*Eur. Polym. J.* Vol. 26, No. 10, pp. 1071–1075, 1990
Printed in Great Britain. 

0014-3057/90 $3.00 + 0.00


# THE COMPRESSION YIELD BEHAVIOUR OF POLYCARBONATE OVER A WIDE RANGE OF STRAIN RATES AND TEMPERATURES

F. RIETSCH

Laboratoire de Physique des Polymères, Université de Lille Flandres Artois, EUDIL Science des Matériaux, 59655 Villeneuve d'Ascq Cedex, France

B. BOUETTE

Etablissement Technique Central de l'Armement, CREA/CM, 16 bis, Avenue Prieur de la Côte d'Or, 94114 Arcueil Cedex, France

(*Received* 22 *December* 1989; *received for publication* 28 *February* 1990)

**Abstract**—The compression yield stress behaviour of engineering polycarbonates in the glassy state has been investigated over a wide range of strain rates ($10^{-4}$–$4500\,sec^{-1}$) and temperatures (−40 to 60°). In this region, the Ree–Erying and Bauwens approach takes into account a distribution of two different relaxation times ($\alpha$ and $\beta$). At high strain rate in the glassy range, this model provides evidence on the secondary transition linking the yield behaviour with the $\beta$ mechanical loss peak.

## INTRODUCTION

Strain rate and temperature are known to have a great influence on the mechanical behaviour of polymers. More particularly, polycarbonate (PC), an amorphous glassy polymer well known for good impact properties, has molecular relaxations which influence its mechanical behaviour at room temperature.

We have shown [1] that study of the compression yield stress of PC over a wide range of temperatures and strain rates reveals a secondary transition due to the local relaxation mode. It was possible to calculate the activation energy associated with this transition by assuming that at the yield point a high polymer exhibits pure viscous flow, in agreement with Erying's theory of non-Newtonian viscosity [2, 3]. The Bauwens approach [4–7], which consists of a modification of the Ree–Erying theory, taking into account a distribution of relaxation times and linking the yield behaviour with the $\beta$ mechanical loss peak, is found to give an acceptable fit to the data. The purpose of this paper is to extend these results in a range of temperatures and strain rates which have few explored before as intermediate strain rate and high strain rate in low temperature test and to compare this description with a thermodynamic approach of plasticity proposed by Escaig *et al.* [8, 9].

## EXPERIMENTAL PROCEDURES

### *Sample*

The samples were machined from extruded sheets of LEXAN PC supplied by General Electric. To avoid any influence of the thermo-mechanical history of the material, the PC sheets were dried and annealed above the glass temperature $T_g$. As has been shown by compression test in the three directions of the sheet, such a thermal treatment leads to about the same mechanical behaviour in all the directions tested. The compression samples were cylinders 8 mm long with dia 5 mm.

### *Compression tests*

The low speed compression tests were carried out using a INSTRON mechanical machine ($10^{-4}$–$10^{-2}\,sec^{-1}$).

The intermediate speed tests with a range of strain rates ($10^{-1}$–$10^{1}\,sec^{-1}$) were carried out using an hydropneumatic MTS machine. Recording the force and the displacement (close the sample) during the test, we were able to calculate accurately the strain rate and to be sure that it was constant during the test.

The high strain rate rests ($350$–$4000\,sec^{-1}$) were performed with a compression split Hopkinson apparatus [10]. A cylindrical sample was placed between two high elasticity limit metallic bars, one called the input bar and the other the output bar, in which a compression wave would pass. Because of the variation of the mechanical impedance when the wave passed through the sample, this input wave, $\epsilon_I$, was partly reflected ($\epsilon_R$), and partly transmitted ($\epsilon_T$). Using a hypothesis [11, 12], we can calculate the strain rate $\dot{\epsilon}(T)$, and the stress $\sigma(T)$, in the sample:

$$\dot{\epsilon}(T) = -\frac{2C}{e}\epsilon_R(t)$$

and

$$\sigma(t) = \frac{EA_b}{A_e}\epsilon_T(t)$$

where $e$ is the thickness of the cylinder and $A_e$ its section; $E$ and $A_b$, are the modulus and the section of the bars respectively; $C$, is the velocity of sound in the bars.

