The Temperature Dependence of Yield of Polycarbonate in Uniaxial Compression and Tensile Tests

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The tensile yield stress is compared with the uniaxial compression yield stress for specimens of polycarbonate tested at constant strain rate from -120 to +120°C. The strain rate dependence of the tensile yield stress is also studied from -140 to +20°C.

The yield behaviour is described by a modification of the Eyring theory of non-Newtonian viscosity where the deformation is supposed to involve two different flow processes.

The validity of a yield criterion previously established by one of us, is checked throughout the range of temperatures explored; the proposed equation gives a good fit to the data provided it is applied separately to each flow process.

Then the present investigation, combining the yield condition with the modified Eyring theory, provides a formalism which agrees with the data and accurately renders the temperature, strain rate and pressure dependence of the yield stress of polycarbonate.

1. Introduction

We have previously shown [1] that the tensile yield stress of polycarbonate (PC), increases linearly with the logarithm of strain rate at constant temperature and decreases linearly with temperature at constant strain rate, over a large range of strain rates and temperatures (from + 20 to 140° C) in the glassy range. This yield behaviour may be fairly well described by the formalism of the Eyring theory of non-Newtonian viscosity [2] where deformation is a rate process.

We intend now:

(1) to check throughout this range the validity of the yield criterion one of us has previously established [3, 4].

(2) to extend to lower temperatures the range explored in order to determine whether at lower temperatures, the Eyring model in terms of a single activated flow process is still applicable to the yield behaviour of PC, and whether and how the yield criterion would fit the data at low temperatures.

This proposed criterion is pressure, temperature and strain rate dependent and has been established for an arbitrary state of stress. Tension-torsion and uniaxial compression experiments conducted at room temperature on polyvinyl chloride (PVC), fit this criterion fairly well [4], but the temperature dependence had not yet been investigated.

We have now performed on PC compression and tensile tests at constant strain rate, and tensile tests at various strain rates over a range of temperatures as broad as possible.

2. Experimental

The material was a commercially available PC (Makrolon Bayer) in the form of sheets 5 mm thick.

The tensile yield stresses were obtained with the equipment described previously [1].

The tensile specimens were dumb-bell shaped with a gauge length of 40 mm and a 8×5 mm cross-section.

The compression test-pieces were of the same cross-section, they were parallel-sided with a length of 8 mm. In order to correct for end constraints, we have performed compression tests on three specimens differing in length and we have extrapolated to infinite length the values obtained for the yield stresses. Compression tests were performed between carefully polished and lubricated steel plates belonging to a compression cage. This compression cage, in conjunction with a tensile load cell of an Instron testing machine, was inside an environmental chamber which allowed us to regulate the temperature to -140° C.

The temperature was measured with a thermometer placed near the specimen in the chamber; the tests were made after the specimen had remained for 1 h at the required temperature.

Load-extension curves exhibit a well defined yield point both in tension and in compression tests.

In both cases, the yield stress was taken as the load at the yield point divided by the initial cross-section (engineering yield stress) for the data of figs. 1 and 3. But in figs. 2 and 4, in order to correct the effect of elastic deformation prior to yielding, the yield stress was calculated from the following equations respectively valid in tensile and in compression tests:

$$\sigma_{\rm t} = \frac{F}{S_0} \left(1 + e \right) \tag{1}$$

$$\sigma_{\rm e}| = \frac{F}{S_0} \left(1 - e\right) \tag{2}$$

where σ is the corrected yield stress, F the load at yield, S_0 the initial cross-section and e the elastic strain corresponding to F (e is measured using an extensioneter). This correction is based upon theoretical considerations; its significance is given in section 4.

All our tests were performed at the same strain rate: $\dot{\epsilon} = 4.16 \ 10^{-3} \ \text{sec}^{-1}$.

3. Results

In fig. 1, we have plotted the engineering yield stress versus temperature, over a wide range of temperatures, for compression and tensile tests performed at the same strain rate. The graph shows clearly that in both cases, over a range of temperatures denoted range I, from about -50 to 120° C, the plot is a straight line; more-over, these two straight lines extrapolated for small stresses meet at zero stress.

Let us show that this type of yield behaviour fits the criterion previously established [3, 4]. For tests performed at the same temperature and



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 $\dot{\epsilon} = 4.16 \ 10^{-3} \ \text{sec}^{-1}$. The curve $\sigma_t = f(T)$ is calculated from equation 15 using the constants given in table II. The curve $|\sigma_c| = f(T)$ gives the best fit of equation 16 to the data, using some constants given in table II.

strain rate, this criterion has been expressed simply by using Nadai's concept [5] of the octahedral shear stress τ_0 :

 $\tau_0 + \mu p = \text{constant}$ (3) where μ is a constant and p is the hydrostatic stress.

