

## The initiation of crazes in polystyrene

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### Summary

The formation of highly reflective assemblages of microvoids or 'crazes' by the influence of stress or solvent action is well known. These crazes are the precursors of cracks in glassy thermoplastic and in some cases stable crazes can be formed in the interior of injection moulded test specimens of polystyrene which do not lead to the immediate failure of the specimen. We have found that the ease of formation and type of internal craze formed on the application of stress is dependent on the injection moulding conditions.

We have studied the processes leading to the initiation of crazes within a glassy thermoplastic and we find that such crazes can only be initiated if the local molecular orientation is favourable. Normally in injected moulded specimens the molecular orientation is not uniform but is complex, being greater at the surface along the direction of melt flow than in the interior of the specimen. We have made detailed measurements of the changes of orientation through the specimen by both birefringence and ultrasonic modulus techniques and find, surprisingly, that in certain cases local orientation may be normal to the direction of melt flow. In such specimens crazing may be induced by stresses applied along the direction of melt flow. In specimens prepared under different processing conditions in which there is no transverse orientation then internal crazing does not occur. We have related the critical stress that will induce crazing to the extent of transverse orientation and have also measured the temperature coefficient for craze initiation with a view to determining the activation energy for the process.

The significance of these results to the fracture of oriented polystyrenes will be discussed.

### Introduction

Recent work has led to important developments in understanding the fracture processes which take place in glassy thermoplastics. In the first place there has been an extension of the Griffiths theory of fracture to include the processes which take place during the growth of a crack in a glassy polymer. This has been summarised by Berry [1, 2], and as a result we now have a fairly clear picture of the way in which a crack can propagate through a glassy plastic and of the forces involved. It turns out that the crack does not extend by a simple process of separation with the formation of a new surface as originally considered by Griffith. Kambour [3, 4, 5, 6] has shown that the growing crack is preceded by the formation of a small volume of material which has been inhomogeneously deformed so that it contains a large number of tiny spheroidal voids, this sponge like structure being called

a craze. Kambour [7, 8, 9] has also shown that the work concerned in the plastic and elastic deformation processes taking place at the crack tip constitutes the main energy sink in the process of crack propagation. The next step in understanding this type of fracture requires a better knowledge of the process of craze formation.

When a stress is applied to a glassy plastic, crazes would be expected to start at the point where the stresses are highest. In isotropic test pieces this will generally be at the surface where local imperfections can concentrate the stress. Further, the craze itself, having a lower modulus than the bulk material will cause a stress concentration at its tip, so that the process becomes auto-accelerating. Thus the application of a stress to a polymeric glass in the absence of any craze stabilizing factor leads to catastrophic fracture before very large crazes have been formed. This situation and the uncertainty which arises concerning the nature of the local stress which occurs at the point of craze initiation have so far made it difficult to investigate quantitatively the crazing process itself.

In our investigation we have taken advantage of previous studies in which it has been shown that injection moulded test pieces of polystyrene can craze internally [10]. We thought that if the conditions under which this type of crazing occurred could be defined, a clearer picture of the crazing process would have been achieved. In particular we sought information on the factors affecting craze formation, which now appears as a controlling factor in fracture.

### Experimental

Polystyrene specimens suitable for internal craze initiation were prepared by injection moulding of clear Carrinex G.P. polystyrene into a standard dumb-bell and impact bar mould (B.S.2782) under different moulding conditions (Table 1). Tensile stressing of the resultant specimens was carried out with an Instron Testing Machine. Craze initiation was detected by shining a collimated beam of light at an angle through a specimen. The first appearance of crazes caused some of the incident light to be reflected, and this reflected light was picked up by a lens and focused onto a cadmium sulphide photo-cell. The change in resistance brought about in the cadmium cell by the incident light was used to activate a switching circuit which automatically operated the event marker on the Instron giving a record of the load at which a predetermined amount of crazing occurred.

The behaviour of the two different test pieces is discussed later. It is sufficient to say here that the dumb-bell gave rise to stable internal crazes whereas the impact bar test piece always failed catastrophically.