The strain is calculated by integration of the strain rate considering that the strain is quasi-isovolumic. So, we have the "true strain" which can be written $\epsilon_v = \ln(1 + \epsilon)$. Direct measurement of the strain during the test and so of the strain rate is achieved with an optical extensometer SIMMER which permits following of the movement of each end of the bar in contact with the sample.

## RESULTS AND DISCUSSION

Bauwens *et al.* have shown, for PC tested in tension at low strain rate, $\dot{\epsilon}$, at temperatures from $-20$ to 145°, that the yield behaviour can be expressed by the exponential form of the Eyring equation [2]:

$$\frac{\sigma_y}{T} = A_\alpha\left[\ln 2C_\alpha\dot{\epsilon} + \frac{Q_\alpha}{RT}\right] \quad (1)$$

where $T$ is the absolute temperature and R is the universal gas constant.

The parameters $A_\alpha$, $C_\alpha$ and the activation energy, $Q_\alpha$ of the molecular movement of glassy transition, $\alpha$, are constants for the material.

When the polymer is capable of revealing a secondary transition, $\beta$, (associated to the local relaxation mode of the macromolecular structure or the relaxation of the side groups), Bauwens showed that, at low temperature or at high strain rate [4–7], the variation of the yield stress with strain rate and temperature can be described by the generalized theory proposed by Ree–Erying [3]:

$$\frac{\sigma_y}{T} = A_\alpha\left[\ln 2C_\alpha\dot{\epsilon} + \frac{Q_\alpha}{RT}\right] + A_\beta \sin^{-1}\left(C_\beta\dot{\epsilon}\exp\frac{Q_\beta}{RT}\right). \quad (2)$$

Obviously, this model is based on the assumption that two processes requiring additive stresses are involved at yield, viz. a low strain rate mode governed by the $\alpha$ transition and a high strain rate process in which the $\alpha$ process is subordinate to the liberation of the local relaxation modes, $\beta$.

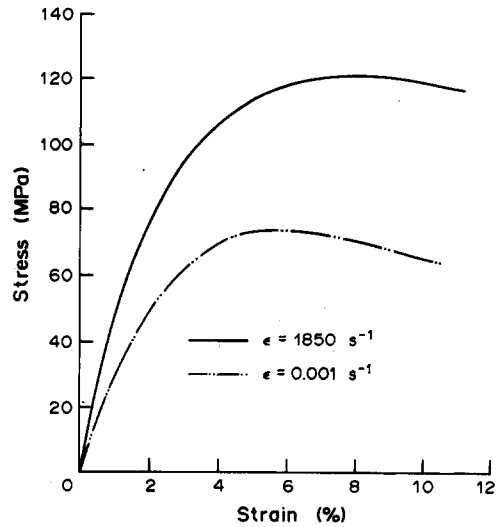


Fig. 1. Typical true stress curves obtained for PC samples deformed at 23° for $\dot{\epsilon} = 1850\ \text{sec}^{-1}$ and for $\dot{\epsilon} = 0.001\ \text{sec}^{-1}$.

The change occurs for a critical strain rate, $\dot{\epsilon}_c$, which obeys the relation:

$$\dot{\epsilon}_c = \frac{1}{2C_\beta}\exp\left(-\frac{Q_\beta}{RT}\right). \quad (3)$$

Figure 1 shows the elastoviscoplastic behaviour of Lexan PC. We see that the yield stress doubles for a five decade increase of strain rate. High strains can be obtained and deformed samples recover their initial dimensions above $T_g$. Figure 2 shows the ratio of the yield stress to absolute temperature, $\sigma_y/T$ vs $\ln\dot{\epsilon}$,

