JOURNAL OF MATERIALS SCIENCE 7 (1972) 577–584

Relation between the Compression Yield Stress and the Mechanical Loss Peak of Bisphenol-A-Polycarbonate in the β Transition Range

J. C. BAUWENS
Institut des Matériaux, Université Libre de Bruxelles, Belgium

The compression yield behaviour of polycarbonate, at constant strain-rate, over a wide range of temperatures, is described by the Ree-Eyring theory of non-Newtonian viscosity linked with a treatment which takes into account a distribution function of activation energies.

The proposed yield mechanism relies on the assumption that the β process considered in the Ree-Eyring theory and the loss peak revealed by oscillatory measurements are related to the same molecular movements.

A relation is given between the β transition conditions in yield measurements and in damping tests; its validity is checked.

The broadness and the shape of the β loss peak are correlated with a spectrum of activation energies.

The compression yield-stress curve, giving the yield stress versus temperature at constant strain-rate, is computed from the measurements of the loss tangent, as a function of temperature, at the frequency corresponding to the strain-rate and is found to fit the data fairly well.

1. Introduction

Polycarbonate possesses a low temperature secondary transition which has been revealed by miscellaneous techniques such as nuclear magnetic resonance, dielectric and mechanical losses, shear creep and stress relaxation. The experimental results obtained by different methods are reviewed in the paper by Locati and Tobolsky [1].

It is the purpose of the present paper to show that the study of the yield stress of polycarbonate over a wide range of temperatures and strain-rates, is also of use in revealing the secondary transition.

In our laboratory, it was previously proposed [2] to describe the yield behaviour of glassy polymers by the Ree-Eyring modification of the Newtonian viscosity theory [3]. It is assumed that two rate-processes, denoted α and β are involved in the deformation at yield. These two processes are characterised by a different activation energy. The value of the activation energy related to the β process, found by this method, for at least five glassy polymers, agrees quite well with the value associated with the secondary transition reported from other types of measurements [4-6]. This fact suggests that the molecular movements are the same in both cases.

We intend here to show the correlation between the shape of the mechanical loss peak observed in damping tests, at low temperatures for polycarbonate, and the compression yield stress curve giving the value of the yield stress as a function of temperature at constant strain-rate. We have previously proposed such a correlation for PVC [7]. We want now to give a more accurate theoretical treatment and to check the validity of the resulting relations using the β transition conditions of polycarbonate.

In this investigation an attempt has been made to link together the Ree-Eyring theory which is useful to describe the compression yield behaviour at constant strain-rate over a wide range of temperatures, and the influence of a distribution

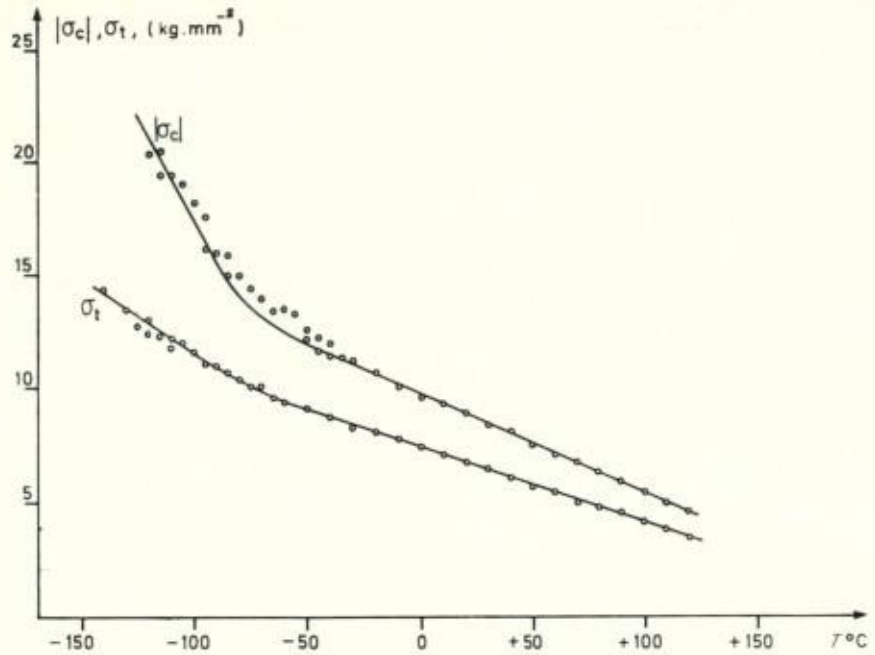

Figure 1 Plot of the engineering yield stress in uniaxial compression $|\sigma_c|$ and in tensile tests σ_t versus temperature at a constant strain-rate $\dot{\epsilon} = 4.16 \times 10^{-3}$ sec^{-1}. The curves are generated from equations 1 and 2 using the constants given in table I.

of activation energies which allows one to obtain a more accurate correlation in the β transition region.

