Letter

Note on the isothermal decay method for determining trap depth from glow curves

We read with interest "A review of the recent methods for determining trap depth from glow curves" by Shalgaonkar and Narlikar [1] and the subsequent letter "On the methods for determining trap depth from glow curves" by Chen [2]. It is considered that the analysis based on the shape of a glow curve over a range of temperature may be perturbed by interfering effects, such as changes in quantum efficiency, frequency factor, or emission spectra of the luminescence, and that the isothermal decay analysis is the only method unaffected with temperature. According to the former authors [1], the isothermal decay method is limited to the monomolecular kinetics and should not be used unless one is sure its application is justified. However, in our opinion, this is not limited to the first order kinetics. In the following we show that the isothermal decay analysis is also applicable to general order kinetics.

In many cases the kinetics of the luminescence should be expressible as follows,

$$I = - \alpha \frac{dn}{dt} = \alpha\beta n^m \qquad (1)$$

where $\beta = \gamma \exp(- E/kT)$, m is a suitable numerical parameter representing kinetics order and α and γ are constants. The solution of Equation 1 (for $m \neq 1$) is given by,

$$(I_0/I)^{1-1/m} = 1 + (m - 1)n_0^{m-1}\gamma t \exp(- E/kT) \qquad (2)$$

where I_0 is the initial intensity and n_0 is the initial concentration of the reaction centre. For any order other than the first, the plot $(I_0/I)^{1-1/m}$ versus time should then be a straight line as reported by May and Partridge [3], and the activation energy, E, will be directly determined from Boltzmann plots of the slope. For a first order isothermal reaction, the log I plotted against time should, of course, be a straight line and the activation energy may also be determined by Boltzmann plots as shown in [1]. The isothermal decay technique, can, therefore, be recommended as a general technique to determine the trap depth.

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Striations on the fracture surfaces of glassy polymers

A characteristic feature of the surfaces of fracture of glassy polymers is a pattern of alternating rough and smooth bands which lie in a direction approximately perpendicular to that of the crack propation; they arise during rapid. unstable fracture whether in cleavage, tension or bending tests and especially if the specimens are notched. Preceding the fracture instability the surfaces of fracture are smooth and the transition between this area and the rougher banded area is marked by a conspicuously sharp boundary line. This general pattern of fracture, shown in Figs. 1 and 2, was first noticed by Rexer [1] and later by others [2-14]; mechanisms for the formation of the bands have also been proposed [15, 16]. In a recent paper, Moskowitz and Turner [17] give an explanation of the banding based on a new phenomenon in which a crack propagating in a craze is diverted towards and then intersects with a microcrack (or advance fracture) formed close-by in another craze propagating roughly parallel with the first. As the direction of the crack propagation changes it leaves a "step" on the surface of fracture, which in their explanation would mark the beginning of the rough band, and it slows down as would be consistent with Hull's explanation of the banding [15]. The mechanism of Moskowitz and Turner, however, occurs entirely
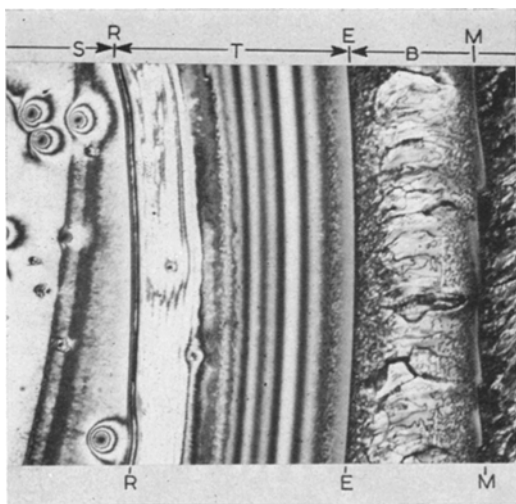
Figure 1 Surface of fracture of polystyrene. Area S: slow crack propagation; area T: transition belt with craze wedge lying on the bulk; area B: fast crack propagation, banding (or striations). The boundary line EE is the beginning of the first band, MM is that of the second band. Cleavage crack propagation left to right; reflected light, $\lambda = 546$ nm, × 62.

