

where T is the temperature in °C. The observed coefficients of expansion at different temperatures are given in Table III along with the calculated values obtained from Equations 1 and 2.

The lattice parameters at room temperature obtained in the present study are higher than the values obtained by other investigators. The thermal behaviour of zinc carbonate is similar to the other compounds of calcite type in having a relatively large coefficient of expansion along the c -axis which is normal to the CO_3 layers and a small coefficient of expansion in the perpendicular direction.

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The strain-rate and temperature dependence of yield of polycarbonate in tension, tensile creep and impact tests

Previous investigations [1-3] have shown that the yield stress of polycarbonate, measured in isothermal tension tests, increases linearly with the logarithm of the strain-rate and fits an Eyring-type equation, provided one operates within a definite range of temperatures located between the α and β transitions. We intend, in this range, to extend the study of the tensile yield stress of polycarbonate to strain-rates which cannot be reached in tension tests. Using tensile creep and impact tests, it is possible to measure the yield stress related to strain-rates varying from 10^{-8} to 10^2 sec^{-1} .

The material and the specimens were the same in the different types of tests. They were described previously as well as the equipment used in tension tests [1]. Tensile creep tests were performed under dead-weight loading inside an environmental chamber provided with windows. Strain was measured with a dial gauge. The impact testing was carried out on a Frank tension impact machine of the pendulum type. The test-piece was placed inside a little oven located in the anvil. One end was clamped in the machine base and coupled with a load cell

operating a storage oscilloscope, so that a load-extension curve was visualized and the yield stress measured.

Fig. 1a is an example of the stress-strain curve related to a tension test. The point Y_t corresponding to the maximum of the curve is taken as the yield point. The stress σ_Y related to this point, fits with accuracy the following Eyring-type equation derived from the theory of non-Newtonian viscosity [4]:

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

where Q denotes the activation energy of the yield process, T the absolute temperature, $\dot{\epsilon}$ the constant strain-rate (proportional to this point to the cross-head speed); A and C are constants and R is the universal gas constant.

A typical creep curve at constant load is shown in Fig. 2a. From A_c to B_c , the strain is increasing at constant strain-rate, while the stress may still be considered as constant. Mindel and Brown [5], have suggested that the mechanism during the yielding in a tension test is the same as that during homogeneous creep. The question of the choice of the yield point may still be raised. In order to characterize the yielding in creep in a similar manner as in tension, we have chosen as the yield point, the inflexion Y_c of the creep

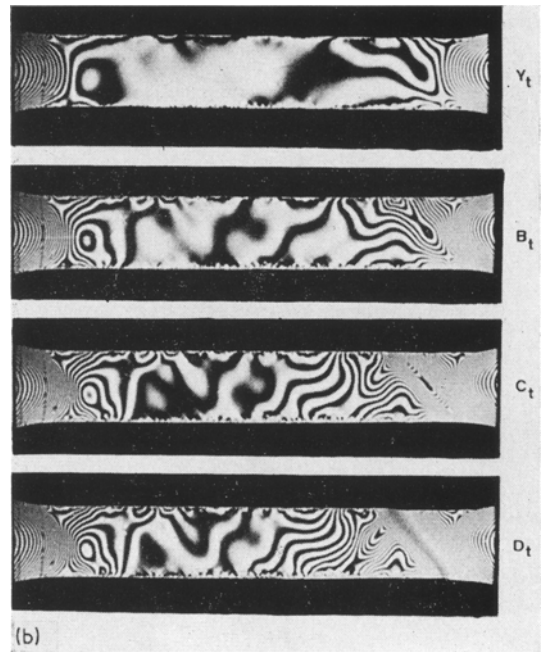
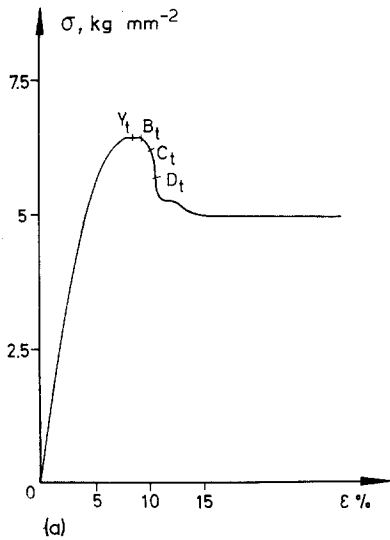