The ratio of the yield stress in compression σ_c to the yield stress in tension σ_t , calculated from equation 3 for tests performed at the same temperature and strain rate, is given by:

$$\frac{|\sigma_{\rm c}|}{\sigma_{\rm t}} = \frac{\sqrt{2} + \mu}{\sqrt{2} - \mu} \tag{4}$$

The expression of this ratio is thus temperature and strain rate independent and agrees with the data of fig. 1 belonging to range I.

From equation 4, we have calculated the value of μ which best fits the data of fig. 1. A value of the same constant can be obtained from the data of Christiansen *et al* [6] and of Sauer, Mears, and Pae [7], who have measured, at room temperature, the tensile yield stress of PC (engineering yield stress) at various values of the hydrostatic pressure. For this last type of tests the correction of the engineering yield stress to allow for elastic strain before yielding, is not significant.

TABLE I Values of the constant μ for PC, calculated
from various data using equation 3

Origin of the data	Type of test	Determination of the yield stress	μ
Christiansen, Radcliffe, and Baer [6]	Tensile tests at various pressures	Engineering yield stress	0.072
Sauer, Mears, and Pae [7]	Tensile tests at various pressures	Engineering yield stress	0.05
Present investigation	Tensile and uniaxial compression tests	Engineering yield stress	0.19
Present investigation	Tensile and uniaxial compression tests	Calculated from equations 1 and 2	0.075

Table I gives the values of μ obtained from various data; a great discrepancy exists between the value calculated from the data of fig. 1 and the values estimated from the tensile tests under hydrostatic pressure. This discrepancy suggests us to correct the engineering yield stress to allow for elastic strain using equations 1 and 2. The corrected data are given in fig. 2; from the data



Figure 2 Plot of the yield stress in compression versus the tensile yield stress (corrected yield stresses) for tests performed at the same strain-rate at various temperatures (one point for each temperature).



Figure 3 Plot of the ratio of the engineering tensile yield stress to temperature as a function of logarithm of strainrate ($\dot{\epsilon}$ in sec⁻¹). The set of curves represents the best fit from equation 15 to the data.

belonging to range I, we have calculated the corrected value of μ which is in agreement with the values given by other authors (see table I).

It is seen in figs. 1 and 2 that, for temperatures below -50° C, the data do not fit equation 4. Thus, in this range of temperatures, which we will refer to as range I', the conclusions we have drawn from the same graph for range I do not hold and we will have to modify the expression of the yield criterion.

We have also performed tensile tests from -140 to $+23^{\circ}$ C at various strain rates. Fig. 3

gives a plot of the ratio of the engineering tensile yield stress to absolute temperature versus the logarithm of strain rate, at several constant temperatures (one curve for each temperature).

Previously [1], we have reported the same type of plot for PC between room temperature and $+ 140^{\circ}$ C. Throughout the data, it was possible to draw a family of parallel straight lines characterised by the fact that the horizontal shift factor *s* between two straight lines respectively related to temperatures T_1 and T_2 , fit with accuracy the Arrhenius equation:

$$s = \text{constant} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) = 1.64 \ 10^4 \\ \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
(5)

Throughout the data plotted in fig. 3, it was not possible to draw a set of parallel straight lines in agreement with equation 5. Only segments of straight lines at $T = -50^{\circ}$ C and $T = -90^{\circ}$ C parallel to the straight line at $T = 23^{\circ}$ C, fit equation 5 with accuracy. Once again, we have separated the graph into two ranges: range I where equation 5 is valid, range I' where it is no more valid.

4. Theoretical Interpretation

4.1. Interpretation of the Results belonging to Range I

The present results confirm that the yield behaviour of glassy polymers may be fairly well described by the formalism of Eyring's theory of non-Newtonian viscosity.