We first thought that the different behaviour was due to residual moulding stresses of the type measured by Peiter [11]. When a test piece cools the outer part solidifies first, so that when the inside cools and contracts it generates an internal tension, which must be balanced by a compression in

the outer parts of the test piece. In order to find out whether stresses of this type were presented in our test pieces we attempted to release the outer compression by machining away the surface, and measuring the retraction of the inner portions. Within the accuracy of our measurements, no retraction was observed showing that the compressive force must be less than 50 Kg/cm<sup>2</sup> for our test specimens. As stresses of up to 50 Kg/cm<sup>2</sup> could well affect test piece behaviour we devised a more accurate technique in which we machined off one half of a dumb-bell test specimen, and attempted to measure any bending of the sample. No bending was detected, indicating the residual stresses to be less than 15 Kg/cm<sup>2</sup>.

On the other hand we found that annealing of the test specimens at 110°C for 2 hours produced gross contraction. Such behaviour is indicative of orientation in the test pieces, and this was confirmed by measuring their birefringence using a Babinet Compensator, which measures the average birefringence of a sample. We then devised a method for determining the variation of birefringence across a sample by measuring its retardation (using a Babinet Compensator) as a function of sample thickness. The sample thickness is gradually reduced by careful milling, and a plot of retardation as a function of sample thickness produced. Numerical differentiation of this plot by Rutledge's method [12] gives the birefringence of points across the sample, and allows birefringence versus thickness plots to be constructed.

As we feared that the milling away of the sample might interfere with its orientation, we adopted the same machining procedure using samples of isotropic poly(methyl methacrylate), as isotropic polystyrene was not readily available. Fig. 1 shows our results, birefringence being plotted against sample thickness for different cutting speeds and feed rates. The cutting speed and feed rate used for the actual measurements (525 r.p.m. and 6.4 cm.min<sup>-1</sup>) appear to have little effect on the sample orientation as long as a very small amount is cut away (generally less than 0.001 in per cut). The conclusions reached from the orientation work are discussed later.

We decided to investigate the effect of temperature and strain rate variation on the crazing behaviour of dumb-bell test specimens. Strain rate variation is easily accomplished with an Instron testing machine and a range of rates from  $6 \times 10^{-4}$  to  $4 \times 10^{-1}$  sec<sup>-1</sup> were employed. Temperature variation within the range 65°C to -75°C was achieved with an Instron Environmental chamber. Crazing stresses were determined for standard test pieces in the manner previously described.

### Results and discussion

In the course of early experiments it became clear that stable internal craze structures of the type discussed by Haward and Mann [10] could be developed in several types of injection moulded specimens. Depending upon the moulding conditions it was possible to cause specimens either to form

stable internal crazes or to fail in a brittle fashion from a crack initiating at the surface.

Our attention was therefore first directed into establishing why these two different behaviours are observed. We thought, at first, that stresses produced by differential cooling during injection moulding might explain the observations. Dumb-bell specimens (which crazed internally) of comparatively thin cross section, would chill quickly and residual stresses should be frozen in, whereas the larger impact bar specimens would allow greater self annealing of the stresses. We thought that the compressive surface stresses produced by cooling would allow the interior of the dumb-bell test piece to reach a stress at which crazing occurred before the outside layer. However, our investigation showed that residual moulding stresses were small, and we concluded that they must be less than  $15 \text{ Kg/cm}^2$ .

Our attention was subsequently directed towards establishing the extent and distribution of molecular orientation of polymer chains within the bulk of the material and to see what effect this might have on the subsequent crazing and fracture behaviour.

Molecular orientation along the direction of flow of thermoplastic melts is well known [13] and such orientation is often frozen into a moulding particularly if the rate of cooling is relatively high. Although it has been generally assumed that the orientation will be at a maximum at the surface of such a moulding, apart from some measurements by Ballman [14] few attempts have been made to measure this orientation, or to relate it to the subsequent behaviour of the material.

The molecular orientation function cannot yet be directly measured for amorphous materials but the measurement of birefringence can be used as a guide to the average orientation within the material [15]. Polystyrene exhibits negative birefringence in the direction of orientation parallel to its molecular axis, since its refractive index transverse to this direction is greater than its refractive index along the chain.