Figure 1 (a) Typical tension curve obtained at 23°C. The strain-rate related to Y_t is equal to $4.16 \times 10^{-4} \text{ sec}^{-1}$. (b) Birefringence patterns related to some points of this curve.

curve, evaluated as the middle of the segment $A_c B_c$. Thus, at both Y_t and Y_c : (a) the strain is increasing at a constant strain-rate; (b) the rate of change of stress may be taken equal to zero; (c) the strain is still homogeneous all along the gauge length of the test-piece; therefore, the

yield behaviour may be represented by a dashpot having a non-Newtonian viscosity: η . Moreover, the value of the strain ϵ_Y corresponding to the yield point, is more or less the same in a tension

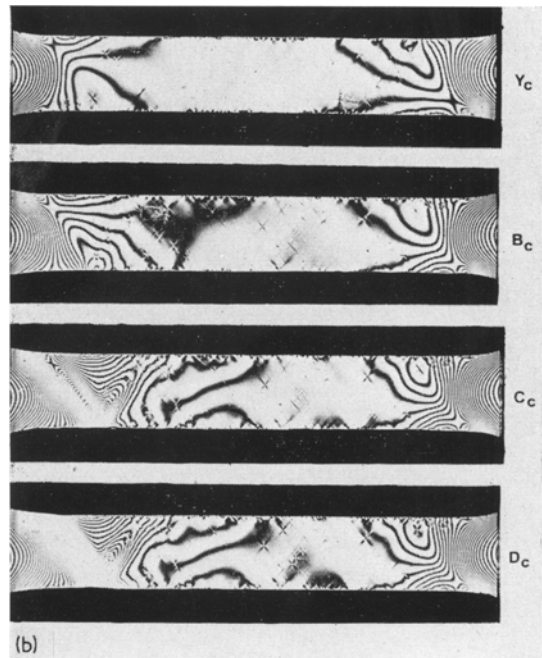
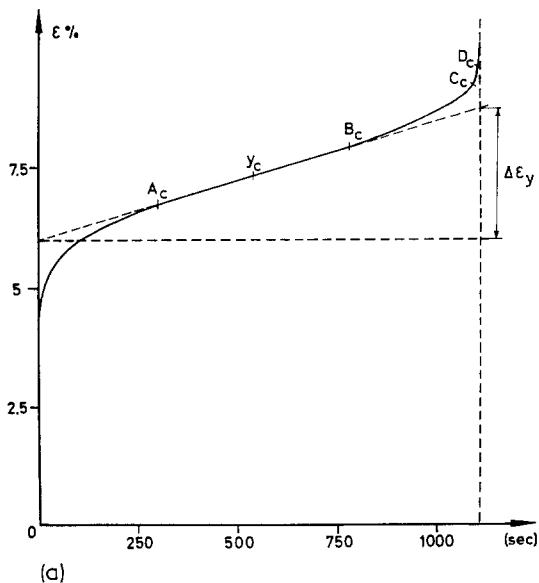


Figure 2 (a) Typical curve obtained at 22.8°C. The engineering stress is equal to 6.05 kg mm^{-2} . The strain-rate at yield (calculated from the slope of $A_c B_c$) is equal to $2.4 \times 10^{-5} \text{ sec}^{-1}$. (b) Birefringence patterns related to some points of this curve.

