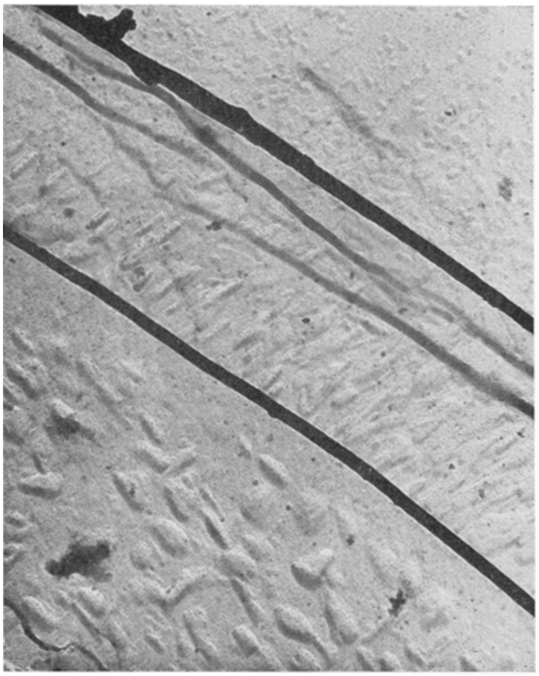

Figure 1 Platinum shadowed carbon replica of (100) cleavage plane of PbTe showing probable tellurium-rich microprecipitates, magnification × 30 000.

surface [5] which is in agreement with the known cleavage plane for PbTe.

Areas near the last end to freeze of an ingot grown only once were sometimes found to have clusters of cigar-shaped surface bumps (Fig. 1). It is suggested that these bumps have their long axes pointing in the ⟨100⟩ directions and represent tellurium-rich microprecipitates. The length and diameter of the precipitates was estimated to be of the order 1500 to 2000 Å and 500 to 1000 Å respectively. These dimensions suggest some of the precipitates are platelets; this is consistent with investigations on PbTe [3, 4] and PbS films [3], precipitates in the latter having dimensions 400 Å × 20 Å. However, others are more cylindrical in shape and are thus similar to the precipitates with approximate dimensions 6000 Å × 1500 Å detected in bulk PbSe [1]. Similar clusters to those shown in the figure were never seen in the ingots which were regrown, but single, smaller cigar-shaped precipitates were sometimes observed.

It is concluded that surface replication of cleaved PbTe allows the easy observation of particles which are thought to be tellurium-rich microprecipitates. It remains to corroborate measurements of this type with transmission electron microscopy of thinned crystals and possibly with reflection electron diffraction. However, because mosaic-free PbTe has so few precipitates it may prove difficult to locate them by either of these methods.

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B. J. SEALY
Department of Physics,
University of Surrey,
Guildford, Surrey, UK

Determination of the K, v diagram of epoxide resins

There is, at present, a great deal of interest in the determination of *K*, *v* diagrams of materials. The *K*, *v* diagram relates the velocity (v) of a crack to the stress intensity factor (K) which causes it to propagate. It provides a valuable method of investigating such effects as the environmentally assisted growth of subcritical cracks in glasses and ceramics; the dependence of fracture energy on crack velocity in viscoelastic polymers; and many other rate-dependent fracture phenomena.

Recently, Evans [1] has shown how the *K*, *v* diagrams of glasses and ceramics may be obtained rapidly and easily by a relaxation technique using the double-torsion specimen geometry first suggested by Outwater [2]. With this geometry the rate of change of compliance (C) with crack length (a) is constant. For such a

