Figure 5 A sketch of the failure face of a specimen that was partly broken at 675 K, unloaded, and the remaining neck, C, broken at room temperature. Examination before the fracture was completed showed that most of the gauge length near the failure zone (e.g. at A and C), was heavily deformed, but over one small arc, at B, there were only a very few slip lines on the gauge length close to the failure face.

undeformed part of the edge of the cracked neck proved to be where the central cleaved region reached the surface.) Since the rim fails after the centre, the experiment establishes that failure by cleavage was prevented by the inability of a large crack front to propagate, rather than through a difficulty of crack nucleation. Non-propagating surface grain boundary cracks were in fact seen in specimens deformed at and above 664K.

The amount of work-hardening preceding failure was negligible in some tests; it appears therefore that crack nucleation takes place first concurrently with or soon after yielding. The remaining question is why cracks can grow to lengths of as much as ~1.45 mm, but not propagate to failure, as is typical of the other Group VIa bcc transition metals. (The observation of fibrous failure in chromium is in itself noteworthy, as even after extensive deformation and necking, frequently, fracture by sharp crack propagation has been observed [2].) A tentative interpretation of the large increase in the surface energy of fracture, which causes the crack front to stop is the pronounced effect of freshly produced dislocations. This hypothesis is consistent with the work on pressurized chromium, for which Mellor and Wronski [7] estimated that an increase in the mobile dislocation density of $< 10^7$ cm^{-2} more than doubled the surface energy of fracture and reduced the ductility transition temperature by 280K.

Acknowledgements

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Anomalous internal friction in linear polyethylene at low temperatures

In linear polyethylene (LPE) the dominant relaxation below room temperature is the γ_I relaxation at $-127°C$ (0.67 Hz) [1-3]. This relaxation is attributed to the relaxation of the non-crystalline fraction since its magnitude increases with decreasing crystal volume fraction [3]. We have examined in torsion pendulum experiments the effect of quenching from room temperature to liquid nitrogen temperature. The

motive for these experiments was an examination of the hypothesis that the γ_I relaxation is the mechanical manifestation of the glass transition [4-6]. It was hoped to make a quantitative measure of the shift of the γ_I relaxation time caused by quenching. It proved impossible to obtain a reliable measure of the shift since the results were obscured by another effect of considerable significance which is described in this note.

A specimen of linear polyethylene of size $8.5 \times 1.0 \times 0.10$ cm was machined from a sheet of Hi-fax 1900 obtained from the Hercules Powder Company. The density of the specimen was 0.936 g/cc at 23°C. Measurements of Λ and G' (logarithmic decrement and shear modulus) were obtained using an inverted torsion pendulum operating at a constant frequency of 0.67 Hz. Two different thermal histories were studied. In a non-equilibrium experiment the specimen (mounted in the torsion pendulum) was quench-cooled* from room temperature by rapid immersion in liquid nitrogen. This was achieved by placing the cryostat immediately below the pendulum, filling it with liquid nitrogen and then abruptly raising it (into its normal position) so as to surround the specimen. The liquid nitrogen boiled off rapidly. The temperature was then maintained at $-180°C$ by passing cold nitrogen gas through the cooling coils of the cryostat. After a period of about 10 min the flow of cold nitrogen gas was stopped and the specimen allowed to warm up due to heat leakage through the thermal shield of the apparatus. Measurements of Λ and G' were obtained "on the run" as the temperature rose. The initial rate of temperature rise was 1.5°C/min dropping to 0.1°C/min near room temperature. In the equilibrium experiment the specimen was cooled slowly from room temperature to the first measuring temperature and then to the next and so on down to liquid nitrogen temperature. Each measuring temperature was maintained for about 1 h before Λ and G' were determined.

The results are shown in Fig. 1. The relaxation behaviour is dominated by the γ_I relaxation for both equilibrium and non-equilibrium specimens. It will be noted, however, that at all temperatures Λ for the non-equilibrium specimen exceeds Λ for the equilibrium specimen. In addition the values of G' differ, being greater for the equilibrium specimen than for the non-
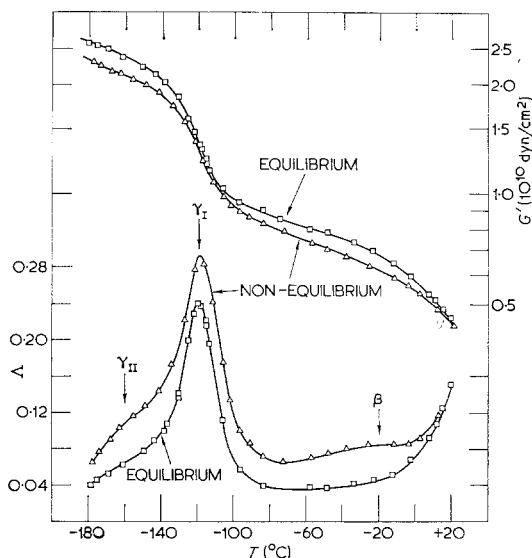

Figure 1 Temperature dependence of logarithmic decrement Λ and shear modulus G' for two thermal histories. (i) *Equilibrium:* specimen cooled slowly and then held at each measuring temperature for 1 h before measurement. (ii) *Non-equilibrium:* specimen quenched to liquid temperature, measurements then being taken as the specimen warmed up.

equilibrium. The non-equilibrium specimen exhibits two subsidiary relaxations $\beta(\sim -20°C)$ and $\gamma_{II}(\sim -160°C)$. In the equilibrium specimen there is no trace of a β peak at $-20°C$. In the region of $-160°C$ the equilibrium specimen exhibits a broad loss region. This radical difference between the two loss spectra resolves the apparent irreproducibility in the experimental evidence recorded in the literature which is now seen to be caused by differences in thermal history at low temperatures during the determination of Λ and G'. For instance, the presence of $\gamma_{II} \gamma_{III}$ peaks in LPE observed in some cases [2] and not in others [3] and the occurrence of a marked β peak in polymethylene [4].

