piston being replaced by a high pressure fluid which surrounds the deforming work piece. Hydrostatic extrusion has the advantage of decreasing the energy dissipated due to friction. We developed a solid-state extrusion process using the latter method for the production of ultra-high modulus polyethylene several years ago which was reported in this journal [7] in 1974. The process is also the subject of a provisional patent application [8].

Capiati *et al.* further remark that they have "developed a much more efficient and, importantly, essentially continuous method for producing high density polyethylene strands of extreme orientation". We wish to comment that continuous methods for the production of tapes and fibres of ultra-high modulus polyethylene by drawing were also developed in our laboratories some years ago, in addition to the hydrostatic extrusion method already discussed. This work has been extensively reported in the literature [9–16], and it has also been emphasized [12] that some of the key guidelines for the production of such materials by drawing, e.g. effect of molecular weight and crystallinization conditions, are applicable to solid-state extrusion. The similarity between the properties and structure of ultra-high modulus polyethylenes produced by solid-state extrusion and drawing is very great [7, 11, 15] because both are solid-state deformation processes which impose substantial elongation deformation. The relationship between high modulus and high draw ratio (or extrusion ratio) has been clearly established by our work [7, 9, 11, 12, 16, 17].

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The temperature pulse method for the determination of the activation energy for creep

The purpose of this letter is to draw attention to a property of a linear viscoelastic solid which has not been noticed previously and which *inter alia* offers the opportunity for an extremely precise determination of the activation energy governing the mechanism of deformation.

We seek the relationship between the creep rate of a specimen in an experiment at a constant temperature T_0 and the creep rate in a second experiment at the same stress in which for a period of time the temperature is switched from T_0 to T. In the second experiment with temperature jumps at $t'(T_0 \rightarrow T)$ and $t''(T \rightarrow T_0)$ the shear strain at time t, $\gamma(t)$, $(t > t'' > t')$ is given, according to the Boltzmann Superposition Principle [1], by

$$\frac{\gamma(t)}{\sigma(J_{\mathrm{R}}^{T_0}-J_{\mathrm{U}}^{T_0})}=\int_0^{t'}\int_{-\infty}^{\infty}\frac{\phi^{T_0}(\ln\tau)}{\tau}\exp\left\{-\frac{1}{\tau}\left[(t'-u)+\frac{(t''-t')}{a_T}+(t-t'')\right]\right\}\mathrm{d}\ln\tau\,\mathrm{d}u$$

$$+b_T\int_{t'}^{t''}\int_{-\infty}^{\infty}\frac{\phi^{T}(\ln\tau)}{\tau}\exp\left\{-\frac{1}{\tau}\left[(t''-u)+a_T(t-t'')\right]\right\}\mathrm{d}\ln\tau\,\mathrm{d}u$$

$$+\int_{t''}^{t}\int_{-\infty}^{\infty}\frac{\phi^{T_0}(\ln\tau)}{\tau}\exp\left[-\left(\frac{t-u}{\tau}\right)\right]\mathrm{d}\ln\tau\,\mathrm{d}u+\frac{J_{\mathrm{U}}^{T_0}}{(J_{\mathrm{R}}^{T_0}-J_{\mathrm{U}}^{T_0})} \qquad (1)$$

in which $J_{\mathrm{R}}^{T_0}$ and $J_{\mathrm{U}}^{T_0}$ are the relaxed and unrelaxed compliances at T_0, $\phi^{T_0}(\ln\tau)$ and $\phi^{T}(\ln\tau)$ are the distributions of relaxation times at T_0 and T, a_T is the shift factor and b_T is a parameter describing the temperature dependence of $(J_{\mathrm{R}}^{T}-J_{\mathrm{U}}^{T})$ [1],

$$(J_{\mathrm{R}}^{T}-J_{\mathrm{U}}^{T}) = b_T(J_{\mathrm{R}}^{T_0}-J_{\mathrm{U}}^{T_0}). \qquad (2)$$