If we assume that deformation is a rate process, say the a process, which consists in the jump of a segment of a macromolecule over a potential barrier, the Eyring viscosity model, valid in simple shear experiments, leads to the following equation:

$$\dot{\gamma} = 2\gamma_{0\alpha} J_{0\alpha} \exp\left(-\frac{Q_{\alpha}}{RT}\right) \sinh \frac{w_{\alpha}}{2kT}$$
 (6)

where $\dot{\gamma}$ is the shear rate, Q_{α} is the activation energy of the α process, $J_{0\alpha}$ is a rate constant. Rand k denote the universal gas constant and Boltzmann's constant respectively and w_{α} means the mechanical energy a segment of macromolecule requires to cross the potential barrier and to produce the permanent elementary shear $\gamma_{0\alpha}$.

Let us consider at the yield point an infinitesimal plastic deformation Γ_0 proportional to the elementary shear $\gamma_{0\alpha}$. Let W_{α} denote the plastic work spent by unit of volume by the applied shear stress τ_{α} to produce Γ_0 , then:

$$W_{\alpha} = K_{\alpha} \frac{w_{\alpha}}{v_0} = \tau_{\alpha} \Gamma_0$$
 (7)

where K_{α} is a constant and v_0 the volume occupied by one segment.

From equations 6 and 7, we see that W_{α} as well as w_{α} are temperature and strain rate dependent. On the other hand, Eyring [8] pointed out that a part of the activation energy is used in providing a momentary volume increase $\Delta v_{0\alpha}$ associated with the formation of an emp⁺y site and this consideration implies that w_{α} and W_{α} are pressure dependent.

The yield criterion is merely a generalisation of relation 7 valid in simple shear to the case where an arbitrary state of stress is applied. As a general state of stress can be split into the sum of a uniform stress equal in all directions p and a deviator, W_{α} becomes in this case the energy required by unit of volume by the deviator to produce an infinitesimal strain equivalent to Γ_0 plus the contribution of the hydrostatic stress pto the momentary formation of a hole having the size $K_{\alpha} \Delta v_{0\alpha}$. We shall consider that plastic deformation are equivalent if they admit the same value of the first plastic strain invariant I_1 which can be expressed as a function of Γ_0 by:

$$I_1 = \Gamma_0^2 + 3 \tag{8}$$

The generalisation of equation 7 is then given by:

$$W_{\alpha} = K_{\alpha} \frac{W_{\alpha}}{v_{0}} = \Gamma_{0} \frac{\sqrt{3}}{\sqrt{2}} \tau_{0\alpha} + K_{\alpha} p_{\alpha} \frac{\Delta v_{0\alpha}}{v_{0}} = \text{const.}$$
⁽⁹⁾

So the yield condition may be stated as follows: for tests performed at equal temperatures and equivalent strain rates, the energy required by unit of volume to produce equivalent plastic strains is a constant. This criterion is expressed by equation 3 as well as by equation 9, provided equivalent plastic strains are considered in each type of test.

Let us point out that when the hydrostatic stress vanishes, equation 3 is an expression of von Mises' yield equation [5]; this last criterion is based on the statement that yield occurs when the elastic strain energy of distortion reaches a critical value. But in our approach the constant energy considered in the yield criterion is related to a rigid-plastic case and has nothing to do with a stored elastic energy. So, although the formalism is the same, we believe that equation 3 is not at all the expression of a modified pressure-dependent von Mises' criterion, whose basic significance is absolutely different from the Eyring theory. In this respect, our point of view differs from that of Sternstein *et al* [9].

Equations 9 and 3 are related to a rigid-plastic case; as in the types of test we have chosen, elastic strain before yielding is significant, we have to take into account these effects to check the validity of the criterion. The correction is based on the assumption that elastic strain before yielding has no influence upon the value of the work W_{α} provided the same value of the equivalent plastic deformation is considered in the rigid-plastic and in the elastic-plastic case. Equations 1 and 2 are merely obtained by the calculation of W_{α} in both cases. Let us remark that this stress calculation relies on the yield criterion and not on the evaluation of the true crosssection area. Both corrections differ substantially when there is a volume change.

Combining equations 6, 7, 8 and 9, we obtain the expression of the tensile yield stress related to the α process $\sigma_{t_{\alpha}}$, as a function of temperature and strain-rate:

$$\frac{\sigma_{t_{\alpha}}}{T} = \frac{6k}{\sqrt{3v_0\gamma_{0\alpha}} + \Delta v_{0\alpha}} \sinh^{-1} \left(\frac{\sqrt{3}\dot{\epsilon}}{2J_{0\alpha}\gamma_{0\alpha}} \exp\frac{Q_{\alpha}}{RT}\right) = A_{t_{\alpha}} \sinh^{-1} \qquad (10)$$
$$\left(C_{\alpha}\dot{\epsilon} \exp\frac{Q_{\alpha}}{RT}\right)$$

