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Crazing Behaviour in Oriented Poly(ethylene terephthalate)

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A study has been made of the two types of crazes formed in oriented sheets of poly(ethylene terephthalate). The crazes have been termed tensile crazes and shear crazes. The tensile crazes formed parallel to the initial draw direction (IDD) whereas the shear crazes formed in a direction close to that of the deformation bands observed when the material yields.

The possibility of applying a yield criterion to shear craze formation has been examined and there appears to be fairly good agreement between theory and experiment. Measurements of crazing stress on the tensile crazes indicated that the criterion for tensile craze formation is not purely dependent on the component of stress normal to the extended chains.

It is concluded that the two types of crazes are formed by two quite different mechanisms, although the exact nature of these mechanisms is still uncertain.

1. Introduction

Since Sauer, Marin and Hsiao's paper [1], there have been a large number of publications describing crazing behaviour in amorphous polymers such as poly(methyl metacrylate) and polystyrene. None of these papers, however, refers to crazing behaviour in anisotropic crystalline polymers such as poly(ethylene terephthalate), (PET). While examining the yield behaviour of 5:1 drawn PET, Rabinowitz (unpublished) observed that, under certain conditions, specimens can become opaque. This opacity was interpreted as being due to crazing of the material.

As a result of these observations, a detailed investigation into crazing in anisotropic PET is now in progress. Experiments on 2:1 drawn PET at 60° C have revealed what are thought to be two distinct types of crazing. The first type, referred to as tensile crazes, form parallel to the initial draw direction (IDD). The second type, referred to as shear crazes, form along a direction which is almost parallel to the deformation bands observed at yield. The shear crazes, as their name suggests, exhibit shear which is absent in tensile crazes. The two craze types are found to form at different stresses.

In this paper, the two types of craze are described in detail, and the possible stress criteria for their formation are discussed.

2. Experimental

2.1. Material

Oriented poly(ethylene terephthalate) sheet was provided by ICI Ltd. The sheet was prepared from isotropic sheet by passing it through heated rollers and drawing it out at constant width as it cools in a temperature gradient, a process which approximates to cold-drawing. The experiments were done on dumb-bell shaped specimens pressed from sheets of nominal draw ratio 2:1. The specimens were cut at various angles, θ, to the IDD. The gauge length of each specimen was 25 mm and the gauge width 4 mm. The thickness varied from 0.40 to 0.55 mm.

2.2. Apparatus

The tensile tests were done on an Instron Tensometer at a strain rate of 0.12 min^{-1}, in an environmental cabinet which maintained the specimens at a temperature of 60° C. The specimens were held in simple grips with universal joints. A bending beam load cell measured the load on the specimens, and this load was monitored on a

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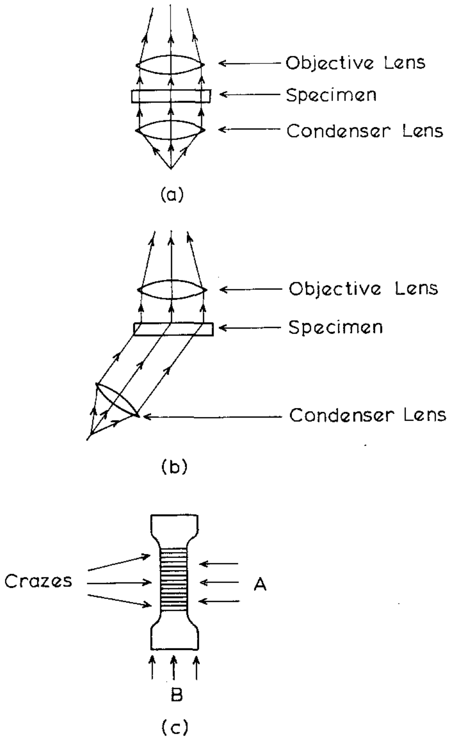

Figure 1 Microscopic examination of crazed PET. (a) Transmitted light; (b) scattered light; (c) orientation of illumination with respect to the crazes.

chart recorder.

The crazes were observed under a microscope. By using the microscope normally, in transmitted light, scratches were often mistaken for crazes. By allowing the light to strike the specimens at an angle, and viewing the light scattered by the crazes, this source of error was considerably reduced (figs. 1a and b).