2. Experimental

The tensile and uniaxial compression data are taken from previous results obtained in our laboratory [6]. The engineering yield stresses, taken as the first maximum of the stress-strain curve divided by the initial cross-section of the specimen, are plotted versus temperature in fig. 1. All the tests were performed at the same strain-rate: $\dot{\epsilon} = 4.16 \times 10^{-3}$ sec^{-1}.

At this strain-rate, we knew that the β transition of polycarbonate is located at about $-80°$C [6]. On the other hand, the loss tangent peak, measured at 1 cps reaches its maximum value at about $-100°$C [1]. We decided then to perform damping tests around 1 cps in order to reveal the β transition in the same temperature range as in tensile and compression tests.

The damping tests were performed using a free-oscillation torsional pendulum operating with samples having dimensions of 11 × 1.5 × 0.2 cm^3.

The samples were cut from the same plate of polycarbonate (Makrolon, Bayer) as the tensile and compression specimens.

The pendulum was set at room temperature at two different frequencies around 1 cps; 0.455 and 2.08 cps. Then, in both cases, the apparatus was placed in an environmental chamber and the loss tangent was measured as a function of temperature from -160 to $-20°$C.

The data are reported in fig. 2 where it is seen that in both cases the shape of the peak and the maximum value of the loss tangent are nearly the same.

3. Theoretical Considerations

The curves of fig. 1 are taken from a previous paper [6]. They were generated using the following equations:

$$\frac{\sigma_t}{T} = \frac{\sigma_{t\alpha}}{T} + \frac{\sigma_{t\beta}}{T} = A_{t\alpha}\left(\ln 2C_\alpha \dot{\epsilon} + \frac{Q_\alpha}{RT}\right) + A_{t\beta} \sinh^{-1}\left(C_\beta \dot{\epsilon} \exp \frac{Q_\beta}{RT}\right) \quad (1)$$

$$\frac{\sigma_c}{T} = \frac{\sigma_{c\alpha}}{T} + \frac{\sigma_{c\beta}}{T} = A_{c\alpha}\left(\ln 2C_\alpha \dot{\epsilon} + \frac{Q_\alpha}{RT}\right) + A_{c\beta} \sinh^{-1}\left(C_\beta \dot{\epsilon} \exp \frac{Q_\beta}{RT}\right) \quad (2)$$

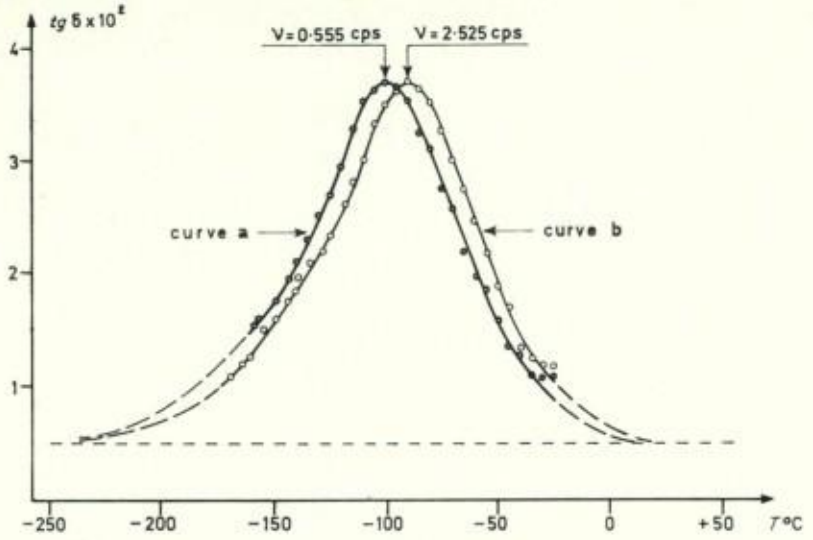

Figure 2 Loss tangent of polycarbonate versus temperature in the β transition range. The frequency varied from 0.63 cps at the lowest temperatures to 0.48 cps at the highest (curve a) and from 3 cps to 2.2 cps (curve b).

where σ_t and σ_c are the measured tensile and compression yield stresses; σ_{t_α}, σ_{c_α} and σ_{t_β}, σ_{c_β} are the α and β contributions to the tensile and to the compression yield stresses; A_{t_α}, A_{c_α}, C_α and A_{t_β}, A_{c_β}, C_β are constants and Q_α and Q_β are the activation energies respectively related to the α and the β processes; T denotes absolute temperature and R is the universal gas constant.