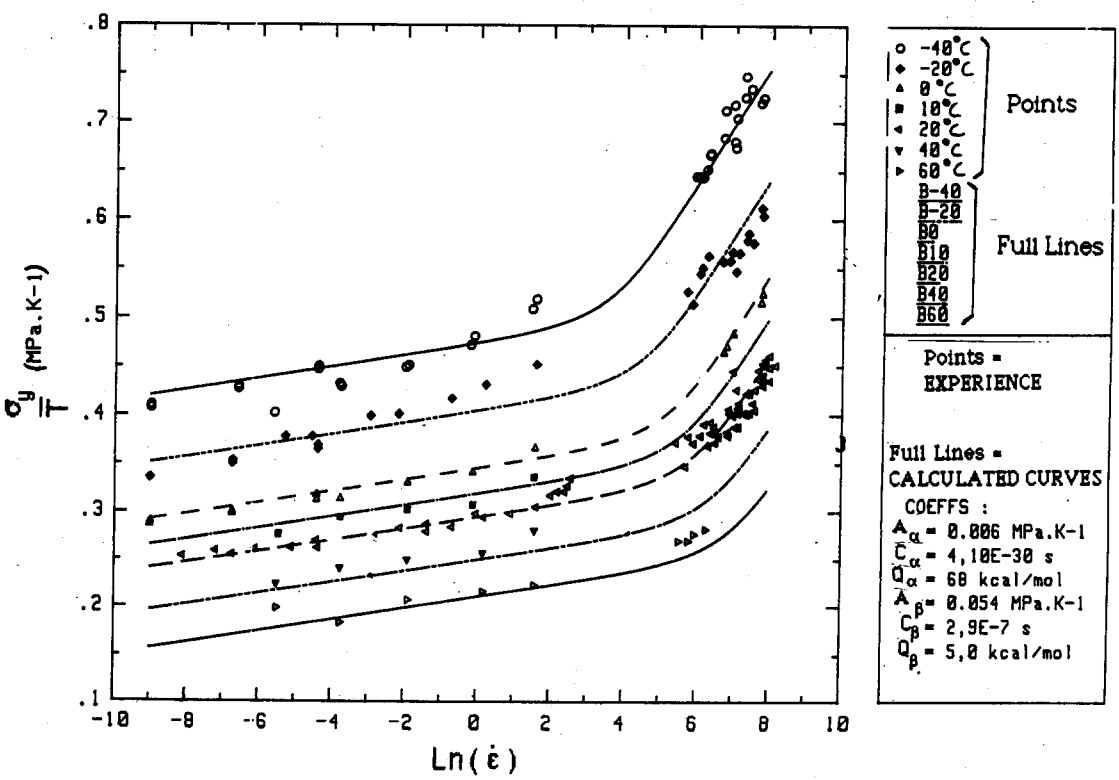


Fig. 2. Measured ratio of yield stress, $\sigma_y$, to temperature as a function of logarithm of strain rate ($\dot{\epsilon}$ in $\text{sec}^{-1}$). The set of parallel curves is calculated from equation (2).

where full lines correspond to theoretical variations [equation (2)]. For low strain rates, our results agree with those published [1, 4]. The yield stress follows an Eyring equation of which coefficients fitting experimental results are:

$$A_\alpha = 6.0 \times 10^{-3}\ \text{MPa} \cdot \text{K}^{-1}$$

$$C_\alpha = 4.1 \times 10^{-30}\ \text{sec}$$

$$Q_\alpha = 68.0\ \text{kcal} \cdot \text{mol}^{-1}.$$

$Q_\alpha$ is close to the proposed Bauwens value ($Q_\alpha$ = 75.4 kcal · mol$^{-1}$), found from test on Markolon PC supplied by Bayer. As has been shown by Bauwens, the yield stress variation can be described with only a deformation mechanism involving the glassy transition, $\alpha$.

For high strain rates, we can observe a great change in the PC behaviour taking into account the activation of the both $\alpha$ and $\beta$ modes as described by the equation (2). The tabulated values of $A_\beta$, $C_\beta$ and $Q_\beta$ are:

$$A_\beta = 54.0 \times 10^{-3}\ \text{MPa} \cdot \text{K}^{-1}$$

$$C_\beta = 2.9 \times 10^{-7}\ \text{sec}$$

$$Q_\beta = 5.0\ \text{kcal} \cdot \text{mol}^{-1}.$$

These coefficients have to be compared to the Bauwens results:

$$A'_\beta = 56 \times 10^{-3}\ \text{MPa} \cdot \text{K}^{-1}$$

$$C'_\beta = 2.76 \times 10^{-9}\ \text{sec}$$

$$Q'_\beta = 9.57\ \text{kcal} \cdot \text{mol}^{-1}.$$

We observe a noticeable difference between our results and the predictions of the Bauwens model (Fig. 3), and the Steer results. The yield stress obtained by us seems to be 30% lower than those given by Bauwens, and the coefficients $C'_\beta$ and $Q'_\beta$ of the model do not exactly fit our experimental results. The activation energy, $Q'_\beta$, is twice $Q_\beta$, but these two energies can be compared with published values [13, 14].