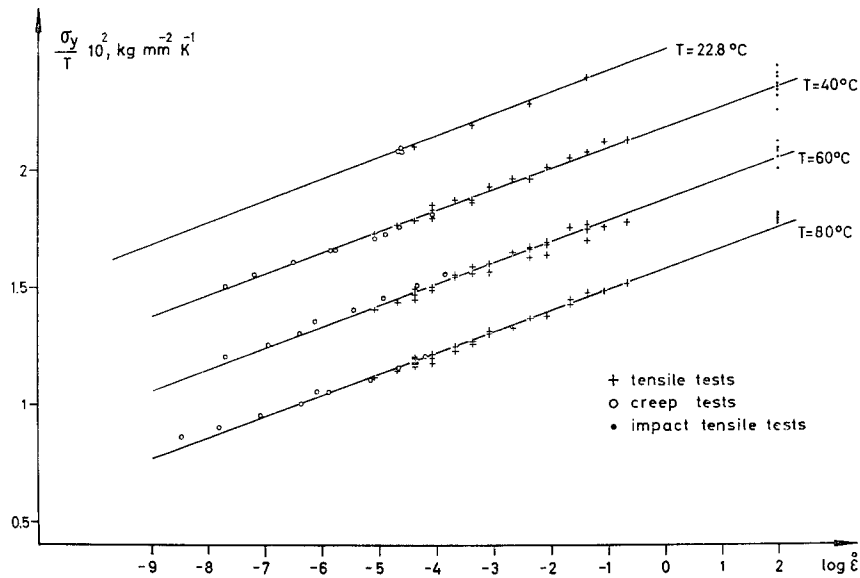


Figure 3 A plot of the ratio of the engineering yield stress to temperature, against the logarithm of the strain-rate at yield ($\dot{\epsilon}$ in sec^{-1}), for tension, creep and impact tests. The set of parallel straight lines is calculated from Equation 1 and Table I.

or in a creep test conducted at the same temperature. Samples were observed between crossed polarizers during both tensile and creep tests conducted at room temperature. Photographs are given in Figs. 1b and 2b, where it may be seen that the birefringence patterns are quite similar for the couple of points Y_t, Y_c . It must be pointed out that, in both cases, a macroscopic deformation band occurs beyond the yield point, at D_t or D_c , where the strain-rate accelerates rapidly.

A plot of σ_Y/T against the logarithm of strain-rate is given in Fig. 3, where it is seen that the data obtained from the different types of tests are in agreement. First, using the linear least-squares method, straight lines are calculated to fit the data related to 40, 60 and 80°C . The mean slope of these straight lines is taken as A . From the horizontal distances between these lines, a mean value of the activation energy is calculated and is taken as Q . C , in turn, is evaluated from A and Q , and the value of the abscissa of each line for $\sigma_Y/T = 0$. The values so obtained for A , Q and C are given in Table I. The set of parallel straight lines drawn on the graph of Fig. 3, is calculated from Equation 1 using Table I. The accuracy of the fit is satisfactory. Some data at 22 and 8°C are also plotted on the graph to check the constancy of the parameters at a

higher level of stress. It has been shown previously [3] that the effect of deformation prior to yielding, must be taken into account in the calculation of the tensile yield stress. However, because it was not possible to measure ϵ_Y in impact tests or in some creep tests related to long times and therefore interrupted before point B_c , the stress, plotted in Figs. 3 and 4, is the engineering stress. Such a plot gives a value of A which is about 6% lower than the one evaluated from the corrected yield stresses, while the values of Q and C are hardly affected.

From Equation 1, the non-Newtonian viscosity at yield may be expressed by:

$$\eta = 2C\sigma_Y \exp \left[\frac{1}{T} \left(\frac{Q}{R} - \frac{\sigma_Y}{A} \right) \right] \quad (2)$$

Let t_D denote the delay time determined by the method suggested by Ender and Andrews [6] as the intersection of the straight-line regions of the creep curve, before and after the neck formation (Fig. 2). Findley [7], amongst others, has shown that t_D can be approximated by an

TABLE I

A ($\text{kg mm}^{-2} \text{ K}^{-1}$)	Q (kcal mol^{-1})	C (sec)
3.96×10^{-4}	85	5.35×10^{-36}