The values of the parameters were estimated from the best fit of equations 1 and 2 to the data previously obtained [5, 6]; they are recalled in table I.

TABLE I Constants of equations 1 and 2 for polycarbonate [5, 6]

α process	β process
$Q_\alpha = 75.5$ kcal mole^{-1}	$Q_\beta = 9.6$ kcal mole^{-1}
$C_\alpha = 2.40 \times 10^{-31}$ sec	$C_\beta = 2.76 \times 10^{-9}$ sec
$A_{t_\alpha} = 4.35 \times 10^{-4}$ kg mm^{-2} . K^{-1}	$A_{t_\beta} = 1.33 \times 10^{-3}$ kg mm^{-2} . K^{-1}
$A_{c_\alpha} = 5.70 \times 10^{-4}$ kg mm^{-2} . K^{-1}	$A_{c_\beta} = 5.57 \times 10^{-3}$ kg mm^{-2} . K^{-1}

Equations 1 and 2 were derived from the Ree-Eyring theory [3] and from a yield criterion previously established [8, 9]. The derivation relies on the following assumptions; 1. both processes move at yield at the same average rate, the stresses being additive, 2. the yield criterion is applied separately to each process.

The curves, expressed by equations 1 and 2, representing the variation of the tensile and compression yield stresses with temperature at constant strain-rate (see fig. 1), admit two asymptotes which intersect at two points having the same abscissa denoted as T_β in the following relation:

$$T_\beta = -\frac{Q_\beta}{R \ln 2C_\beta \dot{\epsilon}} \tag{3}$$

From equations 2 and 3, for tests performed at the same strain-rate, we can write, for a first approximation, that:

$$\frac{\partial \sigma_{c_\beta}}{\partial T} = A_{c_\beta} \ln 2C_\beta \dot{\epsilon} = K = \text{constant} \qquad \text{for } T < T_\beta \tag{4}$$

and

$$\frac{\partial \sigma_{c_\beta}}{\partial T} = 0 \qquad \text{for } T > T_\beta \tag{5}$$

Therefore, pairs of values of temperature and strain-rate which satisfy equation 3, represent the β transition conditions revealed by tensile or compression yield stress measurements when a single activation energy Q_β is considered.

For the constant strain-rate chosen here and the values of the constants of equation 3 given in table I, T_β was found to equal $-77°$C.

Let us assume, now, that the molecular movement related to the β process considered in

the Ree-Eyring theory is the same as the one associated with the β mechanical loss peak. The activation energies found in both types of measurements have similar values (see equation 24 and table I).

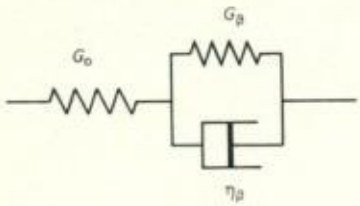

Figure 3 Simple three-element model used to describe, for a first approximation, the mechanical behaviour of polycarbonate in the β transition range.

The response of a high polymer to free oscillation torsional tests, may be calculated, for a first approximation, using the simple three-element model of fig. 3; where G_0 means a spring of high modulus representing the elasticity when both α and β processes are frozen in, $(G_0\, G_\beta)/(G_0 + G_\beta)$ equals the shear modulus when β is completely free and α is completely frozen in, and η_β denotes the Newtonian viscosity of the β process. We may assume that $G_\beta \gg G_0$ because the loss tangent is very small compared to unity. Let $tg\ \delta$ denote the loss tangent, its expression is:

$$tg\ \delta = \frac{G_0\, \omega\, \omega_\beta}{G_\beta\, (\omega^2 + \omega_\beta^2)} \tag{6}$$

where ω and ω_β are the radian frequency and the characteristic radian frequency respectively, with:

$$\omega_\beta = \frac{G_\beta}{\eta_\beta} \tag{7}$$

The quantity η_β may be expressed as a function of temperature using Eyring's equation which gives Newtonian viscosity when the stress is small:

$$\eta_\beta = \frac{A_\beta\, C_\beta\, T}{\sqrt{3}}\ \exp\left(\frac{Q_\beta}{RT}\right) \tag{8}$$

where A_β is a constant.

