–strain curves of different specimens of PC submitted to a tensile test at $T=23°C$ and $\dot{\varepsilon}=2\times10^{-4}\,s^{-1}$: (a) curves A (○), quenched sample; curves B (△), sample aged 6 months at ambient temperature after quenching; (b) curves C (●), quenched sample; curves D (□), quenched sample aged 2 h under stress after predeformation

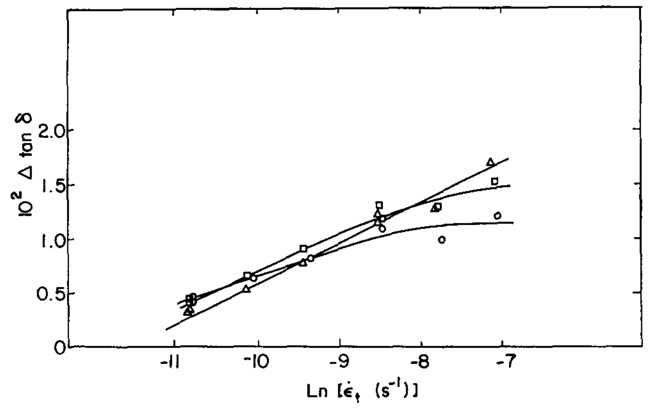

Figure 3 Variation of $\Delta\tan\delta$ as a function of the logarithm of the total strain rate $\dot{\varepsilon}_t$ (○, □ and △ refer respectively to data at 30, 40 and 50 MPa): mean curves are drawn

Influence of the strain rate. Quenched specimens were used to investigate the influence of the strain rate, because such specimens display the greatest increase of mechanical damping during deformation.

Three stress levels were chosen in the homogeneous range of deformation: 30, 40 and 50 MPa. The corresponding values of $\tan\delta$ were measured and the initial ones were subtracted. After this, $\Delta\tan\delta$ related to the three stress levels was plotted *versus* the logarithm of the total strain rate $\dot{\varepsilon}_t$ (see *Figure 3*). Tan δ increased linearly with $\log\dot{\varepsilon}_t$, before reaching a plateau at high strain rates. This behaviour was observed for the data acquired at 30 and 40 MPa.

Creep and creep-recovery tests

All creep and recovery tests were carried out on quenched samples. The measurements were made for a sufficiently long time (about 3 h) to allow $\tan\delta$ to reach a constant value. Examples of the time dependence of $\tan\delta$ and the transient creep strain ε_{tr} are given in *Figure 4*.

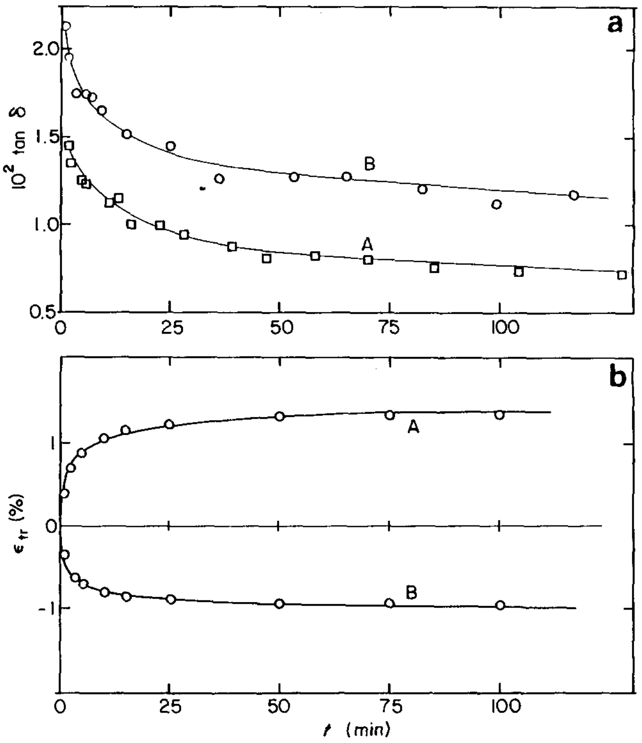

Figure 4 Example of the time dependence of (a) tan δ and (b) ε_{tr} during a creep recovery test realized at $T = 23°C$ on quenched specimens: curves A refer to creep tests with $\sigma = 40$ MPa, curves B to recovery tests. The tan δ curves drawn as full curves are calculated from relation (12) with $t_{id} = 12$ min (A) and $t_{id} = 10$ min (B). The points on the transient creep strain curves are calculated from relation (11) with $t_{ic} = 11$ min, $\tau_{ic} = 3.6$ min (A) and $t_{ic} = 7$ min, $\tau_{ic} = 2.1$ min (B)