By using the milling techniques already discussed we have been able to measure the birefringence of moulded polystyrene specimens as a function of the thickness of the moulding. A typical result for a standard (B.S.2782) dumb-bell test piece is shown in Fig. 2. Here it can be seen that the internal molecular orientation of the moulding is very complex. Near the surface the orientation is high and is parallel to the direction of melt flow while a short distance in from the surface the orientation is preferentially in the transverse direction. There are in this case four separate symmetrical regions of positive birefringence corresponding to transverse orientation within the thickness of the specimen. The application of a suitable stress to this particular test piece caused it to form stable internal crazes. The stress at which crazes were first observed is subsequently referred to as the crazing stress. Careful microscopic examination of these crazes showed that across the thickness of the dumb-bell two typical craze lengths develop

in the positions indicated in Fig. 2. The positions and lengths of these crazes suggest that the short crazes were initiated near the central areas of positive birefringence while the longer crazes had their origin in the larger regions of transverse molecular orientation near the surface.

Other specimens prepared under conditions such that only two positive birefringent peaks are observed gave only crazes of a single length.

By manipulating the injection moulding variables such as melt and mould temperature, injection pressure and cycle times, it was possible to change the birefringence thickness relationship over wide limits. Both impact bars and dumb-bell test pieces could be prepared with positive internal birefringence peaks, and in the latter specimens the size and number of these peaks could also be varied. Further, both types of specimen could be produced so that no positive birefringence were observed, a typical example for a dumb-bell being illustrated in Fig. 3.

In the latter case in which this pattern of no transverse orientation was noted, application of stress to the system caused the sample to fracture without prior internal crazing. Fracture appeared to have initiated at the surface and spread catastrophically across the specimen. Some of the data that has been accumulated on the birefringence-crazing behaviour is illustrated in Table 2 in which moulding conditions and subsequent crazing behaviour of both impact bar and dumb-bell specimens are tabulated.

Qualitative observation suggested that the crazing stress decreased as the positive birefringence became more pronounced. This was found to be the case, as results of crazing experiments on a number of dumb-bell test pieces prepared under conditions detailed in Table 1 show, a straight line relationship between crazing stress and birefringence being observed (Fig. 4). Extrapolation of this line to zero birefringence gives a figure of  $430 \text{ Kg/cm}^2$  for the crazing stress of unoriented polystyrene.

The correlation we have shown between direction of orientation and ease of crazing is supported by the evidence of several other workers, namely Maxwell and Rahm [16] and Kline *et al.* [17]. Thus there is now strong reason to believe that a correlation exists between stress crazing and molecular orientation transverse to the applied stress. We believe that it is comparatively easy to form a craze by stressing a material perpendicular to its direction of orientation, and very difficult to form one by stressing a material in the direction of its main orientation. Crack propagation studies in these laboratories would support these ideas, since it is generally not possible to propagate a crack transverse to the direction of orientation of hot stretched polystyrene or poly (methyl methacrylate) [18]. Presumably this is due to the impossibility of crazed structures forming in the transverse direction, and therefore the impossibility of cracks propagating.

Since we have shown that the stress required to generate a visible craze depends on the local conditions of orientation we must assume that the

only representative condition for measuring crazing stress would be in isotropic material. On the other hand, we found that test pieces without positive internal birefringence did not form stable crazes but broke catastrophically from an edge. We therefore decided to work with specimens having a small amount of positive birefringence in which the crazing stress would differ insignificantly from that obtained by extrapolation to zero birefringence. A large number of specimens of this type were prepared for use in the work described below.

As with most mechanical properties of visco-elastic materials craze structure and crazing stress are markedly affected by both temperature and rate of straining. At high temperatures (65°C) the gross structure of typical polystyrene crazes is much coarser and more granular than those formed at room temperature, while those formed at -75°C are very fine. Typical photographs of such crazes produced at different temperatures are shown in Fig. 5.

As temperatures are increased and the strain rate decreased so the stress required to initiate crazed structures decreases. These effects are illustrated in Fig. 6. At lower temperatures the effect of strain rate is much less marked, as might be anticipated. The factors which are concerned with this crazing process may be elucidated in a number of ways. In the first place, by plotting crazing stress against temperature (Fig. 7) we see that the value for the crazing stress obtained falls to zero at about the glass transition temperature of the material at the strain rate used. The same behaviour is observed for the compressive yield stress plotted on the same figure, from the data of Binder and Muller [19]. This supports the concept that the crazing process is essentially one of plastic yielding. The interaction of strain rate and temperature may also be represented as by Sternstein and Sims [20] by an Arrhenius plot and described in terms of an activation energy for the craze propagation process. The value they obtained for poly (methyl methacrylate), 20 kcal, compares with our results of 30-32 kcal for polystyrene and those of Bucknall [21] who has used the data of Maxwell and Rahm [16] to calculate the energy of activation of formation of crazes in polystyrene as 35 kcal.