Let us consider the value of the characteristic radian frequency related to free oscillation torsional tests conducted at the temperature T_β defined by equation 3. From equations 3, 6, 7 and 8, we obtain the relation between the frequency and the strain-rate at which the transition of a β element having an activation energy equal to Q_β, occurs at temperature T_β:

$$\omega_\beta = \frac{2\sqrt{3}\, G_\beta}{A_\beta\, T_\beta}\, \dot{\epsilon} \tag{9}$$

In order to improve the approximation, we will consider, now, a distribution of activation energies $P(Q)$ expressed by:

$$\int_0^\infty P(Q)\, \mathrm{d}Q = 1 \tag{10}$$

and whose half-width value is denoted as $\Delta\, Q$.

If one takes into account such a distribution, equation 4 becomes:

$$\frac{\partial\, \sigma_{c\beta}}{\partial\, T} = K \int_{Q_T}^\infty P(Q)\, \mathrm{d}Q \tag{11}$$

where Q_T denotes the activation energy of an element whose β transition occurs at temperature T.

The problem arises how the $P(Q)$ function is to be calculated from experimental data. We propose to obtain the shape of this function from the measure of the loss tangent versus temperature in the β transition range. Using the concept of a distribution of activation energies, the extension of the derivation which led to equation 6, gives:

$$tg\ \delta = \frac{G_0}{G_\beta} \int_0^\infty P(Q)\, \frac{\omega\, \omega_\beta}{\omega^2 + \omega_\beta^2}\, \mathrm{d}Q \tag{12}$$

Equations 7 and 8 imply that:

$$\mathrm{d}Q = -\, RT\, \mathrm{d}\,(\ln \omega_\beta) \tag{13}$$

and then, an approximation of first order of the loss tangent may be expressed by:

$$tg\ \delta = \frac{\pi\, G_0\, R\, T\, P(Q)}{2\, G_\beta} \tag{14}$$

It results from equation 14 that $(tg\ \delta)/T$ is proportional to the distribution function of the activation energies. Furthermore, equation 9 implies that:

$$\nu\, T = \nu_{max}\, T_{max} = \text{constant} \tag{15}$$

where ν denotes the frequency of the oscillations and ν_{max} and T_{max} correspond to the maximum value of the $(tg\ \delta\ (T))/T$ curve.

Therefore, using the approximation that the maximum of $P(Q)$ may be expressed by:

$$P(Q) = \frac{1}{\Delta\, Q} \tag{16}$$

it follows from equations 9 and 14 that:

$$\nu_{max} = \frac{\sqrt{3}\, G_0\, R}{2A_\beta\, (tg\ \delta)_{max}\, \Delta Q}\, \dot{\epsilon} \qquad (17)$$

where $(tg\ \delta)_{max}$ is related to the maximum value of the $(tg\ \delta\ (T))/T$ curve.

Equations 15 and 17 give as a function of $\dot{\epsilon}$, the frequency at which the β transition occurs at the same temperature in tensile, compression and damping tests for elements having the same activation energy.

Equations 7, 8 and 15 imply that:

$$\frac{Q_T}{RT} = \text{constant} \qquad (18)$$

which means that the β transition of an element having an activation energy equal to Q_T, occurs at a temperature T proportional to Q_T. Then from equation 18, it is possible to express the quantity ΔQ as a function of ΔT, the half-width value of the $(tg\ \delta\ (T))/T$ curve, by:

$$\Delta Q = \frac{\Delta T}{T_{max}}\, Q_{max} \qquad (19)$$

where T_{max} and Q_{max} are the temperature and the activation energy corresponding to the maximum of the $(tg\ \delta\ (T))/T$ curve.