In the range of temperatures and strain rates investigated the stress level is sufficiently high to use the approximation:

 $\sinh X \approx 1/2 \exp X$ therefore equation 10 becomes:

$$\frac{\sigma_{t_{\alpha}}}{T} = A_{t_{\alpha}} \left(\ln 2C_{\alpha} \, \dot{\epsilon} \, + \, \frac{Q_{\alpha}}{RT} \right) \tag{11}$$

In the same manner we can establish the expression of the yield stress in compression related to the α process:

$$\frac{|\sigma_{\mathbf{e}_{\alpha}}|}{T} = A_{\mathbf{e}_{\alpha}} \left(\ln 2C_{\alpha} \,\dot{\boldsymbol{\epsilon}} + \frac{Q_{\alpha}}{RT} \right) \qquad (12)$$

From 11 and 12 we obtain the ratio of the compression yield stress to the tensile yield stress, both related to the a process, for tests performed at the same temperature and strain rate:

$$\frac{\sigma_{c_{\alpha}}}{\sigma_{t_{\alpha}}} = \frac{A_{c_{\alpha}}}{A_{t_{\alpha}}} = \text{constant}$$
(13)

Because equation 11 implies equation 5, and because equation 13 is another manner to write equation 4, we may state that range I, as defined in equation 3, is the range of temperatures and strain rates where the formalism of Eyring's theory in terms of a single simply activated flow process (the α process) is applicable with accuracy to the data. Therefore throughout range I:

$$|\sigma_{\rm c}| = |\sigma_{\rm c_{\alpha}}| \text{ and } \sigma_{\rm t} = \sigma_{\rm t_{\alpha}}$$
 (14)

4.2. Interpretation of the Results belonging to Range I'

In order to describe the yield behaviour of PC throughout range I', we assume that in this range, deformation at yield involves two rate processes α and β , and that the stresses due to these processes are additive.

This modification of Eyring's theory first made by Ree and Eyring [8], appeared to be successful to describe the tensile yield behaviour of at least four glassy polymers (see the papers by Roetling [10] and by ourselves [1, 11]).

This hypothetical mechanism of deformation may be depicted as follows:

At the yield point, pure viscous flow takes place and results in both ranges (I and I') from the α process, i.e. from jumps of segments of the backbone chain of the macromolecule from one equilibrium position to another under the action of the yield stress and thermal energy.

Throughout range I', the α process is hindered by the fact that the molecular movements are partially frozen in even when $\sigma_{t_{\alpha}}$ or $\sigma_{c_{\alpha}}$ act. To liberate these movements it is necessary to supply a supplementary energy by applying a supplementary stress. One may thus consider that in range I' the observed yield stress is the sum of two stresses respectively related to the α and β processes.

Throughout range I, the thermal energy is sufficient to activate the β process, one may then consider that the deformation at yield involves a single process.

The similarity of the activation energies suggests that the β flow process observed at yield is the same process observed in damping tests. One of us [12] has shown the correlation between the β mechanical loss peak (loss tangent versus temperature at a given frequency) and the

yield stress curve (yield stress versus temperature at a given strain rate) for PVC.

The problem is now to establish the expression of the yield stress related to the β process in compression and in tensile tests. We shall try to express $|\sigma_{c_{\beta}}|$ and $\sigma_{t_{\beta}}$ in the same manner as $|\sigma_{c_{\alpha}}|$ and $\sigma_{t_{\alpha}}$. We will therefore write Eyring's equation for the β process as if it was a single process. Thus we obtain the expression of the resultant yield stress in tensile and in uniaxial compression tests:

$$\frac{\sigma_{t}}{T} = \frac{\sigma_{t_{\alpha}}}{T} + \frac{\sigma_{t_{\beta}}}{T} = A_{t_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + A_{t_{\beta}} \sinh^{-1} \left(C_{\beta} \dot{\epsilon} \exp \frac{Q_{\beta}}{RT} \right)$$
(15)
$$\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) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_{c_{\alpha}} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + C_$$

$$A_{c_{\beta}} \sinh^{-1} \left(C_{\beta} \in \exp \frac{Q_{\beta}}{RT} \right)$$
 (16)

where $A_{t\beta}$, $A_{c\beta}$, C_{β} and Q_{β} have the same meaning as in 10 and 12 but are related to the β process.