MODEL

In a first approach, let us propose a simple model based on the following assumptions:

(1) The structural state of each sample may be defined in terms of a temperature θ at which the sample would be in equilibrium[5].

(2) The mechanical behaviour of glassy PC in the range of experimental conditions investigated in this work may be simulated by a simple rheological system (*Figure 5*) consisting of a Hookean spring connected in series with a dashpot and a non-Hookean spring in parallel. The viscosity η of the dashpot conforms to the Eyring formalism of non-Newtonian viscosity[6]. E_1 and E_2 denote respectively the modulus of the Hookean and of the non-Hookean springs. The response of the model is linear with regard to the small periodical stress superimposed on the creep stress.

The transient creep strain ε_{tr} derived from the rheological system of *Figure 5* is given as a function of time by:

$$\varepsilon_{tr} = (\sigma/E_2)[1 - \exp(-tE_2/\eta)] \qquad (1)$$

where σ is the applied stress and $\eta/E_2 = \tau_c$ denotes the relaxation time of the creep process.

In agreement with the above assumptions, the viscosity η may be expressed in the non-linear range of viscous deformation by:

$$\eta = \frac{\sigma}{\dot{\varepsilon}_0}\exp\left(\frac{Q}{RT} - \frac{\Delta S(\theta)}{R}\right) \times \frac{1}{\sinh(\sigma/AT)} \qquad (2)$$

where Q is an activation energy, R is the universal gas constant, T is the temperature, A is a constant, $\Delta S(\theta)$ is the change in configurational entropy and $\dot{\varepsilon}_0$ is a frequency factor containing the entropy factor related to the initial structural state.

Damping measurements performed at a frequency ν of 1 Hz and at ambient temperature lie in the high-frequency tail of the α transition where $\omega^2\eta^2 \gg G_2(G_1 + G_2)$ (here $\omega = 2\pi\nu$ and G_1 and G_2 denote the shear moduli). In this range of experimental conditions, the mechanical damping tan δ may be expressed by:

$$\tan\delta = G_1/\omega\eta \qquad (3)$$

and $\eta/G_1 = \tau_d$ represents the characteristic relaxation time of the mechanical damping.

Following relation (3), the decrease of tan δ observed during creep must result from a progressive increase of the viscosity with time, which we attribute to a change of the structural state occurring during transient creep. As a strain-hardening effect has been observed[7,8] when a glassy polymer is submitted to low stresses, let us assume that the structural change occurring during creep is similar to that produced by physical ageing. To derive the influence of time on the viscosity η, let us express the change in configurational entropy $\Delta S(\theta)$ by the following relationship used successfully to describe the enthalpy relaxation of rejuvenated samples[9]:

$$\Delta S(\theta) = C(\theta - \theta_i) \qquad (4)$$

where C is a constant, θ the actual and θ_i the initial structural temperatures, and $\theta - \theta_i$ denotes the structural change occurring during creep.

The variation of θ with time and temperature may be expressed by:

$$d\theta = -(\theta - T)J\,dt \qquad (5)$$

where J, the frequency of configurational changes, can be written as:

$$J = J_0 \exp\left(\frac{\Delta S(\theta)}{R} - \frac{Q}{RT}\right) \qquad (6)$$

where J_0 is a rate constant.