In studying mechanical relaxation of high melting point crystalline polymers at low temperatures, it has been considered unnecessary to programme the thermal history. Experimental reports rarely contain a precise statement of thermal history. It is clear in the light of the data shown in Fig. 1 that mechanical relaxation is profoundly affected by thermal history which must therefore be carefully defined both in

*The term " quench-cooled " is often used for a specimen quenched from the melt. In this note the term refers to specimens quench-cooled from room temperature to liquid nitrogen temperature by immersion in liquid nitrogen.
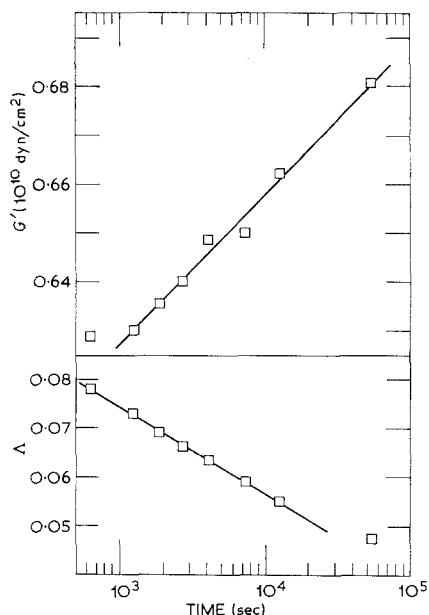
Figure 2 The dependence of logarithmic decrement Λ and shear modulus G' for a quenched specimen on storage time at $-19°$C.

planning and in reporting an experiment. The majority of workers studying mechanical relaxation cool their specimens rapidly from room temperature to liquid nitrogen temperature (and then sometimes to liquid helium temperature) and record data continuously as the specimen heats up. Clearly, this procedure will lead to a result different from the equilibrium result. If for any reason the rate of rise of temperature is checked, then both Λ and G' will exhibit marked time dependence. Fig. 2 shows the effect of storage time at $-19°$C on Λ and G' for a quenched specimen. The natural rate of temperature rise was interrupted by switching on the thermostat when the temperature had risen to $-19°$C. It will be seen that both Λ and G' depend approximately linearly on the logarithm of storage time at $-19°$C. In effect, if the non-equilibrium experiment of Fig. 1 is interrupted, and the temperature held constant, the specimen will anneal and Λ and G' move from the non-equilibrium curve to the equilibrium. The curves shown in Fig. 1 thus approximate the envelopes to the data for both Λ and G'. For instance, data for a specimen cooled to a liquid nitrogen temperature over a period of 3 h with values of Λ and G' taken "on the run" as the specimen

warmed up lay within the envelope.

The simplest explanation of the increase in background damping of the non-equilibrium specimen is that the quench to liquid nitrogen temperature induces thermoelastic micro-stresses. It is known that the anisotropy of thermal expansion of hexagonal [7] and orthorhombic metals [8, 9] leads to pronounced mechanical effects. In α-uranium, thermal cycles of $\pm40°$ at $500°$C increase the minimum creep rate by factors between 25 and 45 [9]. A comparable effect on creep of LPE has been observed in the temperature range 20 to $40°$C [10].

In LPE the detailed explanation is as follows. In the a, b and c directions of the crystal and in the non-crystalline fraction the thermal expansion coefficients at $20°$C are 2.3, 0.7, -0.13 and $3.4 \times 10^{-9}\,°C^{-1}$ respectively [11, 5]. This marked anisotropy is maintained down to liquid nitrogen temperature [11]. It is proposed that thermoelastic micro-stresses are introduced on cooling due to the mismatch of expansion coefficients and the peculiar arrangement of the crystals. If the specimen is cooled extremely slowly, the thermoelastic stresses are largely eliminated at the temperatures at which they are introduced. A most likely mechanism will be stress relaxation processes within the low modulus amorphous fraction. But if the specimen is quenched, then the thermoelastic stresses will not relax during cooling. When the quenched specimen is heated however, marked relaxation will occur and the measured Λ and G' for the non-equilibrium experiment will depend on the rate at which the specimen is heated from liquid nitrogen temperature. If the rate of rise of temperature is interrupted and the specimen maintained at constant temperature, then the measured Λ and G' will depend on storage time, as shown in Fig. 2.

It is obvious therefore that the most reliable and reproducible method to obtain data on crystalline polymers, is to cool slowly and maintain the specimen at a constant temperature before measuring Λ and G'. It is to be expected that comparable effects will be observed in other crystalline polymers since the thermal expansion of polymer crystals is invariably anisotropic.

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