If equations 15 and 16 are valid, the curves giving σ_t and $|\sigma_c|$ versus temperature at constant strain rate throughout the glassy range (i.e. range I and range I') must admit two asymptotes which intersect at two points having the same abscissa denoted as T_{β} in the following relation:

$$T_{\beta} = -\frac{Q_{\beta}}{R \ln 2C_{\beta} \epsilon} \tag{17}$$

From the best fit of equation 15 to the data of fig. 3 we have evaluated the constants related to each process. Table II shows the values obtained; $A_{t_{\alpha}}$, C_{α} and Q_{α} agree well with the previous determinations [1].

 TABLE II Constants calculated from the fit of equation 15 to the data of fig. 3

α process	β process
$ \overline{Q_a = 75.5 \text{ kcal/mole}} \overline{C_a} = 2.40 10^{-81} \text{ sec} A_{ta} = 4.35 10^{-4} \text{kg/mm}^2 . ^\circ \text{K} $	$Q_{\beta} = 9.6 \text{ kcal/mole} \ C_{\beta} = 2.76 10^{-9} \text{ sec} \ A_{t\beta} = 1.33 10^{-3} \text{kg/mm}^2.^{\circ} \text{K}$

The values of the constants given in table II were used to generate the curve $\sigma_t = f(T)$ in fig. 1; the accuracy of the fit is very good.

From these results and from equation 17, we are able to determine the value of T_{β} corresponding to $\dot{\epsilon} = 4.16 \ 10^{-3} \ \text{sec}^{-1}$, we obtain:

$$T_{\beta} = -77^{\circ}\mathrm{C}$$

The constants $A_{c_{\alpha}}$ and $A_{c_{\beta}}$ were estimated from the best fit of equation 16 to the data of fig. 1 using the values of Q_{α} , Q_{β} , C_{α} and C_{β} given in table II. With the following values:

$$A_{c_{\alpha}} = 5.7 \ 10^{-4} \ \text{kg/mm}^2$$
. °K
 $A_{c_{\beta}} = 5.57 \ 10^{-3} \ \text{kg/mm}^2$. °K

we found a good fit for the curve $|\sigma_c| = f(T)$, except in a narrow range of temperatures around T_{β} . But the poor agreement around T_{β} is not surprising because for a first approximation we have considered the average yield behaviour. We intend to show in a future paper that a better approach can be obtained if one takes into account a distribution of relaxation times and activation energies to calculate the curve $|\sigma_c| = f(T)$ at constant strain rate throughout range I'.

The hypothetical mechanism of deformation at yield we have proposed, implies the following consequences:

(1) The ratio of the measured yield stresses $(|\sigma_c|)/\sigma_t$ for tests performed at the same temperature and strain rate throughout range I' is not a constant.

(2) The α and β processes are viewed as a single kind of flow unit characterised by an average volume v_0 and possessing two degrees of freedom. Each degree of freedom requires for being freed a momentary volume increase $\Delta v_{0\alpha}$ and $\Delta v_{0\beta}$ associated with the formation of an empty site. The shear rates of each process: $\dot{\gamma}_{\alpha}$ and $\dot{\gamma}_{\beta}$ are supposed to be equal.

(3) The ratio of the yield stresses related to the β process $(|\sigma_{c_{\beta}}|)/\sigma_{t_{\beta}}$ is a constant for tests performed at the same temperature and strain rate.

It follows from these consequences that the yield criterion remains valid throughout range I' provided it is applied separately to each process. So, in addition to equation 9 which still holds throughout range I', we must write:

$$W_{\beta} = K_{\beta} \frac{w_{\beta}}{v_0} = \Gamma_0 \frac{\sqrt{3}}{\sqrt{2}} \tau_{0\beta} + K_{\beta} p_{\beta} \frac{\Delta v_{0\beta}}{v_0} = \text{constant}$$
(18)

where W_{β} , w_{β} , K_{β} , $\tau_{0\beta}$ and p_{β} have the same meaning as in equation 9, but are related to the β process.

Then in the special case where tensile and compression tests are performed at the same temperature and strain rate in range I', we know from 15, 16 and 18 that:

$$\frac{|\sigma_{\rm c} - \sigma_{\rm c_{\alpha}}|}{\sigma_{\rm t} - \sigma_{\rm t_{\alpha}}} = \frac{|\sigma_{\rm c_{\beta}}|}{\sigma_{\rm t_{\beta}}} = \frac{\sqrt{2} + \mu'}{\sqrt{2} - \mu'} = \text{constant} \quad (19)$$

 μ' having the same meaning as μ in equation 4 but being related to the β process.