Figure 2 Surface of fracture of polymethyl-α-cyanoacrylate adhesive. Cleavage crack propagation from left to right; reflected light, $\lambda = 546$ nm, × 150.

at low crack speeds usually of a few centimetres per second or less whereas in all cases so far observed, in several different polymers and shown in Figs. 1 and 2 for example, the bands are formed at much higher crack speeds; it cannot explain the periodicity of the bands nor how the rough bands are formed in the first place for several reasons.

The phenomenon which they have described does show, however, one mechanism by which level differences may arise *within* the rough band *after* it has been initiated or under some conditions within the first transition belt. It is also a factor in the formation of the striations on the fracture surfaces of cast (high molecular weight) polymethyl methacrylate but which are not typical of the bands observed on the fracture surfaces of most other glassy polymers.

Observations of the banded surface of fracture show clearly that the rough bands consist of closely spaced multiple layers of cracking and crazing to a depth, in some cases, of a millimeter or so below the actual fracture surface which itself shows irregular and sharp level differences where the crack has evidently jumped from one craze to another within the multiple craze bundle. Between the rough bands the surface of fracture is relatively smooth and usually shows
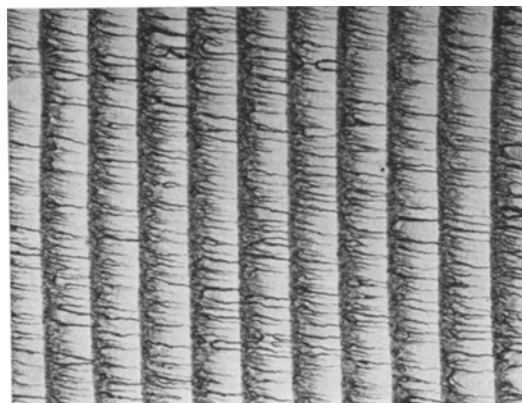
no subsurface cracking or crazing. The essential characteristics of the banding phenomenon, present in the simplest cases and shown in Fig. 1 are the periodic formation of the bands of multiple cracking and crazing and the characteristically sharp boundary line between the smooth band and the next rough band.