The transition at $-80°$ is in fact the deconvolution of three maxima. The first, at $-80°$ ($\beta$ peak) is associated with an activation energy between 8.3 kcal · mol$^{-1}$ and 10.8 kcal · mol$^{-1}$, depending on the authors. It corresponds to the movement of the phenyl group in the main chain. A second maximum located around $-140°$ for which the associated energy is 6.2 kcal · mol$^{-1}$ or 10.9 kcal · mol$^{-1}$ ($\gamma$ transition) can be associated with the interaction of the carbonate and phenyl movements. The third is located at $-152°$ and the associated energy is 5.8 kcal · mol$^{-1}$.

We can say therefore that the activation energies determined by Bauwens or by the authors are in the same range as those found in the literature. This establishes that there is a mechanism which correlates the yield strain to the characteristic movements of the glass transition and of secondary transitions.

Figure 2 reveals transition of the materials, which are expressed in term of critical rate, $\dot{\epsilon}_c$, determined by extrapolation of the straight lines in each scale of strain rate. We plot the critical rate vs temperature (Fig. 4). These rates correspond to the transition

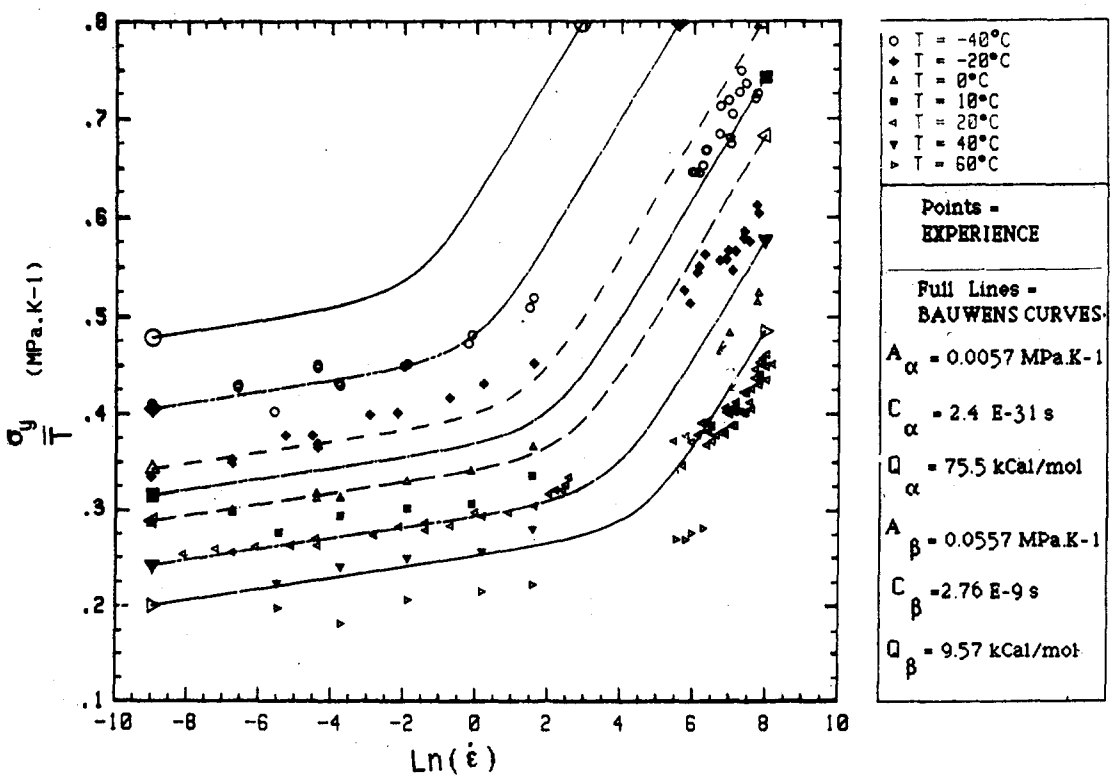


Fig. 3. Measured ratio of yield stress, $\sigma_y$, to temperature as a function of logarithm of strain rate ($\dot{\epsilon}$ in sec$^{-1}$). The set of parallel curves is calculated from equation (2) and the Bauwens coefficients.