In fig. 1c, the crazes are invisible if the light is coming from the direction A. It is only after the specimen is rotated so that the light comes from the direction B, that the crazes become visible. This factor becomes important when viewing crazes which have formed at different angles in the same specimen. By merely rotating the specimen, one set of crazes can be made invisible.

3. Results and Discussion

The microscopic examination of the specimens suggested that two quite different types of craze had formed in the material, referred to in this paper as tensile and shear crazes. Since the two mechanisms responsible appear to be in no way connected, the two phenomena will be discussed separately.

3.1. Tensile Crazes

Tests were done on specimens for values of θ ranging from 0° to 90° Tensile crazes were observed for $\theta = 90°$, $\theta = 75°$, and in a few specimens for $\theta = 60°$ No tensile crazes were seen for $\theta < 60°$ The main characteristic distinguishing tensile crazes was the fact that they always formed parallel to the IDD. Sternstein [2] has suggested that crazes in amorphous polymers form perpendicular to the major principal stress, and this is observed in poly(methyl methacrylate) Hsiao and Sauer [3] showed that in bending tests on polystyrene, crazes formed normal to the direction of maximum tensile stress. They attempt to explain this with a theory based on the orientation of molecular domains. Initially all the domains are randomly oriented. Under the action of a uniaxial stress all the domains try to reorientate themselves parallel to the stress direction, except for those domains which happen to lie normal to this stress, since they are physically incapable of reorientating themselves. Instead, neighbouring domains which are so oriented, separate and form microvoids which ultimately develop into crazes, which of course lie normal to the stress direction. In anisotropic material, however, this reorientation process is very much harder and it seems reasonable to suppose that the domains will find it easier to separate, forming crazes parallel to the preferred orientation of the domains (IDD), than to reorientate themselves.

The lengths of the crazes formed in this way vary from 10 to 100 μm, and are shown at two levels of magnification in figs. 2 and 3. There appeared to be an upper limit of 100 μm on the length of craze, which suggests an intensive strain-hardening mechanism. The stress at which they first formed was approximately 80% of the yield stress. Specimens which were loaded to yield did not show any crazes of lengths appreciably longer than those specimens observed immediately after crazing had started, but the total population of crazes had increased. It therefore appears that the measured "crazing" stress is the stress required for initiation rather than propagation of crazes.

Tests made on 5:1 drawn PET failed to produce any crazing on clean specimens. If the specimens were lightly squeezed between the fingers leaving a fingerprint on the surface, a craze pattern formed on applying a stress. The pattern showed up the details of the fingerprint, but crazes did not appear anywhere else on the

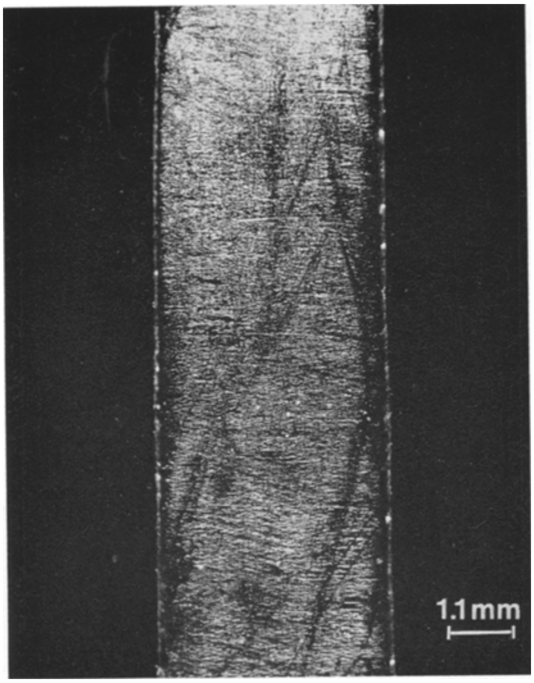

Figure 2 Tensile crazes in 2:1 drawn PET for $\theta = 90°$.