At low speeds a crack propagating in polystyrene (viscosity molecular weight 2×10^5) is preceded by a wedge-shaped layer of craze; the tip of the craze is very sharp while that of the crack which propagates within the craze is blunt (Fig. 3). As the craze is parted at or near its median plane the surfaces of fracture are then covered by a smooth continuous layer of craze. At lower temperatures, or if the molecular weight is higher, the stress to rupture the craze at the crack tip is increased and subsidiary or satellite crazes may be initiated in the high stress regions ahead of the crack tip, above and below the craze layer in which fracture takes place (Fig. 4). In the latter case, the fracture surfaces formed by slow cleavage fracture are again smooth but appear irridescent due to the increased reflection of light from the many parallel crazes below the fracture surfaces. In either case, as the crack velocity is increased, in a cleavage test for example, there is a change in fracture mechanism and an approximately brittle type of fracture occurs at the craze-bulk interface in the primary craze [16]. Following the detachment of the craze wedge, the crack tip is then the edge of the disrupted craze wedge; as a consequence of the change in fracture mechanism the crack tip becomes much sharper and the
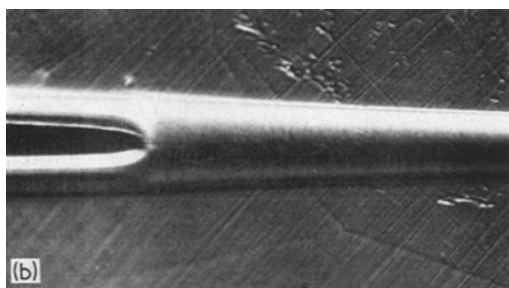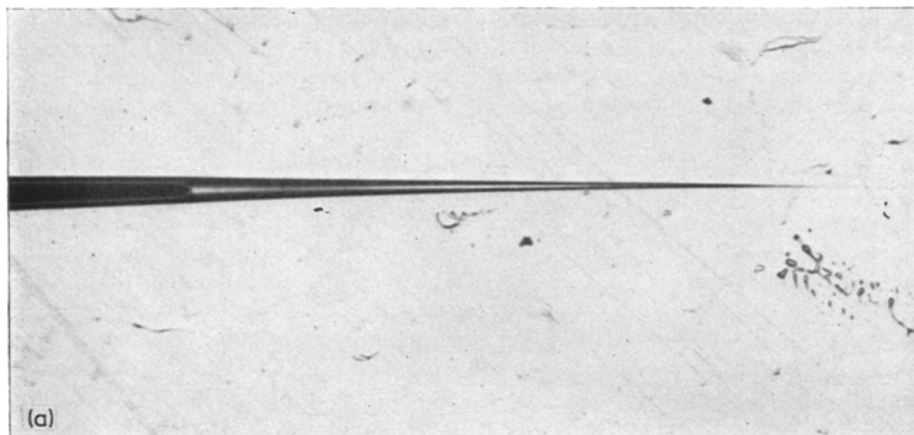
Figure 3 (a) Surface of polystyrene block, side view of crack and craze wedge advancing slowly from left to right. Reflected light, × 190. (b) Crack tip; Nomarski interference, × 780.
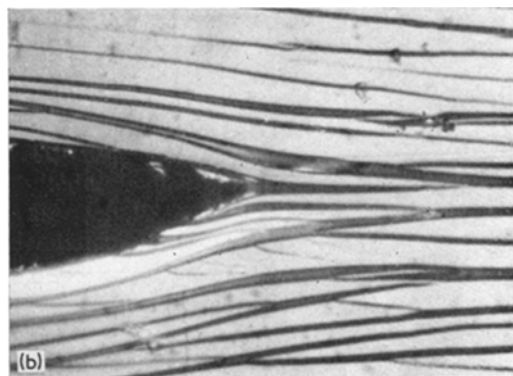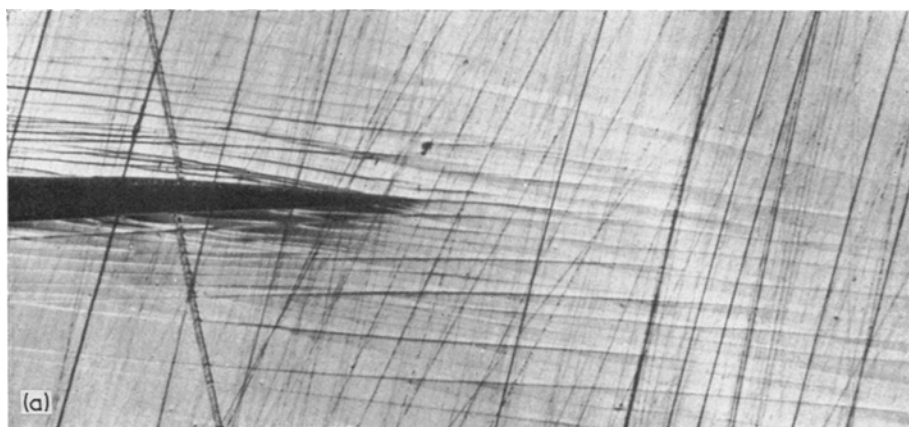

Figure 4 (a) Surface of polystyrene block, side view of crack and satellite crazes (horizontal lines) propagating slowly from left to right. Reflected light, × 80. Vertical lines are surface scratches. (b) Crack tip and satellite crazes. Reflected light × 525.

stress in the bulk ahead of the crack is suddenly and greatly increased so that many crazes and cracks are initiated in the regions around its tip. The roughness within the bands arises probably because after the detachment of the craze wedge and the sudden increase in stress concentration ahead of the crack tip, fracture is initiated at many different sites in crazes at different levels; as these cracks propagate and overlap they join up resulting in steep level differences on the surface of fracture within the band. The boundary line in the first transition belt is long and sharp because it is the edge of a single craze wedge formed during slow crack propagation and often extends continuously along the entire fracture front. After the first rough band the boundary lines are shorter and less straight because they are formed from craze wedges which have extended irregularly from the bundle of discontinuous craze layers within the preceding rough band (see Figs. 6 and 7). The presence of the multiple crazing effectively blunts the crack and slows the fracture down; one of the crazes emerges ahead of the bundle, accelerates, and the process is repeated. The bands of multiple cracking and crazing arise from the change in fracture mechanism and the consequent concentration of the stress at the edge of the detached craze wedge. The oscillation in the fracture mechanism arises because after each rough band the crack is blunted and the fracture is momentarily slowed down; the conditions are sufficient to initiate many crazes but not to propagate all of them.