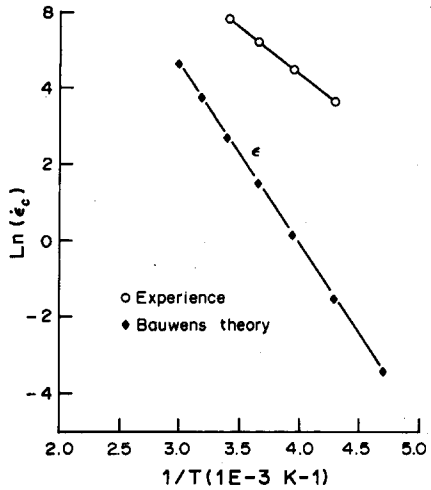


Fig. 4. Critical strain rate vs $1/T$ from experimental results and calculated values from equation (3).

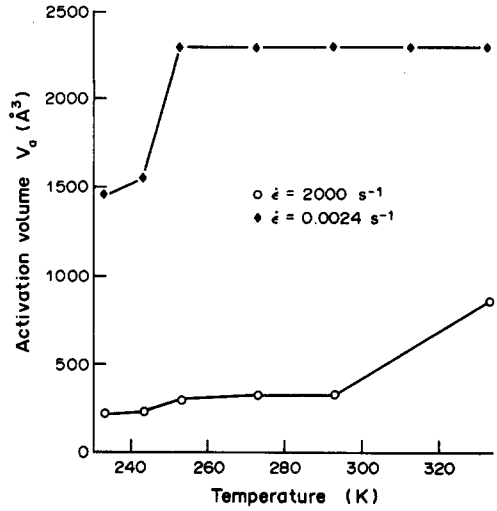


Fig. 5. Variation of the volume of activation with temperature for: $\dot{\epsilon} = 0.024\ \text{sec}^{-1}$ (◆) and for $\dot{\epsilon} = 2000\ \text{sec}^{-1}$ (○).

between the activation of a single mode (the $\alpha$ mode) and the activation of several modes of deformation. The plot of $\ln \dot{\epsilon}_c$ vs $1/T$, is a straight line as indicated by equation (3).

On the other hand, a thermodynamic approach to plasticity has been proposed by Escaig [8, 9]. Plastic deformation appears as a thermal activated mechanism for which two parameters can be easily calculated. The activation energy, $\Delta G_a$, and the activation volume, $V_a$, are given by:

$$\Delta G_a = \left[\Delta H_a + \frac{T}{\mu}\frac{d\mu}{dT}\right]\left[1 - \frac{T}{\mu}\frac{d\mu}{dT}\right]^{-1} \quad (4)$$

with

$$\Delta H_a = kT^2\left[\frac{\partial \ln \dot{\epsilon}}{\partial T}\right]_\sigma$$

$$\mu = \frac{E}{2(1+\nu)}$$

and

$$V_a = kT\left[\frac{\partial \ln \dot{\epsilon}}{\partial \sigma_a}\right]. \quad (5)$$

The model predicts a low temperature and a high temperature mechanism. For a temperature, $T$, below a critical temperature, $T_c$, we have a thermally activated mechanisms, with $V_a$ constant of $\Delta G_a$ proportional to $T$, then for $T > T_c$ a vacancy migration mechanism with $\Delta G_a$ constant and $V_a$ increasing with $T$.

Moreover, the study of PC behaviour with a wide range of strain rates can reveal some characteristic transitions of the material; these transitions can be expressed in term of critical strain rate or critical temperature.