So, provided equations 15 and 17 are satisfied, where all the parameters can be computed from the data here reported (except G_0 which is taken from the literature), we can express $P\,(Q)$ as a function of $tg\ \delta\,(T)$. It then follows from equations 11 and 14 that:

$$\frac{\partial\, \sigma_{c\beta}}{\partial\, T} = K \frac{\int_T^\infty \frac{tg\ \delta\,(T)}{T}\, dT}{\int_0^\infty \frac{tg\ \delta\,(T)}{T}\, dT} \qquad (20)$$

Equation 20 allows to state that the double integral

$$\int_T^\infty \int_T^\infty \frac{tg\ \delta\,(T)}{T}\, dT^2$$

which can be computed from the β peak is proportional to the β contribution to the tensile or compression yield stress. This consequence of the proposed mechanism of yield deformation may be expressed from equations 1, 2 and 20, by writing:

$$\sigma_t\,(T) = \sigma_{t_\alpha}\,(T) + B_t \int_T^\infty \int_T^\infty \frac{tg\ \delta\,(T)}{T}\, dT^2 \qquad (21)$$

and

$$\sigma_c\,(T) = \sigma_{c_\alpha}\,(T) + B_c \int_T^\infty \int_T^\infty \frac{tg\ \delta\,(T)}{T}\, dT^2 \qquad (21a)$$

where B_t and B_c are constants.

We will try to check the validity of these last relations.

4. Results

4.1. Evaluation of A_β

From equations 1 and 2 and from Eyring's equation applied to the β contribution to the shear yield stress τ_β, we obtain the following relation:

$$\frac{\sigma_{t\beta}}{A_{t\beta}} = \frac{\sigma_{c\beta}}{A_{c\beta}} = \frac{\tau_\beta}{A_\beta} \qquad (22)$$

On the other hand, the yield criterion applied to the β process gives another relation between $\sigma_{t\beta}$, $\sigma_{c\beta}$ and τ_β, i.e.:

$$\tau_{0\beta} + \mu_\beta p_\beta = \frac{\sigma_{t\beta}}{3}\,(\sqrt{2} + \mu_\beta) = \frac{\sigma_{c\beta}}{3}\,(\sqrt{2} - \mu_\beta) = \tau_\beta \sqrt{\frac{2}{3}} \qquad (22a)$$

where $\tau_{0\beta}$ and p_β denote the β contribution to the octahedral shear yield stress and to the hydrostatic stress respectively and μ_β is a constant.

Then, from equations 22 and 22a, using the values of $A_{t\beta}$ and $A_{c\beta}$ given in table I, we find the following value for A_β:

$$A_\beta = \frac{A_{c\beta}}{\sqrt{3}\left(1 + \frac{A_{c\beta}}{A_{t\beta}}\right)} = 1.24 \times 10^{-3}\ \text{kg mm}^{-2}\ \text{K}^{-1} \qquad (23)$$

As $A_{c\beta}$ and $A_{t\beta}$ are evaluated from the engineering yield stresses, there results an error in the constant A_β which arises from failure to take elastic deformation prior to yielding into account. This error was evaluated using the treatment given previously [6] and was found to reach less than 4%; therefore it may be neglected here according to the approximations done.

4.2. Evaluation of Q_{max}

Q_{max} is evaluated from the data of fig. 2 and the Arrhenius relation. The following value is found

$$Q_{max} = 9.6\ \text{kcal mol}^{-1} \qquad (24)$$

4.3. Evaluation of ν_{max}

The quantity ν_{max} is calculated from equation 17

using the following values of the constants:

$$G_0 = 230 \text{ kg mm}^{-2} \quad (25)$$

This value is taken from the literature [1]; as G_0 means the maximum value reached by the shear modulus at low temperature, it is expected to be independent of material differences and of frequency.

$(tg\ \delta)_{max}$ is assumed to be nearly equal to the maximum of the loss tangent. This last quantity does not change significantly with the frequency within a narrow range. After subtraction of the background, whose level is estimated on the graph to reach 5×10^{-3}, the following value is taken, for a first approximation:

$$(tg\ \delta)_{max} = 3.2 \times 10^{-2} \quad (26)$$

ΔQ is given by equation 19, where ΔT is obtained by iteration from the data. As a first approximation, we have assumed that $T_{max} \approx T_\beta = -77°C = 196K$, and we have taken for ΔT the half-width value of the loss tangent peak measured as a function of temperature at about 1 cps. When the background is subtracted from the β loss peak, we have found from the data of fig. 2, that

$$\Delta T = 80°C \quad (27)$$

Then from equations 17, 19, 23, 24, 25, 26, 27 and $\dot{\epsilon} = 4.16 \times 10^{-3} \text{ sec}^{-1}$, a first approximation is calculated for ν_{max}:

$$\nu_{max} = 10.7 \text{ cps} \quad (28)$$

In order to obtain a better approximation, the $(tg\ \delta\ (T))/T$ curve related to the value, equation 28, of ν_{max}, is then generated from the data of fig. 2 using the Arrhenius relation. From this curve we got the following values of the constants:

$$\Delta T = 90°C \quad (29)$$

$$T_{max} = -80°C = 193K \quad (30)$$

$$(tg\ \delta)_{max} = 3.1 \times 10^{-2} \quad (31)$$

Putting these last values in equation 17, we found:

$$\nu_{max} = 9.5 \text{ cps} \quad (30)$$

4.4. Determination of the $(tg\ \delta(T))/T$ Curve related to $\nu_{max} = 9.5$ cps

The β loss peak related to $\nu_{max} = 9.5$ cps may be generated from the data of fig. 2. The resulting curve, from which the background has been subtracted, is then corrected in order to take into account equation 15. In fig. 4 we give the plot of $(tg\ \delta\ (T))/T$ deduced from the extrapolated β peak. It is seen on the graph that the half-width value of the curve, the temperature and the value of the loss tangent related to the maximum of the curve quite agree with equations 29, 30 and 31 respectively. Moreover the value of T_{max} is nearly equal to the value of T_β determined from equation 3, which was deduced from the compression and tensile yield stress curves.

In fig. 4 we have also plotted the double

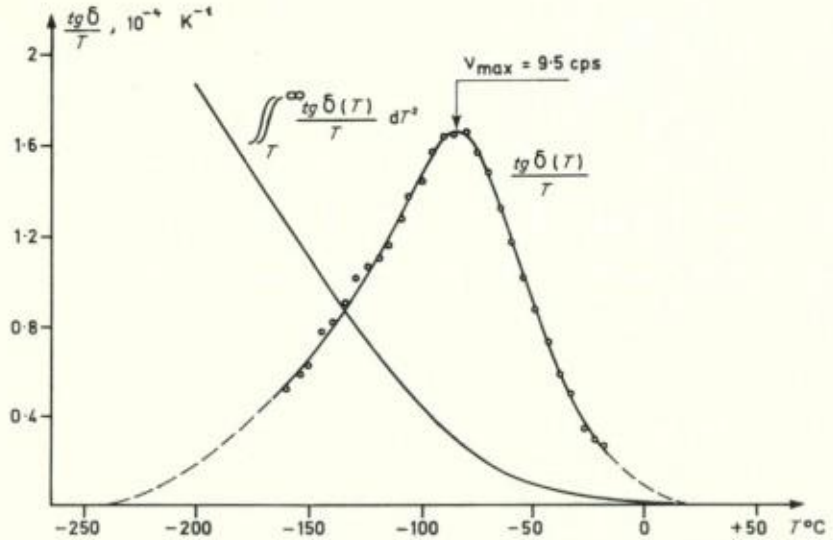

Figure 4 β contribution to the $(tg\ \delta\ (T))/T$ curve and double integral of $(tg\ \delta\ (T))/T$ from T to ∞.

integral of $(tg\ \delta\ (T))/T$ integrated from T to ∞.

4.5. Correlation between the Compression Yield Stress Curve and the Curve giving $(tg\ \delta(T))/T$

The determination of the curve expressed by equation 21 was done as follows

1. The curve giving σ_{c_α} as a function of temperature at constant strain-rate is assumed to be a straight line and is extrapolated from the compression data obtained at temperatures between $-$ 50 and $+$ 120°C where equation 5 is valid.
2. The value of the constant is chosen to obtain the best fit of the computed curve to the data.

Results are given in fig. 5 where it is seen that the accuracy of the fit is quite good and better than in fig. 1.

Obviously, the same treatment may be followed to generate, from the β peak, the curve giving the tensile yield stress as a function of temperature at constant strain-rate, but the theoretical curve so calculated, and the one computed from equation 1 are very close together. Both curves fit the data fairly well. Therefore, in the case of tensile tests, the treatment proposed here, although it does not give a more accurate fit than the Ree-Eyring theory, is more interesting because it provides a distribution of the activation energies in the β transition range.

5. Conclusions

A yield mechanism, relying on the following assumptions, is proposed for polycarbonate.

1. Two activated flow processes, α and β, moving at the same rate, are involved in the deformation at yield.
2. The β yield process and the β peak revealed by oscillatory measurements, arise from the same molecular movements.