It may be presumed that only small changes of the structural state will occur during transient creep, so that $\theta - T \simeq \theta_i - T$. Then integration of (5) taking account of (4) and (6) gives:

$$\exp\left(-\frac{C(\theta - \theta_i)}{R}\right) = \frac{t}{t_i} + 1 \qquad (7)$$

with

$$t_i = \frac{R}{C(\theta_i - T)J_0}\exp\left(\frac{Q}{RT}\right) \qquad (8)$$

Relations (2), (7) and (8) yield:

$$\eta = \eta_i\left(\frac{t}{t_i} + 1\right) \qquad (9)$$

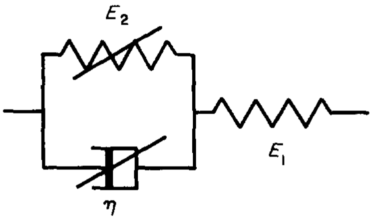

Figure 5 Model to describe transient creep strain and mechanical damping. η denotes an Eyring dashpot

with

$$\eta_i = \frac{\sigma}{\dot{\varepsilon}_0}\exp\left(\frac{Q}{RT}\right)\frac{1}{\sinh(\sigma/AT)} \qquad (10)$$

At a given temperature, η_i is a decreasing function of σ for $\sigma > AT$ and is a constant for $\sigma \ll AT$.

At large times compared with t_i, equation (9) yields:

$$\mathrm{d}\ln\eta/\mathrm{d}\ln t = 1$$

The kinetics of viscosity change are consistent with the value of the shift factor (1.18) deduced by Struik for the ageing behaviour of PC submitted to short-time creep tests[10].

TESTING OF THE MODEL AND DISCUSSION

Creep tests

Transient creep strain. Taking account of relations (1) and (9), the transient creep strain is given by:

$$\varepsilon_{tr} = \varepsilon_{tr}^{\infty}\left[1 - \exp\left(-\frac{tt_{ic}}{\tau_{ic}(t + t_{ic})}\right)\right] \qquad (11)$$

where $\varepsilon_{tr}^{\infty} = \sigma/E_2$ and the subscript c denotes the parameters used to describe the transient creep deformation recorded through creep and recovery experiments. The derived values of t_{ic} and τ_{ic} are given in *Figure 6 versus* the applied stress σ together with the measured values of $\varepsilon_{tr}^{\infty}$. No systematic dependence of t_{ic} and τ_{ic} on σ may be deduced. This behaviour is predicted for t_i by relation (8) as long as no structural change is induced by the stress. The independence of τ_{ic} on σ may be explained by taking account of the expression given for τ_{ic}, namely:

$$\tau_{ic} = \eta_i/E_2 = \varepsilon_{tr}^{\infty}/\dot{\varepsilon}_i$$

As both $\varepsilon_{tr}^{\infty}$ (*Figure 6*) and $\dot{\varepsilon}_i = \sigma/\eta_i$ (relation (10)) are increasing functions of σ, the observed independence of τ_{ic} on the stress is consistent.

Theoretical values derived from relation (11) are given as points in *Figure 4b*. The agreement with the experimental (full) curves is quite satisfactory.

Mechanical damping. Assuming that the level of tan δ under zero stress is close to the background level, Δ tan δ may be expressed following (3) and (9) by:

$$\Delta\tan\delta = \frac{(\Delta\tan\delta_i)t_{id}}{t + t_{id}} \qquad (12)$$

where $\Delta\tan\delta_i = 1/\omega\tau_{id}$ denotes the maximum value of Δ tan δ under stress; the subscript d is used to characterize the parameters related to damping. The values of t_{id} deduced from the fit of relation (12) to the damping data are plotted *versus* σ in *Figure 7*, together with the measured values of Δ tan δ_i. The constancy of t_{id} confirms the validity of relation (8) with θ_i constant; moreover, the mean values of t_{id} and t_{ic} are close together (see *Table 1*), supporting the above hypothesis linking the creep strain and the damping to the same time-dependent viscous process. Theoretical curves derived from relation (12) with appropriate parameters listed in the figure caption are drawn as full curves in *Figure 4a*. A good fit is obtained.