For specimens with internal crazes, stresses appreciably higher than the crazing stress may be required to cause ultimate failure of the specimen. However, there is a considerable difference in the fracture behaviour of specimens in which the internal crazes have been generated at one temperature and then subsequently fractured at another temperature. Some results of this kind are contained in Table 3. Here samples pre-crazed at temperatures lower than that at which fracture stress measurements are made break at consistently higher stress levels than those pre-crazed at the fracture temperature or higher.

This raises a point of some importance in relation to the fracture of the specimens as a whole. It is apparent that a specimen which has crazed at a

temperature of -75°C is actually stronger than an uncrazed test piece, when broken at a higher temperature. At first sight this seems an improbable result since there is no obvious reason why, at 65°C, new crazes should not be formed. For this to happen it is not only necessary that the low temperature crazes should be ineffective as stress concentrating agents, but also that the low temperature crazing process should have a small reinforcing effect. We would suggest that this is the result of the expansion which takes place when the large number of low temperature crazes are formed. This puts the internal part of the specimen into a state of compression which must be overcome before more crazes can be initiated or the low temperature craze enlarged. It must be noted however, that this effect could also be explained if the low temperature crazing process had used up the limited number of favourable sites for craze initiation. On the other hand, the fact that pre-crazing at a higher temperature leads to a weaker test piece must mean that the high temperature crazes are more effective in initiating fracture.

These experiments showing the inter-relationships between craze initiation and growth and the presence of orientation within the sample are obviously of interest in developing the study of fracture processes of polymeric glasses. We are endeavouring to follow up these experiments by measurements of crack propagation in oriented glassy and crystalline polymers, by investigating the morphology of crazes, and also by a study of the nature of flow of polymer melts into moulds and its relevance to the properties of oriented specimens.

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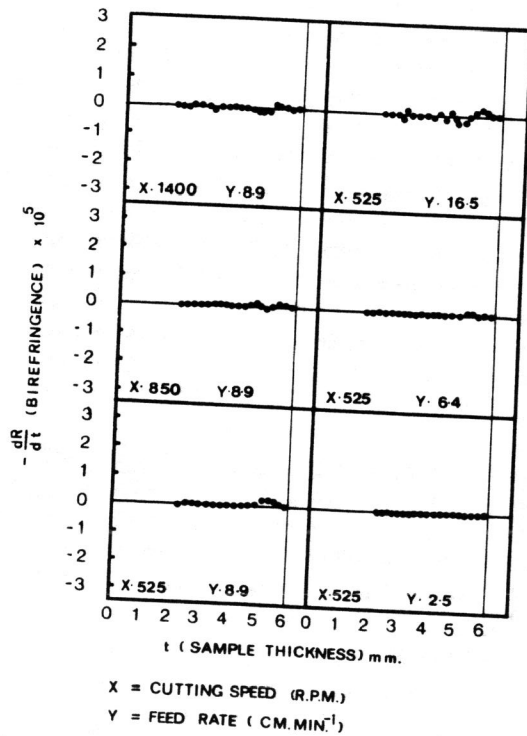
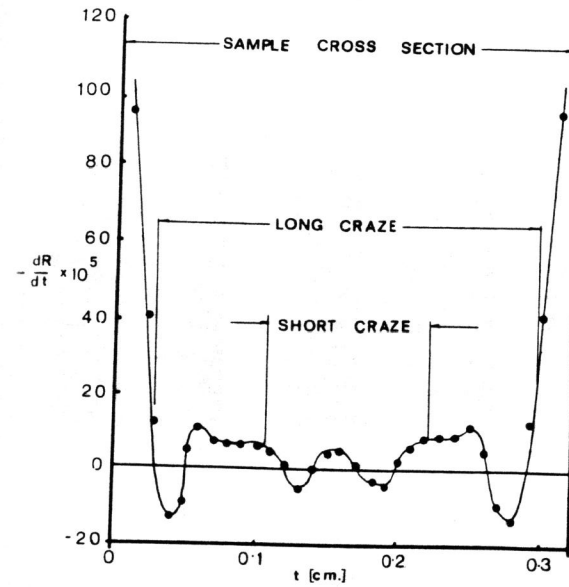