In the mechanism described by Moskowitz and Turner (shown in their Fig. 3 [17]) it appears that the crack deviates into an adjacent layer (thus giving rise to a step on the fracture surface which they identify as the beginning of the rough band) by a process of rupture at about the middle of the craze layer thickness. It would follow then that the thickness of the craze layer on the surface of fracture immediately preceding the beginning of the rough band would hardly change; in addition, the appearance of the two fracture surfaces in this area would be identical, with a layer of craze of the same thickness on each. Observations of the fracture surfaces of polystyrene (PS), styrene-acrylonitrile (SAN), injection moulded polymethylmethacrylate (PMMA) and polycarbonate (PC) show that in each case the thickness of the craze layer preceding the first rough band decreases to less than a few hundred Ångstroms as would be

expected in the craze wedge detachment mechanism. In the latter, since fracture appears to be initiated simultaneously at both craze-bulk interfaces, patches of the disrupted craze layer remain attached to either one fracture surface or the other, thus giving a patchwork or tree-bark pattern.

If the presence of the advance fracture (or microcrack) in the adjacent craze layer causes the deviation of the main crack, then since advance fractures (fracture parabolas or "events" [18]) are initiated approximately at a point, the boundary line marking the beginning of the band would spread from that point. This does not appear to be so; the boundary line in the first transition belt (see for example Fig. 1) in PS and in SAN is a sharp, straight or smoothly curving line which may extend continuously through the thickness of the specimen (up to 1.9 cm thick) with no indication of having initiated at any one point along the front. In the craze wedge detachment mechanism the boundary line at the beginning of the rough band is the edge of the craze wedge. The mechanism shown in Fig. 3 of [18] applies to *slow* crack propagation in SAN polymer which fractures by continuous propagation of a bundle of crazes ahead of a crack propagating in one of them as shown in Fig. 4. In the absence of the satellite craze bundle during slow crack growth, as may occur for instance in PS or SAN at higher temperature, it would seem that the mechanism could not operate since no explanation is given for the periodic formation of craze bundles under the above conditions and yet the banding effect is observed in the usual form.

Fig. 5 shows, in reflected monochromatic light, the interference pattern in the single craze wedge ahead of a cleavage crack in a block of polystyrene and viewed from a direction perpendicular to the fracture plane; the edge of the craze wedge is at E, the crack tip is at R. The crack was "loaded" by forcing in a metal wedge but remained stationary for some time while under observation in the microscope. The loading wedge was then slowly forced again when suddenly the crack was observed to jump very rapidly forwards a small distance before coming to rest as shown in Fig. 6. It was evident, and confirmed by observation of the separated fracture surfaces later, that the sudden crack jump corresponded to the detachment of the craze wedge between RR and EE and the formation of the first rough band. Beyond EE
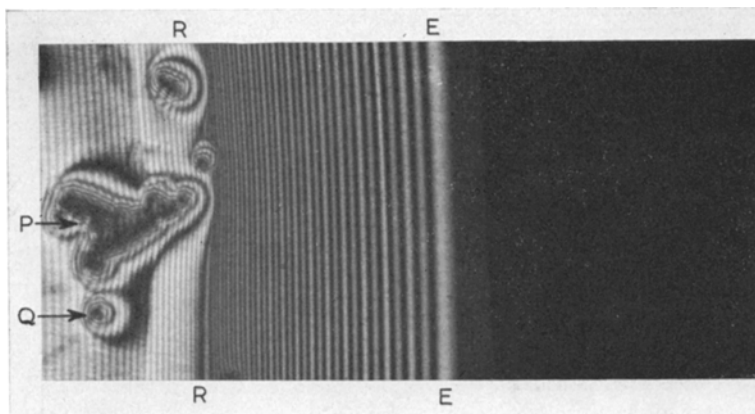
Figure 5 Interference fringes at the crack tip (RR) and in the craze wedge (RR to EE) preceding it. Viewed from a direction normal to the plane of fracture. Reflected monochromatic light, $\lambda = 546$ nm, × 65. The feature P is an "event" and Q is a fracture "parabola".
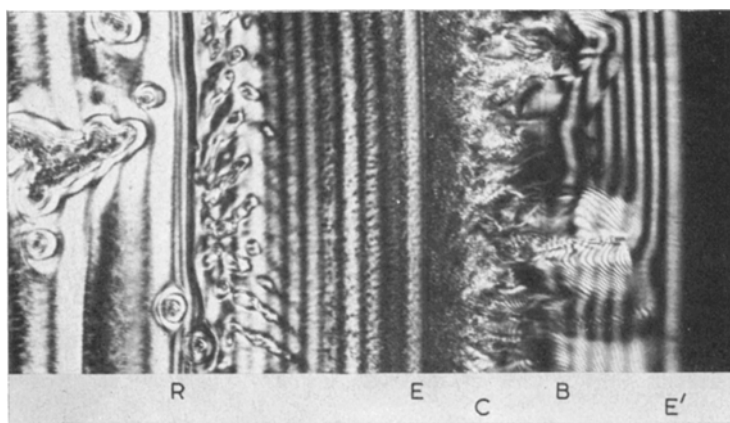