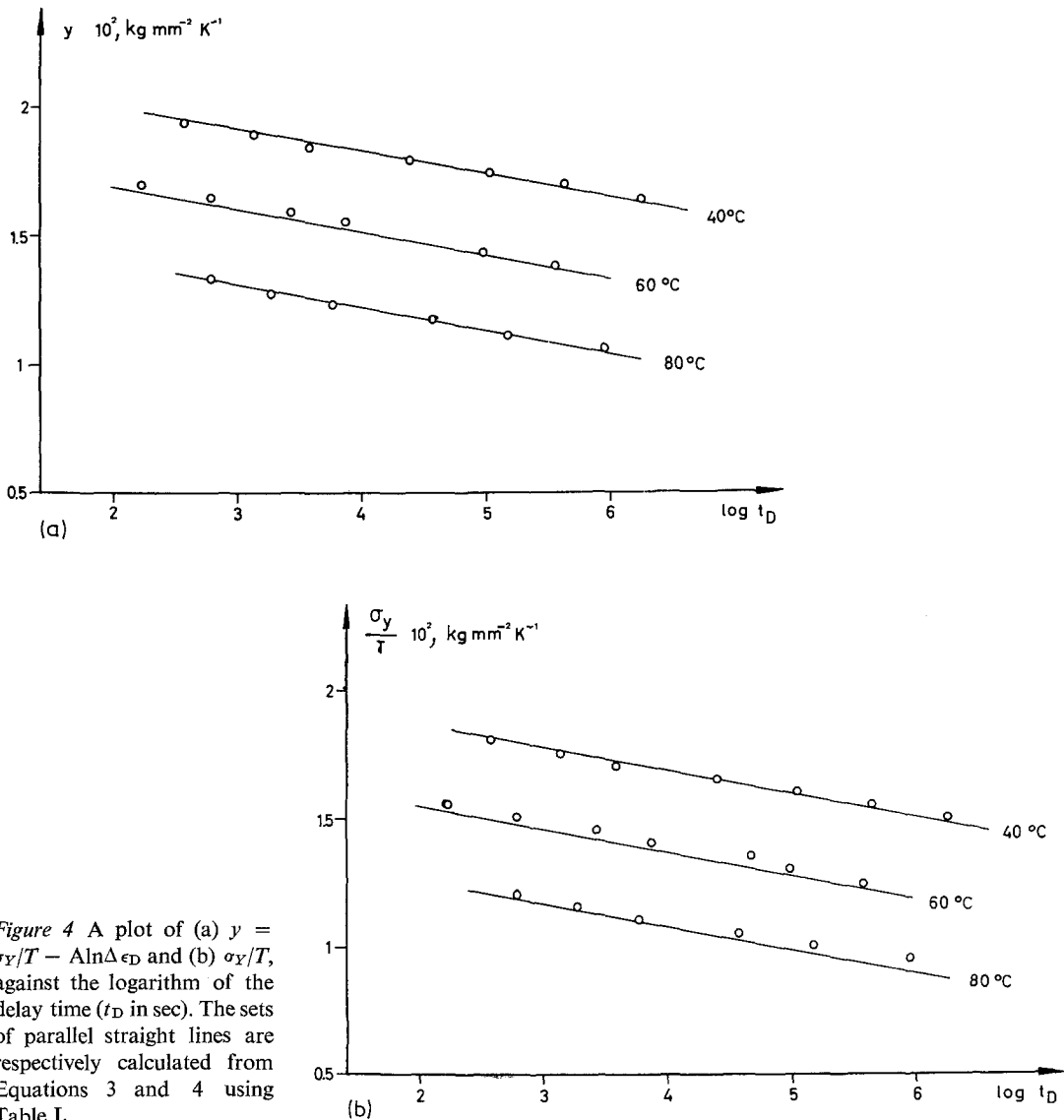


Figure 4 A plot of (a) $y = \sigma_Y/T - A \ln \Delta \epsilon_D$ and (b) σ_Y/T , against the logarithm of the delay time (t_D in sec). The sets of parallel straight lines are respectively calculated from Equations 3 and 4 using Table I.