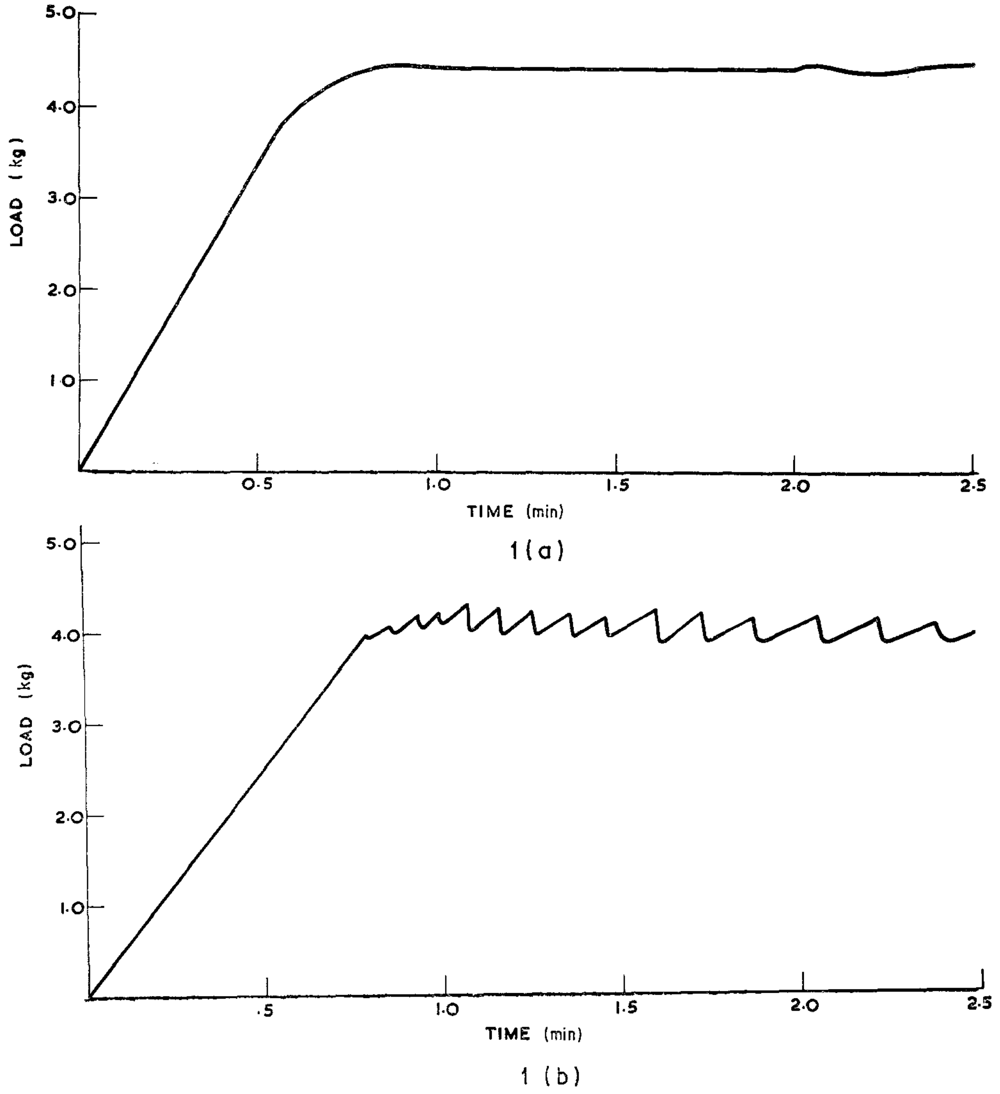

Figure 1 (a) Continuous fracture, (b) stick-slip fracture.

specimen of glass or ceramic, a crack will propagate under constant load at a fixed velocity which is determined by the rate of displacement of the loading point. This is because, for such materials, the fracture energy remains constant during the experiment. The relaxation technique relies on loading such a material rapidly so that the crack is driven at a high velocity. The loading point is then suddenly halted so that the displacement is fixed, and because the compliance of the specimen decreases as the crack grows, the load (P) and thus the stress intensity factor driving the crack decrease until the crack is finally arrested. Evans has shown that the rate of change of load with time (t) is directly related to the crack velocity at that load, and hence that the relaxation curve $P(t)$ provides all the information necessary to calculate the K, v diagram, provided the crack length which corresponds to some point in the relaxation curve is known.