Integrating Equation 1, making use of [1] $\phi^{T_0}(\ln\tau)=\phi^{T_0}[\ln(\tau/a_T)]$ and differentiating,

$$\frac{\dot\gamma(t)}{\sigma(J_{\mathrm{R}}^{T_0}-J_{\mathrm{U}}^{T_0})}=-\int_{-\infty}^{\infty}\phi^{T_0}(\ln\tau)\frac{1}{\tau}\exp\left[-\frac{(t-t'')}{\tau}\right]$$

$$\left\{\exp\left[\frac{-(t''-t')}{a_T\tau}\right]\left[1-\exp\left(\frac{-t'}{\tau}\right)\right]\right.$$

$$\left.+b_T\left\{1-\exp\left[\frac{-(t''-t')}{a_T\tau}\right]\right\}-1\ \mathrm{d}\ln\tau\right\} \qquad (3)$$

Making the approximation $b_T=1$ (the validity of which we return to later) we have after reduction

$$\frac{\dot\gamma(t)}{\sigma(J_{R}^{T_0}-J_{\mathrm{U}}^{T_0}}=\int_{-\infty}^{\infty}\frac{\phi^{T_0}(\ln\tau)}{\tau}$$

$$\exp\left\{-\frac{1}{\tau}\left[(t-t'')+\frac{(t''-t')}{a_T}+t'\right]\right\}\mathrm{d}\ln\tau \qquad (4)$$

In the first experiment conducted at the same stress σ but without T-jump the strain rate at time t_0 is

$$\frac{\dot\gamma(t_0)}{\sigma(J_{\mathrm{R}}^{T_0}-J_{\mathrm{U}}^{T_0})}=\int_{-\infty}^{\infty}\frac{\phi^{T_0}(\ln\tau)}{\tau}\exp\left[-\ \frac{t_0}{\tau}\right]\mathrm{d}\ln\tau \qquad (5)$$

Equations 4 and 5 show that the two strain rates would be the same function of time if we equate the exponential factors in the integrands, that is,

$$t_0 = (t-t'')+\left(\frac{t''-t'}{a_T}\right)+t' \qquad (6)$$

or

$$\frac{(t-t_0)}{(t''-t')} = \left(1-\frac{1}{a_T}\right) \qquad (7)$$

Thus the two creep rate curves at $t>t''$ are separated along the time axis by the constant quantity $(t-t_0)$, which depends only on the jump interval $(t''-t')$ and the shift factor a_T. For a crystalline polymer [1] the shift factor is controlled by the Arrhenius equation,

$$\ln a_T = -\frac{(T-T_0)}{RTT_0}\Delta H. \qquad (8)$$

Thus by measuring $(t-t_0)$ for various values of $(t''-t')$ and T it is possible to determine ΔH at T_0.

The validity of the theory was tested in torsional creep experiments on a thin-walled tube of polypropylene. The specimen was equilibrated in a water bath at $T_0=40.0^\circ$ C for 60 h. Three experiments were then performed (with periods of 3 h recovery between experiments), for which $\Delta T=T-T_0=5.9$, 8.8 and 2.9° C, and $t'\sim 60$ sec, $t''\sim 120$ sec. Each experiment lasted 600 sec except the $\Delta T=2.9^\circ$ C experiment which lasted 400 sec. The temperature jumps were made very rapidly by use of the apparatus described by Mathews and McCrum [2]. After the third experiment the specimen was allowed to recover for 5 h before a final experiment performed isothermally at 40.0° C and over a longer creep time (1000 sec).