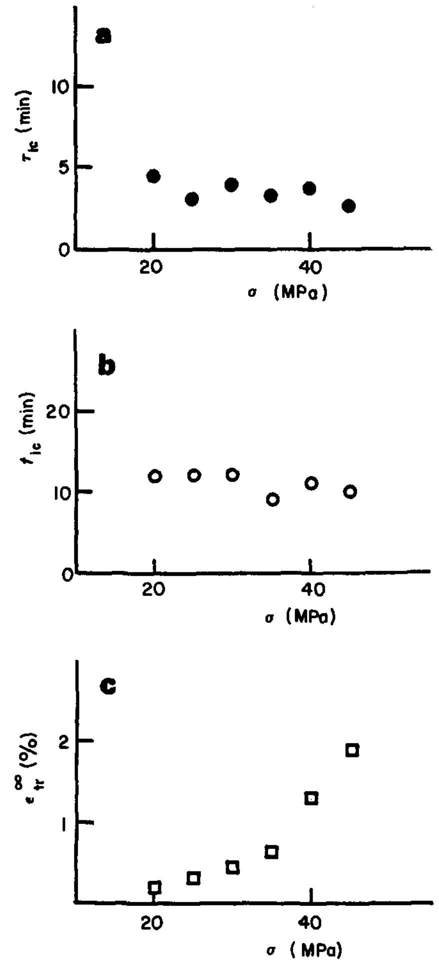

Figure 6 (a) τ_{ic} and (b) t_{ic}, evaluated from the fit of relation (11) to the creep data, *versus* the applied stress. (c) Variation of the measured values of $\varepsilon_{tr}^{\infty}$ with the applied stress

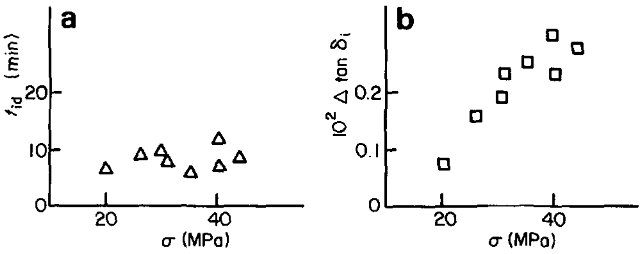

Figure 7 (a) t_{id} evaluated from the fit of relation (12) to the mechanical damping data recorded during creep, *versus* the applied stress. (b) Variation of the measured values of Δ tan δ_i with the applied stress

Tensile tests

Influence of the thermal treatment. Owing to the limited number of experiments and the diversity of applied treatments, only a qualitative interpretation of the influence of the thermal treatment can be given.

The differences observed at ambient temperature in the initial damping levels of tan δ under zero stress in *Figures 1* and *2* reflect to a much lesser extent than at higher temperatures[11] the influence of the thermal pretreatment. The decrease of tan δ after annealing or ageing is consistent with an increase of the relaxation time as may be deduced from relation (3) with $\eta = \tau_d/G_1$. This interpretation is in agreement with the measured shift of the spectrum of relaxation times during ageing to longer times reported in the literature[12].

The influence of the initial structural state on the damping during straining occurs through the frequency

Table 1 Mean constants t_i deduced from the fit of relations (11) and (12) to the variation of ε_{tr} or $\Delta \tan \delta$ with time, by creep or recovery experiments

		t_i (min)
Mechanical damping	Creep	8.5
	Recovery	10.0
Transient creep strain	Creep	11.0
	Recovery	7.5

factor $\dot{\varepsilon}_0$ (see relation (2)); at high stresses the effect of ageing at room temperature (*Figure 2*) becomes progressively erased, when it may be emphasized that the structural state is destroyed by plastic deformation.

Stress-ageing at room temperature (*Figure 2*) allows the sample to reach a relaxation time close to the value of τ_d under zero stress, accounting for the parallelism of the initial part of the $\tan \delta$ curves before and after stress ageing.

Influence of the strain rate. At low strain rates, the amplitude of $\Delta \tan \delta$ results from competition between the increase of damping with rising stress and its concomitant decrease with time. At higher strain rates, the relaxation process does not have enough time to proceed and the damping keeps a constant value. To evaluate the damping level at low strain rates, let us consider in a first approximation that $\Delta \tan \delta$ recorded at a given stress σ during continuous tensile loading is equal to $\Delta \tan \delta$ measured during a creep test, performed under the same constant stress after a lapse of time equal to the time needed to reach σ on the tensile curve.