Eyring-type equation, but some authors, like Matz *et al.* [8], restrict the applicability of such an equation to a range of experimental conditions where the stresses are not too low and the temperatures below and not too close to T_g , the glass transition temperature. We believe that the range of applicability of Eyring's formalism is the same in tension, compression and creep tests, for the yield stress, the strain-rate at yield or the delay time, this range has been referred to as range I in previous communications [2, 3]. From Equations 1 and 2 the expression of σ_Y/T as a function of the delay time may be written:

$$\frac{\sigma_Y}{T} = A \left(\ln 2C \Delta \epsilon_D + \frac{Q}{RT} - \ln t_D \right) \quad (3)$$

where $\Delta \epsilon_D$ denotes the deformation at t_D related to a dashpot having a viscosity equal to η (Fig. 2a). This quantity may be evaluated with accuracy from the creep curves. Therefore, if Equation 3 is valid, the variation of $y = \sigma_Y/T - A \ln \Delta \epsilon_D$ as a function of the logarithm of the delay time may be predicted from the value of the constants given in Table I. A set of parallel straight lines expressed by:

$$\left[y = A \left(\ln 2C + \frac{Q}{RT} - \ln t_D \right) \right]_{T=\text{const.}} \quad (4)$$

is drawn on Fig. 4a and compared with the data measured on the creep curves. The accuracy of the fit is quite satisfactory. Fig. 4b gives a plot of σ_Y/T against $\log t_D$ compared to a set of parallel straight lines calculated from Equation 3, using the constants given in Table I and a mean value of $\Delta\epsilon_D$ taken equal to 3%. The fit is acceptable except for the lowest values of the stresses related to 80°C where $\Delta\epsilon_D$ becomes much greater than 3%. We believe that this region of experimental conditions belongs to the edge of range I. This assumption is in agreement with the results of Matz *et al.* [8], who found that at 90°C the delay time becomes independent of the stress for values greater than $t_D = 10^8$ sec.

In conclusion, it appears that:

(1) the tensile creep yield behaviour of polycarbonate may be compared to the tension yield behaviour, provided one takes as the yield point the inflexion of the creep curve;

(2) the yield behaviour of polycarbonate may, therefore, be described by an Eyring-type equation over ten decades of strain-rate, in a range of temperatures, from room temperature to 80°C;

(3) within this range, the delay time can also be approximated by an Eyring-type equation

having the same constants A , C and Q as the former one.

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Observation of microprecipitates in PbTe single crystals

The presence of microprecipitates has long been assumed in the lead chalcogenides. However, direct observation, although very difficult, has been achieved for PbSe by transmission electron microscopy of thinned crystals [1]. Similar experiments on PbTe have proved inconclusive [2] but the presence of precipitates in evaporated PbTe [3, 4] and PbS [3] films has been demonstrated.

Attempts to thin PbTe crystals for transmission electron microscopy have proved difficult. However, platinum-shadowed carbon replicas can be readily produced and allow the speedy examination of the topography of large surface areas provided that a sufficient number of separate replicas are made over the required area. Therefore, replication was used to examine and assess the quality of freshly cleaved single crystals of PbTe taken from large Bridgman grown ingots. The ingots were grown from a melt containing 0.5 at. % excess tellurium so that

tellurium rich (i.e. p-type) material was obtained over the whole length [5]. Samples were taken from various positions along the ingot so that the effects of the variation in tellurium content could be assessed. This is possible because ingots become progressively rich in tellurium as one proceeds from the front (first end to freeze, FETF) to the rear (last end to freeze, LETF) [5]. Many ingots were examined along their lengths both before and after etching to produce dislocation etch pits [6]. In order to eliminate mosaics, that is, low-angle grain boundaries, ingots were regrown after removing the LETF [5]. As the latter was rich in tellurium, regrown ingots contained less tellurium than those grown only once.

Replicas of unetched surfaces consisted of cleavage steps and rivulets separated by microscopically flat regions similar in appearance to optical micrographs of identical areas at much smaller magnifications. Etched surfaces contained etch pits having square cross-sections indicating that the cleaved surface was a (100)