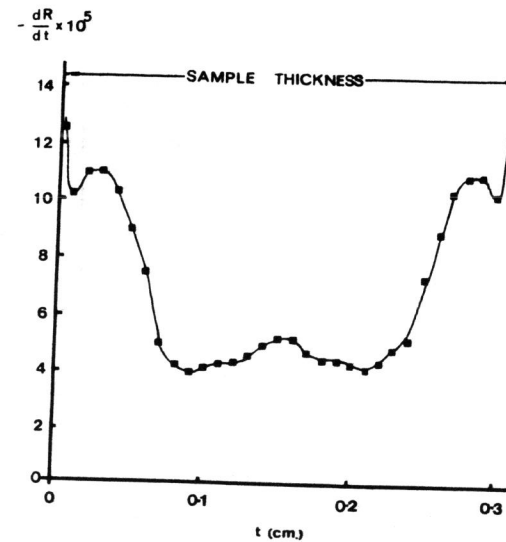
Fig. 1. Effect of milling on the birefringence of isotropic test pieces.

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*show internal crazes.*

Fig. 2. Birefringence distribution of a dumb-bell test piece (positive internal birefringence present).



*typical of specimen which crazes from outside*

Fig. 3. Birefringence distribution of a dumb-bell test piece (positive internal birefringence absent).

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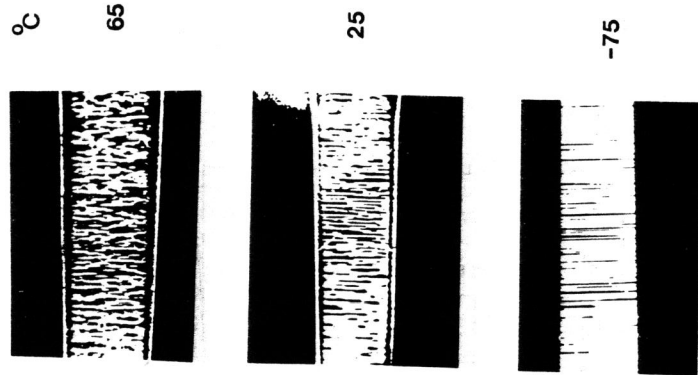


Fig. 5. Photographs of crazes produced at different temperatures.

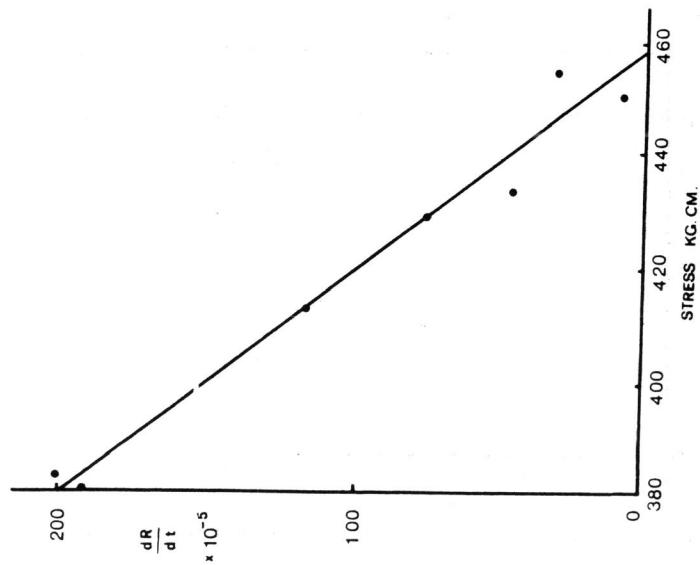


Fig. 4. Crazing stress versus maximum positive internal birefringence for a series of dumb-bell test pieces.