Fig. 1a shows for $t>t''$ the dependence of $\dot\gamma$ on t for values of $\Delta T=2.9^\circ$ C ($t''-t'=61$ sec), $\Delta T=5.9^\circ$ C ($t''-t'=62$ sec) and $\Delta T=8.8^\circ$ C

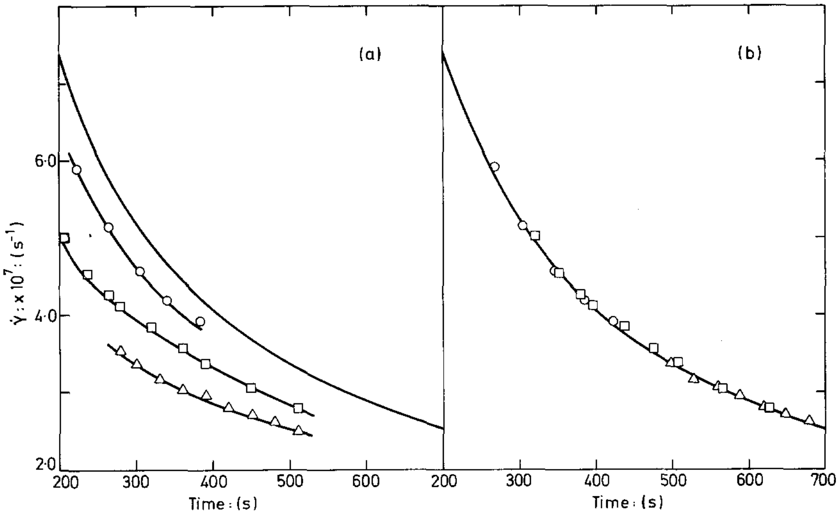

Figure 1 (a) Dependence of $\dot{\gamma}(\text{sec}^{-1})$ on time for experiments conducted with $T_0 = 40.0°$ C and with $\Delta T = 2.9°$, ○; $\Delta T = 5.9°$, □; and $\Delta T = 8.8°$, △. The solid curve gives the dependence of $\dot{\gamma}$ on time for an experiment at 40.0° C at the same stress but without T-jump. (b) Data of (a) plotted with horizontal shifts along the time axis: $\Delta T = 2.9°$, shifted by 40 sec; $\Delta T = 5.9°$ shifted by 115 sec; $\Delta T = 8.8°$ shifted by 197 sec.

$(t'' - t' = 61\,\text{sec})$. Also shown is the dependence of $\dot{\gamma}$ on t for the specimen creeping at 40.0° C without T-jump. The latter curve is obtained from a least squares fit to the data when plotted $\log \dot{\gamma}$ against $\log t$. The x-axis is plotted linear in time so as to demonstrate the constant shift in time of the T-jump data from the data with no T-jump. That each of the T-jump curves is separated by a constant quantity $(t - t_0)$ along the time axis from the curve with no T-jump is illustrated in Fig. 1b. The shifts are $-(t - t_0) = 40$, 115 and 197 sec respectively for $\Delta T = 2.9$, 5.9 and 8.8° C. These values together with the appropriate values of $(t'' - t')$ yield $\Delta H = 34.2$, 35.3 and 32.8 kcal mol^{-1} respectively with mean value 34.1 kcal mol^{-1}. It will be seen therefore that not only is the theory obeyed in that each T-jump curve is shifted from the isothermal curve by a constant time $(t - t_0)$ for all values of $\dot{\gamma}$ but the magnitudes of ΔH are in quantitative agreement one with another. These values of ΔH are in good agreement with those calculated from experiments with negative values of ΔT.

The error which might have been introduced by the approximation $b_T = 1$ in Equation 6 has been computed using a model consisting of 18 single relaxation time elements in the range $\tau = 0.6$ sec to $\tau = 3 \times 10^5$ sec. It is found to be appreciable only for times immediately after the second T-jump: that is, for values of $(t - t'') < 30$ sec. Although we recorded data in this range it was not used in computing ΔH. In fact data points in the range $0 < (t - t'') < 40$ sec were not used. The values of ΔH computed from data taken at $(t - t'') > 40$ sec are not therefore affected by the approximation $b_T = 1$ in Equation 4.