This hypothetical yield mechanism implies the following consequences.

(*a*) The study of the yield stress over a wide range of temperatures and strain-rates must reveal the β transition.

(*b*) The activation energies respectively associated with the β yield process and the β loss peak must be equal.

(*c*) If the β transition, revealed by yield measurements, is located at temperature T_β and strain-rate $\dot{\epsilon}$, there must exist a relation between $\dot{\epsilon}$ and the frequency at which the β loss peak occurs at temperature T_β.

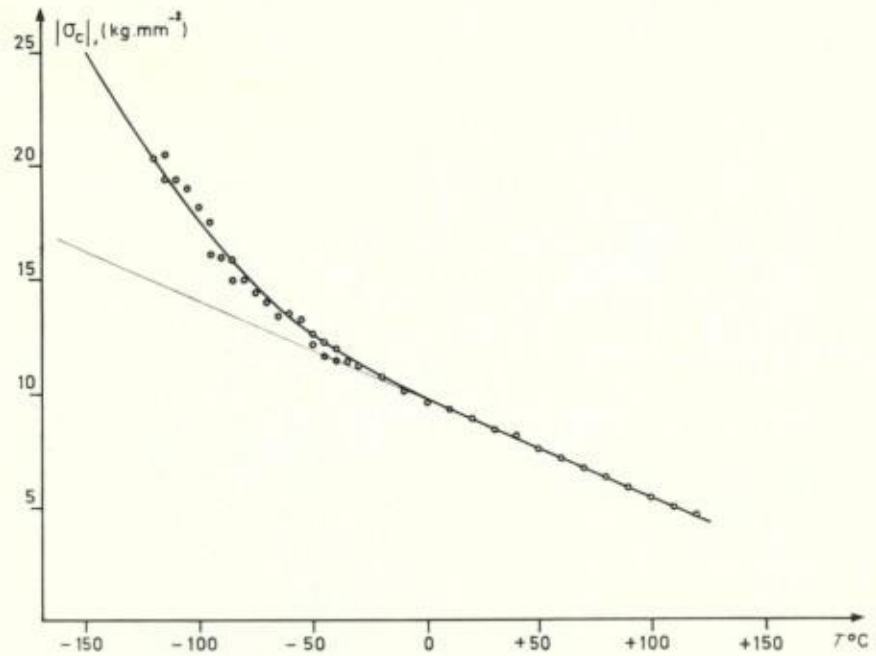

Figure 5 Plot of the compression yield stress versus temperature at constant strain-rate. The data are the same as in fig. 1, but the curve is generated from equation 21.

(*d*) The broadness and the shape of the β loss peak may be associated with a distribution function of the β activation energies.
(*e*) The β contribution to the yield stress curve, giving the yield stress versus temperature at constant strain-rate, may be computed from the β peak measured as a function of temperature at the corresponding frequency.

All these consequences are checked here; the quite good accuracy of the fit confirms that the proposed treatment linked with the Ree-Eyring theory, is able to describe the yield behaviour of polycarbonate over a wide range of experimental conditions, in tensile and in uniaxial compression tests.

Acknowledgements

We wish to thank Professor G. Homès, Directeur de l'Institut des Matériaux de l'Université libre de Bruxelles and C. Bauwens-Crowet, chef de travaux à l'Université libre de Bruxelles.

References

1. G. LOCATI and A. V. TOBOLSKY, *Adv. Mol. Relaxation Processes* **1** (1970) 375.
2. C. BAUWENS-CROWET and G. HOMÈS, *C.R. Acad. Sci. (Paris)* **259** (1964) 3434.
3. T. REE and H. EYRING, in Rheology, Vol. II, F. R. Eirich, Ed. (Academic Press, New-York, 1958).
4. J. A. ROETLING, *Appl. Polymer Symp.* **5** (1967) 161.
5. C. BAUWENS-CROWET, J. C. BAUWENS, and G. HOMÈS, *J. Polymer Sci.* **A-2, 7** (1969) 735.
6. *Idem, J. Mat. Sci.* to be published.
7. J. C. BAUWENS, *J. Polymer Sci.* **C 33** (1971) 123.
8. J. C. BAUWENS, *J. Polymer Sci.* **A-2, 5** (1967) 1145.
9. *Idem, ibid* **A-2, 8** (1970) 893.

Received 28 September and accepted 1 November 1971.