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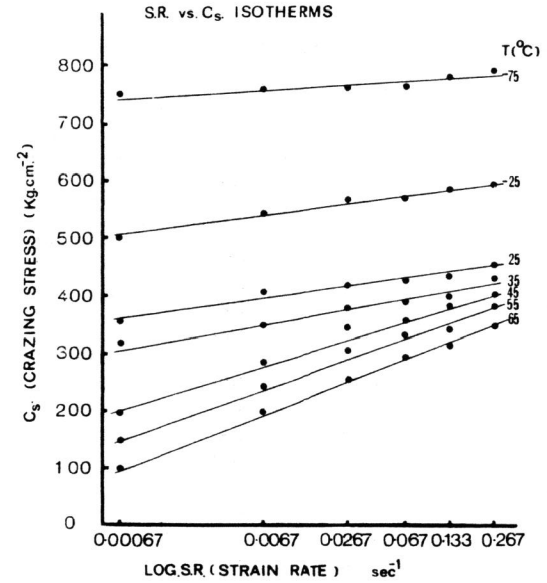


Fig. 6. Crazing stress versus rate of strain and temperature for standard dumb-bell test piece.

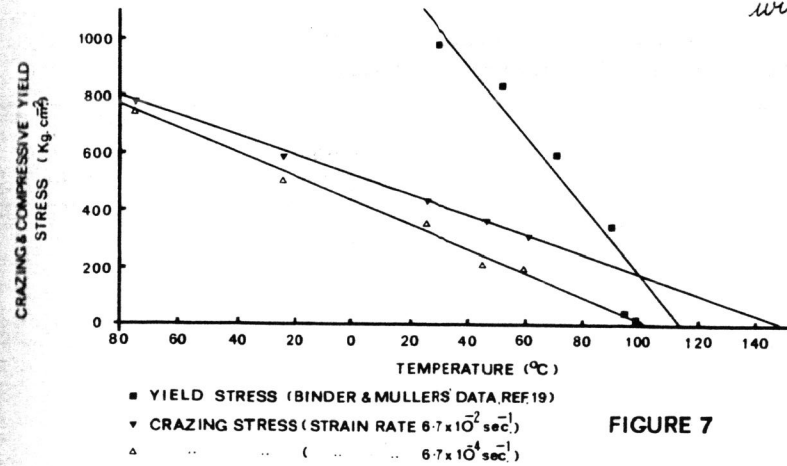


FIGURE 7

Fig. 7. Crazing stress/temperature relationship of dumb-bell test piece at two different strain rates. The yield stress/temperature relationship obtained by Binder and Muller [19] is shown on the same axes.

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Table 1  
Moulding conditions dumb-bell and impact bar specimens

Sample	Mould temp. (°C)	Inj. press (p.s.i.)	Melt temp. (°C)	Inj. time (sec)	Cooling (sec)
A	22	1000	180	15	15
B	22	1000	230	15	30
C	22	1000	300	15	35
D	22	500	230	15	15
E	22	500	300	15	35
F	22	250	300	15	35
G	50	1000	180	15	25
H	50	1000	230	15	35
I	50	1000	300	15	35
J	50	500	230	15	30
K	50	500	300	15	35
L	50	250	300	15	35
M	70	1000	180	15	35
N	70	1000	230	15	35
O	70	1000	300	15	35
P	70	500	230	15	35
Q	70	250	300	15	35

Table 2  
The effect of birefringence distribution on the crazing behaviour of dumb-bell and impact bar samples

Dumb-bell sample (see Table 1)	Internal birefringence (see Key)	Crazing behaviour (see Key)
A	1	3
B	1	3
C	1	3
D	1	3
E	1	3
F	1	3
G	2	4
H	1	3
I	1	3
J	2	4
K	2	4
L	1	3
M	2	4
N	2	4
O	1	3
	1	3

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Table 2-(contd.)

P	1	3
Q	2	4
A (Impact Bar)	1	3
K (Impact Bar)	2	4
Q (Impact Bar)	2	4

Key

1. Positive Internal Birefringence Present
2. Positive Internal Birefringence Absent
3. Crazes internally
4. Crazes externally/fractures

Table 3  
The effect of pre-crazing and temperature on the fracture stress of dumb-bell test pieces

Pre-craze temperature °C	Fracture temperature °C	Ultimate fracture stress Kg/cm <sup>2</sup>
65	65	370
25	65	390
-75	65	420
No pre-craze	65	380
65	25	580
25	25	640
-75	25	660
No pre-craze	25	645
65	-75	730
25	-75	860
-75	-75	910
No pre-craze	-75	900