The thermodynamic and kinetic analysis of the plastic deformation necessarily needs determination of the activation parameters of the deformation. So, we determine the activation volume and the activation energy, for which the change with temperature is shown in Figs 5 and 6. For the range of temperature explored, we noted that for high strain rates the activation volume determined by equation (5) increases with temperature (contrary to the Escaig theory). For low strain rates, we note that this volume is constant after an abrupt increase. The activation energy, as indicated by the theory [equation (4)], can be represented by an Arrhenius equation which is characteristic of a thermally activated phenomenon (for $T < 70°$). The Arrhenius equation can be written as:

$$\Delta G_a = \alpha kT \text{ with } \alpha = 3.0 \text{ for } \dot{\epsilon} = 2000\ \text{sec}^{-1}$$

$$\alpha = 19.5 \text{ for } \dot{\epsilon} = 2.4 \times 10^{-3}\ \text{sec}^{-1}.$$

A second determination of the activation energy has been performed by integrating the activation volume. We obtain the same result, so we can conclude that the calculated activation volume is the true value.

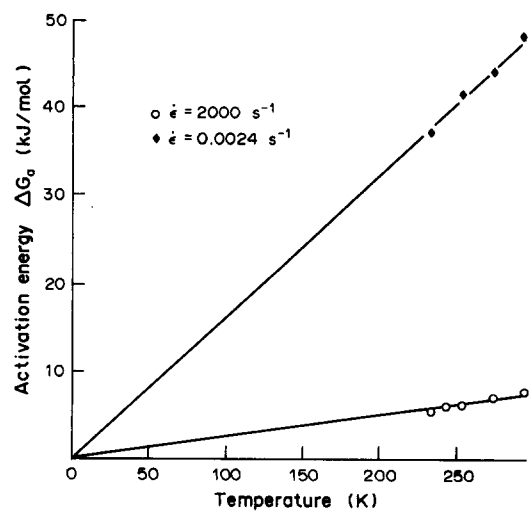


Fig. 6. Variation of the Gibbs free energy of activation with temperature for: $\dot{\epsilon} = 0.024\ \text{sec}^{-1}$ (◆) and for $\dot{\epsilon} = 2000$ sec (○).

The range of high temperature ($T - T_c = 70°$) has not been explored in this work.

## CONCLUSION

The yield stress of PC is greatly influenced by the temperature and the strain rate. At low strain rates, the results are consistent with the literature but we note a noticeable difference with the Bauwens predictions and the Steer results at high strain rates. Nevertheless, the Eyring equation can be used to describe the PC behaviour over the range of temperature and strain rates explored. The change of the critical range is consistent with equation (5) given by Bauwens.

The thermodynamic model of Escaig seems not to apply (for the range of temperature and strain rates used).

The tests at intermediate rate allow us to point out the critical rates ($c$ 300 $sec^{-1}$ at room temperature), which is the boundary between two modes of deformation (from the $\alpha$ mode to the $\alpha$ mode combined with the $\beta$ local deformation modes).

## REFERENCES


1. P. Steer and F. Rietsch. *Eur. Polym. J.* **24,** 7 (1988).
2. H. Eyring. *J. chem. Phys.* **4,** 283 (1936).
3. T. Ree and H. Eyring. *Rheology*, Vol. III (edited by F. R. Eirich). Academic Press, New York (1958).
4. C. Bauwens-Crowet, J. C. Bauwens and G. Homes. *J. Mater. Sci.* **7,** 176 (1972).
5. J. C. Bauwens and C. Bauwens-Crowet. *J. Mater. Sci.* **9,** 1197 (1974).
6. J. C. Bauwens. *Polymer* **25,** 1523 (1984).
7. J. C. Bauwens. *J. Mater. Sci.* **7,** 577 (1972).
8. J. Haussy, J. P. Cavrot, B. Escaig and J. M. Lefebvre. *J. Polym. Sci.* **18,** 311 (1980).
9. J. M. Lefebvre and B. Escaig. *J. Mater. Sci.* **20,** 438 (1985).
10. R. Davies. Vol. 240, p. 275. Cambridge University Press (1985).
11. H. Holsky. N. Y. Dover Publication Inc. (1953).
12. P. Davies and N. Hunter. *J. Mech. Phys. Solids* **11,** 155 (1963).
13. E. Sacher. *J. Macromolec. Sci.* **B11,** 403 (1975).
14. Y. Aoki and J. O. Brittain. *J. appl. Polym. Sci.* **20,** 2879 (1976).