We have extended this technique to obtain the K, v diagrams of a common DGEBA epoxide resin at various states of cure. Experimentally, there are two factors which complicate the technique when applied to epoxides. First,

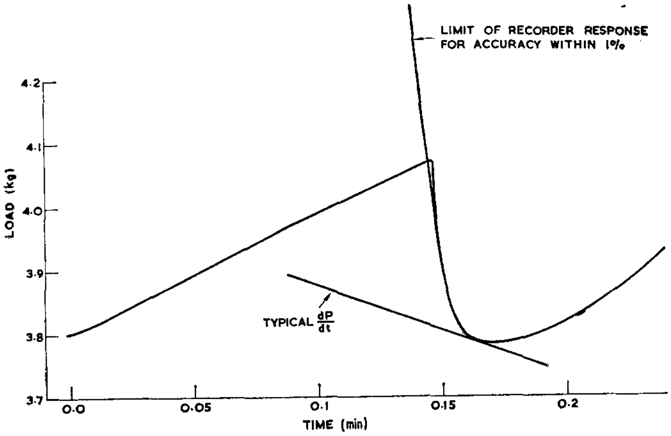

Figure 2 Stick-slip relaxation.

the resins creep and, therefore, a relaxation due to creep deformation is superimposed on the relaxation due to the propagating crack. Second, cracks in the resins do not all propagate continuously as shown in Fig. 1a; instead they frequently propagate intermittently in a stick-slip manner as shown in Fig. 1b.

The problem of creep in a K, v determination can be solved by carrying out two measurements. One on a specimen containing a sharp crack, and the other on a specimen containing a blunt crack. A suitable sharp crack may be introduced by starting a cleavage crack with a sharp razor blade. The length of the crack can be controlled by gripping the specimen in a vice so that the cleavage crack runs into a compressive stress field. A blunt crack for the control experiment can be introduced by cutting a notch of the same length with a jeweller's saw. On loading the two specimens at the same rate to the same load, two different relaxations are obtained. One is due to a combination of crack propagation and creep, $(\mathrm{d}P/\mathrm{d}t)_1$, the other is due only to creep $(\mathrm{d}P/\mathrm{d}t)_2$. The relaxation due to crack propagation alone is obtained by subtracting $(\mathrm{d}P/\mathrm{d}t)_2$ from $(\mathrm{d}P/\mathrm{d}t)_1$, both measured at the same time interval after maximum load.

When stick-slip crack propagation occurs, the relaxation technique described by Evans cannot be applied. It is, however, sometimes still possible to obtain a K, v diagram. The deflection (y) of the load point in the double-torsion specimen is

$$y = P(A_1a + A_2) \tag{1}$$

where A_1 and A_2 are constant. Since the compliance $C = y/P$ it follows that

$$A_1 = \partial C/\partial a$$

and

$$y = P\left(a\frac{\partial C}{\partial a} + A_2\right)\cdot \tag{2}$$

Differentiating Equation 1 with respect to time, gives the crack velocity

$$v = \frac{\mathrm{d}a}{\mathrm{d}t} = \frac{1}{A_1P}\left[\frac{\mathrm{d}y}{\mathrm{d}t} - A_1a\frac{\mathrm{d}P}{\mathrm{d}t} - A_2\frac{\mathrm{d}P}{\mathrm{d}t}\right]\cdot \tag{3}$$

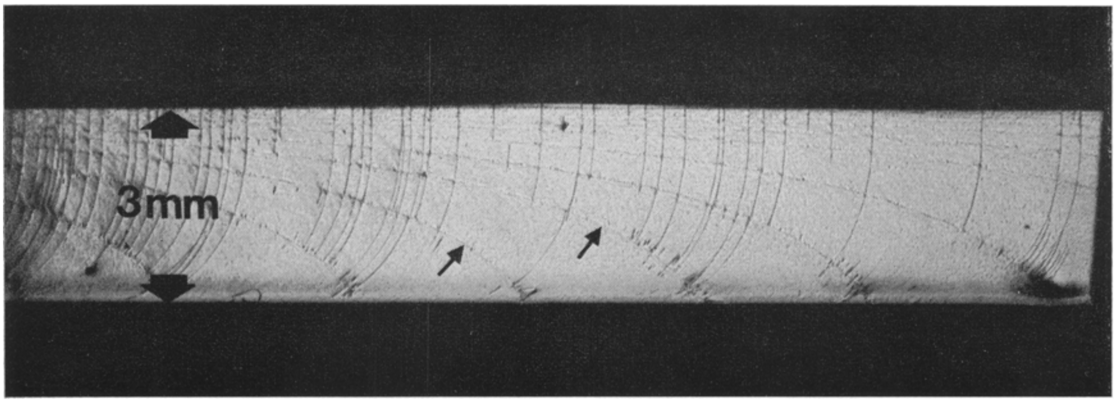

Figure 3 Crack arrest marks (arrowed).