Figure 6 Same as Fig. 5 after detachment of the craze wedge between R and E. The crack tip is within the first band EB at about the position C. A new single craze wedge is developing between C and E'. Reflected monochromatic light, $\lambda = 546$ nm, × 65.

the crossing interference patterns indicate multiple layers of cracks and crazes but beyond this shattered band a single craze wedge, CE′ is beginning to form. The photomicrograph in Fig. 7 is a view of the crack shown in Fig. 6 taken at the side surface of the block. The multiple crazes which constitute the first band radiate from the point E which was the edge of the craze wedge before it was broken off the bulk; the rear of the craze wedge, R, was further to the left (off the photograph). The distribution of stress close to a crack-craze as in Fig. 3 would be quite different from that around a sharp crack in the bulk as would occur immediately after the detachment of the craze wedge. The conclusion is that the bundle of crazes radiating from E arises *after* the detachment of the craze wedge and that the latter mechanism of fracture is the cause of the banding.

The mechanism of crack jumping described by Moskowitz and Turner is dependent on a specific mechanism of craze branching which

has been observed in polystyrene and cast polymethylmethacrylate and which can occur even without the presence of the adjacent satellite crazes; it appears to be an important
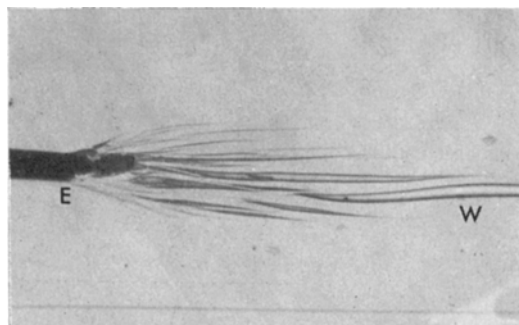

Figure 7 Same specimen as shown in Fig. 6; view of crack at side surface of polystyrene block. The edge of the fractured craze wedge was at E, a new craze wedge is forming at W. Reflected light, × 300.

factor in the striations formed on the fracture surfaces of cast (high molecular weight) PMMA as they suggest [17] but it is not the cause of the banding on the surfaces of fracture of PS, SAN, PC, polymethyl-α-cyanoacrylate, or moulding grade PMMA.

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Striations on the fracture surfaces of glassy polymers—a reply

Work on the fracture of a styrene-acrylonitrile co-polymer (SAN) [1] terminated several years ago and we are no longer in a position to review experimental procedures in the light of the interesting observations reported by Doyle [2]. Therefore, we do not have detailed information about the microstructure of the bands, i.e. striations, which would allow informed comments about their relationship to the phenomenon of crack jumping in the detail considered by Doyle in paragraph 5. In this respect it should be noted that Doyle's criticism depends on the validity of his assertion that microstructural details of the fracture surface of SAN are invariably similar to those reported by Doyle et al. in their work on polystyrene (PS) [3]. This assertion, along with its generalization to other glassy polymers mentioned in paragraph 5, clearly needs to be documented in the scientific literature.