$\Delta \tan \delta$ was evaluated at three stress levels using relation (12), where the parameter t_{id} is the mean value (8.5 min) derived from *Figure 7* and the time t was measured on each tensile curve. The values of $\Delta \tan \delta_i$ are the measured ones at 30 and 40 MPa; a linear extrapolation was made to evaluate $\Delta \tan \delta_i$ at 50 MPa.

The theoretical curves, giving $\Delta \tan \delta$ *versus* the logarithm of time are plotted as full curves in *Figure 8* for the three stress levels; the tensile data of *Figure 3* are reported in the same figure. Good agreement is obtained, giving support to the validity of the model.

CONCLUSIONS

The proposed model is able to describe the transient creep strain and the mechanical damping variation during creep. It is based on the following assumptions:

(a) creep strain and mechanical damping are controlled by the same viscous process; and

(b) the increase of viscosity during creep may be ascribed to a structural change similar to that produced by physical ageing.

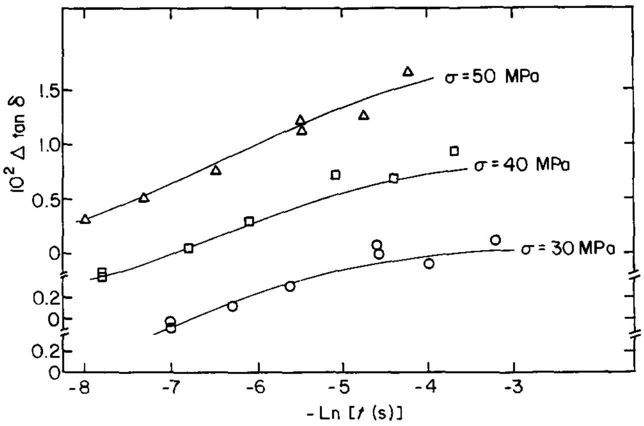

Figure 8 Values of $\Delta \tan \delta$ *versus* $\ln t$, at $T = 23°C$. The curves are calculated from equation (12) where the time constant is taken equal to the mean value deduced from creep relaxation of $\tan \delta$ (*Table 1*); the measured values of $\Delta \tan \delta$ taken at three stress levels from tensile results are plotted *versus* the logarithm of the time (○, □ and △ refer respectively to 30, 40 and 50 MPa)

This latter hypothesis leads to a linear time dependence of the viscosity, well fitted by creep and damping data.

The model allows us, moreover, to describe accurately the influence of the strain rate on the damping data recorded during tensile tests, using the time parameter deduced from creep experiments.

ACKNOWLEDGEMENTS

Grateful acknowledgement is given to Professor J. C. Bauwens, Université Libre de Bruxelles, for helpful discussions, comments and suggestions during the course of this work.

REFERENCES

1 Parisot, J., Astier, J., Fernandez, A. and Rafi, O. *J. Physique* 1981, **42**, C5, 569
2 Parisot, J., Rafi, O. and Choi, W. J. *J. Physique* 1983, **44**, C9, 177
3 Kolman, H. J., Ard, K. and Beatty, C. L. *Polym. Eng. Sci.* 1982, **22**, 950
4 Bauwens-Crowet, C. and Bauwens, J. C. *Polymer* 1986, **27**, 709
5 Bauwens-Crowet, C. and Bauwens, J. C. *Polymer* 1982, **23**, 1599
6 Eyring, J. *J. Chem. Phys.* 1936, **4**, 283
7 Sternstein, S. S. and Ho, T. C. *J. Appl. Phys.* 1972, **43**, 4370
8 Struik, L. C. E. *Polymer* 1980, **21**, 962
9 Bauwens-Crowet, C. and Bauwens, J. C. *Polymer* 1987, **28**, 1863
10 Struik, L. C. E. 'Physical Ageing in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978, p. 20
11 Bauwens-Crowet, C. and Bauwens, J. C. *J. Mater. Sci.* 1979, **14**, 1817
12 Struik, L. C. E., in ref. 10, p. 13