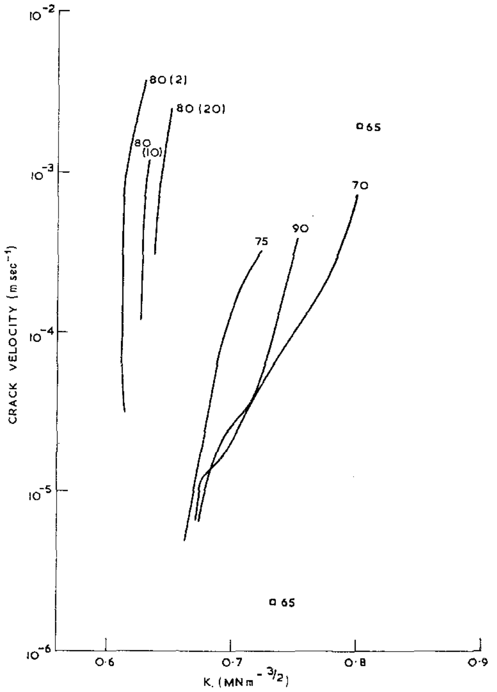

Figure 4 *K*, *v* relationships in epoxide resins.

TABLE I

Comsition	Cure schedule	Fracture mode
100:65:1	2 h at 120°C	Stick-slip
100:70:1	2 h at 120°C	Continuous
100:75:1	2 h at 120°C	Continuous
100:80:1	2 h at 120°C	Stick-slip and continuous
100:80:1	10 h at 120°C	Stick-slip and continuous
100:80:1	20 h at 120°C	Stick-slip and continuous
100:90:1	2 h at 120°C	Continuous

Constants A_1 and A_2 may be determined from a compliance calibration; dy/dt is the constant cross-head velocity of the testing machine; and a is the crack length at the point at which P and dP/dt are measured. Fig. 2 shows a stick-slip relaxation obtained experimentally by running the recording chart at a high rate and expanding the load scale. An Instron machine is very suitable for this procedure and P and dP/dt can be quite easily determined from such a relaxation. The crack length, a, at the onset of sudden fracture can be measured to a high accuracy from the fracture surface since crack arrest lines are well defined, as shown in Fig. 3. It is not possible to measure this during the rapid crack movement stage. However, in our experiments, the separation of crack arrests (Δa) was small compared with the length of the crack. We assumed, therefore, a constant crack length value for each crack arrest relaxation. Since Δa was typically 4 mm at a crack length 30 mm, the uncertainty in a was $\pm$ 7%. When used in Equation 3, this results in an error in v of less than 6%. Because the *K*, *v* diagram has a large slope, this error is tolerable. In the calculation of our data, further accuracy was achieved by taking into account the shape of the crack front (Fig. 3) by assuming the area of the crack surface to be a quadrant of an ellipse with semi-major axis equal to the crack length.

Fig. 4 shows data obtained in this way from Ciba-Geigy epoxide resin MY750 cured with MNA, accelerated by BDMA. Specimens have been prepared containing 65, 70, 75, 80 and 90 parts of MNA to 100 parts of MY750 and 1 part of accelerator, with a cure schedule of 2 h at 120°C. Additional specimens were prepared from 100:80:1 composition with cure schedules of 10 h at 120°C, and 20 h at 120°C. The mode of fracture is given in Table I. Some of the data have been obtained from stick-slip relaxation and some from the conventional relaxation. Some of the crack velocities obtained from the conventional relaxation techniques have been verified by driving the crack at a constant velocity, filming its movement, and measuring the crack velocity from the film. Good agreement was obtained.

These techniques, therefore, appear to be useful for studying the fracture of epoxides, plastics and adhesives. This work is part of a larger programme of study of the matrix dominated properties of fibre composites.

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D. C. PHILLIPS
J. M. SCOTT
Process Technology Division,
AERE, Harwell, Didcot, Oxon.