We have checked equation 19 from -50 to $+120^{\circ}$ C. Values of $|\sigma_{c_{\alpha}}|$ and $\sigma_{t_{\alpha}}$ are obtained by extrapolating from range I the straight lines giving $|\sigma_c|$ and σ_t as a function of temperature. Results are given in fig. 4; it is seen that the fit of equation 19 to the data is quite good. From the graph we have calculated the following value of μ' :

$$\mu' = 0,86$$



Figure 4 Plot of the β contribution to the yield stress in compression versus the β contribution in tension (corrected yield stresses). The tests are performed at the same strain-rate at various temperatures from -120 to -50° C.

5. Discussion

The value of the activation energy Q_{β} is in agreement with the value reported from dielectric measurements which is about 8 kcal/mole [13]. We obtained previously the same coincidence with PVC [1].

Only Q_{β} may be compared with other types of measurements. We know from a previous paper [14] that Q_{α} may not be compared with the apparent activation energy of the loss peak related to the primary transition observed in dielectric or mechanical damping tests. The molecular process associated with this loss peak is governed by the theories based on the concept of free volume (the WLF equation for example) and differs from the α process considered here.

Polycarbonate possesses a low-temperature β transition and a high-temperature primary transition. The broadness of the temperature range between both transitions is particularly interesting because the proposed hypothetical yield mechanism implies that this range corresponds to range I. Throughout range I, the Ree-Eyring theory reduces to the Eyring theory in terms of a single simply activated flow process (here called the α process) and in this case, the plots of yield stresses versus log (strain-rate) or versus temperature, must give straight lines.

The fit of the formalism of Eyring's theory to the data, over a wide range of experimental conditions, has convinced us to use the Ree-Eyring model instead of the one proposed by Robertson [15]. Robertson's approach predicts a definite curvature in the yield stress curve even in the range of temperature here called range I. The treatment is based on the hypothesis that the mechanism of yielding is a stress-activated change of structure from a glassy to a more fluid state. This "yielding state" is considered to have the structure of a melt but the vibrational temperature of a glass. This assumption is undoubtless attractive, but, unfortunately, the theory does not give an acceptable fit to the data.

Ward *et al* [16] have recently modified the Robertson theory to include the effect of hydrostatic component of stress on yield; they have used optimised values of the coefficients of Robertson's equation and they obtained a good fit to the data, especially on PMMA. But the tensile behaviour of PMMA has also been described by the Ree-Eyring theory [10, 17] and the accuracy of the fit was fairly good too. Perhaps it will be interesting to apply the present treatment to the compression behaviour of PMMA over a range of temperatures as broad as possible in order to compare the results with those of Ward *et al.*

Just below the glass temperature, at slow and moderate strain-rates, we know from a previous paper [14] that for polycarbonate the formalism of Eyring's theory is no longer valid. We have established [14] the existence of a range of temperatures (denoted as range III in the paper) where the yield behaviour does not follow Eyring's formalism, nor the WLF equation, but may be governed by a temperature-dependent activation energy. Perhaps this range III, is the one where a good fit of Robertson's theory can be obtained for polycarbonate.

6. Conclusions

(1) The validity of a yield criterion previously established by one of us, is checked for PC throughout a range of temperatures covering 170° C (from -50 to $+120^{\circ}$ C) for tensile and uniaxial compression tests performed at a strain rate equal to $4.16 \ 10^{-3} \ \text{sec}^{-1}$.

In this range, the accuracy of the fit is convincing as well as the remarkable agreement of the data with the formalism of the Eyring theory where a single flow process governed by a constant activation energy is supposed to be involved in the deformation at yield.

Throughout this range the ratio of the measured yield stress in compression to the measured yield stress in tension is a constant for tests performed at the same temperature and strain rate; and the constant μ deduced from this ratio agrees with the values reported from measurements of the tensile yield stress under hydrostatic pressure.

(2) Below -50° C, the existence is revealed of a range of temperatures and strain rates where it is necessary to assume that two activated flow processes are involved in the yield deformation of PC for being allowed to apply the Eyring model.

In this range, to obtain an accurate fit, it is necessary to apply the yield criterion separately to each process.

(3) The similarity of the activation energies suggests that the second flow process revealed by the compression and tensile yield behaviour, is the same as the molecular movement which gives rise to the β mechanical damping peak observed at about -100° C for PC.

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