Doyle also questions whether data obtained at low crack velocities, as are presumed to occur in the wedge technique, can be pertinent to an understanding of more common modes of fracture which involve high crack velocities. While the need for caution is acknowledged the existing evidence does indicate that this may be the case. First, in some experiments on SAN, not mentioned previously [1], the crack got out of control when the wedge was driven in and generated fracture surfaces by fast fracture. Nevertheless, the fracture surfaces appeared similar to those generated by fractures which were sufficiently slow to be followed conveniently under the microscope. However, it should be repeated that neither detailed nor documented comparisons were made because at that time this distinction had not been recognized as a significant issue. Second, in the case of PS, Doyle's own data and analysis are adduced as evidence that the wedge technique can generate fracture surfaces which are similar, apparently even in microstructural detail, to those observed after fast fracture.

The implication, in paragraph 6, that the phenomenon of crack jumping, as stated by us, is dependent on any specific mode of crazing is a misunderstanding. On the contrary, we deliberately avoided any commitment in this matter. Therefore Doyle's objection that both PS and SAN, at higher temperature, form banded fracture surfaces and yet do not display a particular form of crazing ("satellite" crazing) seems to be irrelevant to our case.

Another source of misunderstanding would arise if paragraph 1 is intepreted to mean that we have stated any views about crack deceleration

i.e. "it slows down". In fact, we are uncertain about the detailed behaviour of the crack tip relative to the cleaving of a complete band. However, in stating this, we do note that Doyle *et al.* [3] have adduced good evidence from secondary fracture markings in PS that crack acceleration occurs in one part of the band and also that Doyle now states that a sudden jump was observed under the microscope in the same region. Our usage of the word "jump" referred to the observed coalescence of the crack tip with an advanced microcrack. These distinctions may appear to be rather refined but they are made in order to deny any commitment concerning questions of crack acceleration which are regarded by Doyle *et al.* as important in deciding between their mechanism of band formation, by craze wedge splitting, and one which they attribute to Hull [4].

The main criticism offered by Doyle is that the mechanism of crack tip jumping *cannot* explain band periodicity. This criticism is valid although it would be more judicious to state that the phenomenon *does not* explain periodicity. However, it can be incorporated with additional observations and assumptions to provide explanations along the lines suggested, for example, either by Hull or by Doyle *et al.* This, in fact, is what Doyle has done in a revision of the craze wedge mechanism. Our own reticence to enter into this level of detail is due to an inability to explain certain phenomena at a gross level including periodic band formation in polymethyl methacrylate. In this case microstructural details apparently similar to those documented in PS appear as a special case observed only within a narrow range of molecular weights [5]. This observation would appear to call for a more general mechanism which would explain all cases and, more critically, account for a dependence of band spacing on molecular weight [6]. The need to explain this latter relationship was pointed out previously by Benbow [7]. It would be helpful to know whether any dependence on molecular weight is observed in PS and other glassy polymers.

Finally, apology must be made for the discursive nature of this exchange of views. To some extent this is due to a primitive means of communication involving descriptions of pictures of fracture surfaces. There is not yet any agreement about terminology and redundance in the use of terms such as "striations", "bands", "ribs" etc. Neither is there agreement about which experimental variables should be specified, chemical composition, molecular weight, sample geometry, strain rate etc. These matters seem ripe for discussion at some future conference on fractography.

Acknowledgement

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On the thermal oxidation resistance of some Intermetallic compounds

In a recent systematic study [1], Stone has reported on the thermal oxidation behaviour of several intermetallic compounds. As in his previous work on the oxidation of metals [2], he chose a parameter T_p as the index of the oxidation resistance of the material. T_p is the temperature which yields a weight change of 1 mg cm^{-2} over 4 h on thermal oxidation of the material in air. Higher T_p values would thus indicate higher resistance to oxidation and vice versa. The classification of the oxidation behaviour of various intermetallic compounds was attempted in terms of the ratio of T_p to the melting point of