For a precise and reliable determination of ΔH the new technique is far superior to the alternative methods. The superposition of isothermal creep curves is erroneous unless appropriate corrections are made for the temperature dependence of the limiting compliances [1]. The corrections often take the form of vertical shifts which are invariably difficult and normally impossible to assess. The Dorn method involves an unguided data extrapolation procedure [3]. The chief virtues of the new method are: (a) the linear theory leads to a closed form prediction that the T-jump data should be separated from the data without T-jump by a constant time $(t - t_0)$; (b) the experimental data for each (T-jump experiment can be checked against this theoretical prediction; (c) if (b) is observed then the measured values of $(t - t_0)$ can be used reliably with the relevant values of ΔT and $(t'' - t')$ to obtain ΔH. No subjective procedure is involved, such as a vertical shift. The extent to which values of ΔH agree for different experiments is a quantitative measure of the precision of theory and experiment.

This work will be described in detail elsewhere with an assessment of research areas opened up by this significant development. The same experimental principle may be applied to creep strain rather than creep-strain rate. The power of the technique is not limited to linear viscoelastic solids but to any slow rate process governed by an analogous first order differential equation.

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A calculation of the surface energy of α-rhombohedral boron

In a preceding investigation, Vega *et al.* [1] applied the Griffith criterion for the fracture of brittle materials to tensile failure in boron fibres. The application was restricted to fractures initiated at a particular type of imperfections, the geometry of which was observed to be similar to that of a Griffith crack, i.e. the proximate voids existing in the vicinity of the core–mantle interface. The application of the Griffith equation permitted the authors to estimate experimentally the surface energy γ for boron with a Young's modulus of $4.4 \times 10^5\,\text{N mm}^{-2}$ as calculated by Talley [2]. The values of the surface energy obtained were 2.77 to $6.43\,\text{J m}^{-2}$, which is of the same order as available values in the literature for bulk tungsten [3, 4]. As neither experimentally measured nor theoretically calculated values of γ have earlier been reported, it is the purpose of the present work to calculate γ by some simple fundamental considerations.

Elemental boron can exist in three different allotropic forms: α-rhombohedral, tetragonal and β-rhombohedral. The structure of boron in fibres has most commonly been referred to as amorphous [5–7]. Others have interpreted the amorphousness of boron in terms of a fine grained polycrystalline structure with crystallite sizes of 20 to 30 Å [8–10]. By now there is some agreement on the microcrystalline nature, but on the other hand, it has not yet been possible to determine the exact crystal structure of the microcrystallites.

Considering the uncertainty in crystal structure, and the fact that tetragonal and β-rhombohedral boron are relatively more complicated structures, we have decided to make our calculations on the simpler α-rhombohedral allotrope.

A complete description of the three allotropic forms of boron can be found in [11] and [12]. Data for α-rhombohedral boron have been taken from a textbook by Adams [11]. Only the most relevant data will be summarized here.

All three allotropic forms are characterized by lattice arrangements of B_{12} icosahedra. The B_{12} icosahedral unit is shown in Fig. 1. The α-rhombohedral structure consists of nearly regular icosahedra in a slightly deformed cubic close packing. The rhombohedral unit cell can be more conveniently described in terms of the related hexagonal cell with $a = 4.908$ Å and $c = 12.567$ Å and containing three icosahedra.

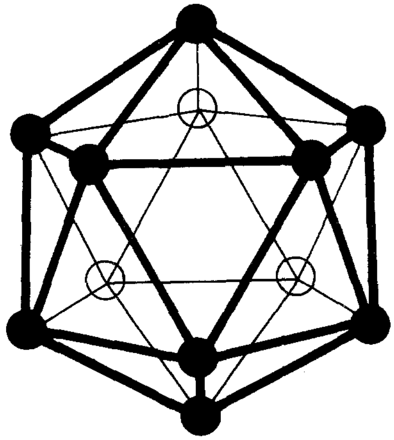

Figure 1 The B_{12} icosahedral unit in boron structures.