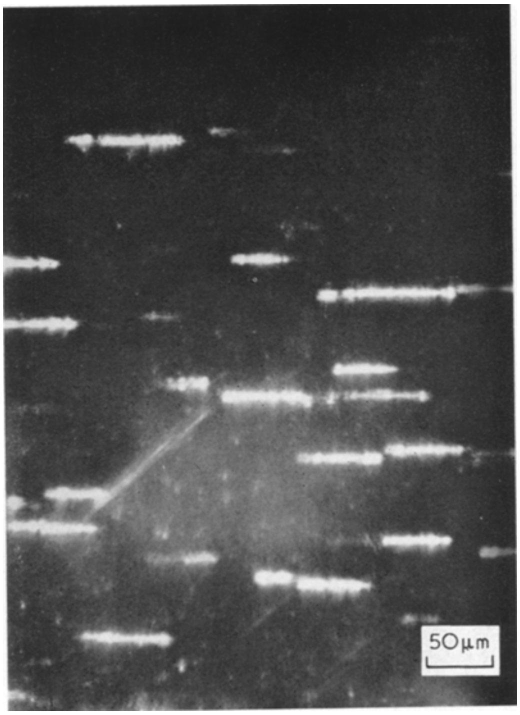

Figure 3 Tensile crazes in 2:1 drawn PET for $\theta = 90°$.

specimen. Clearly the condition of the surface is very important in crazing experiments. It seems that these tensile crazes, like crazes formed in amorphous polymers, start at the surface, and presumably grow inwards.

Measurements were made of the stress at which crazing first appeared, the crazing stress, in specimens for $\theta = 90°$ and $\theta = 75°$, and they showed that the stress for $\theta = 75°$ was less than that for $\theta = 90°$. This is a surprising result. Sternstein [2] suggested that the criterion for craze formation depended on the component of stress normal to the crazes. On his reasoning it would be expected that the stress for $\theta = 75°$ would be higher than for $\theta = 90°$. Clearly, in anisotropic material at any rate, there are other factors which must affect the crazing stress; factors not taken into account by Sternstein.

The similarity between crazes and cracks has often been remarked on, the only difference being that crazes, instead of forming two *surfaces*, do in fact form two *interfaces*, which form a sandwich with a thin plate-like region of low density polymer and the mother polymer [4].

If the criterion is as Sternstein suggests, it clearly requires modifications. One of these could be the introduction of a term to take shear into account. Although it has not been detected so far, there may be some shear involved in the crazing process. This is at present being examined.

3.2. Shear Crazes

In addition to the tensile crazes, crazes formed along directions close to the direction of the deformation bands (fig. 4). Their appearance (fig. 5) suggests that some shear was taking place, and the crazes are referred to as shear crazes.

Comparing figs. 3 and 5 reveals several differences between the two types of crazing. When a void or crack first forms in a material under tension, it is normally expected to be elliptical in shape. The tensile crazes in fig. 3 are unusual in this respect as they appear to be more rectangular. The shear crazes, on the other hand, have the appearance of elliptical openings which have consequently sheared. Also, the shear crazes are much longer than the tensile crazes, often several hundred microns long.

It was found that shear crazing occurred at a slightly higher stress than tensile crazing. Shear crazing was seen in specimens of all orientations from $\theta = 0°$ to $\theta = 90°$. It was found that, in those specimens that were loaded to yield, the

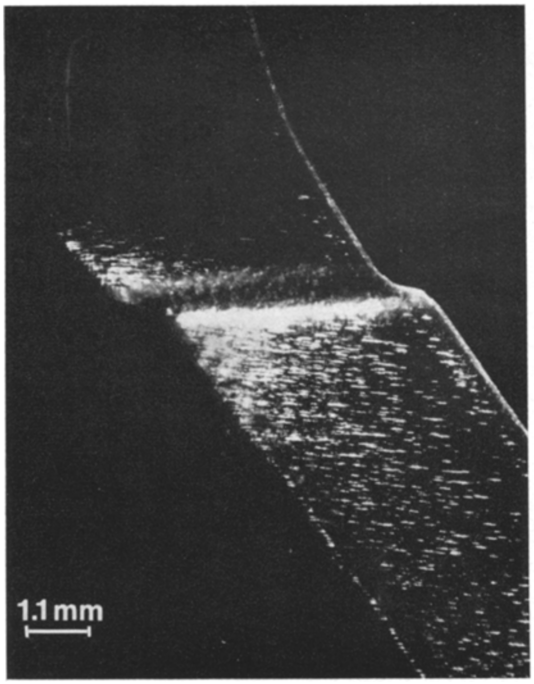

Figure 4 Shear crazes and deformation band in 2:1 drawn PET for $\theta = 90°$.

Figure 5 Shear crazes in 2:1 drawn PET for $\theta = 90°$.

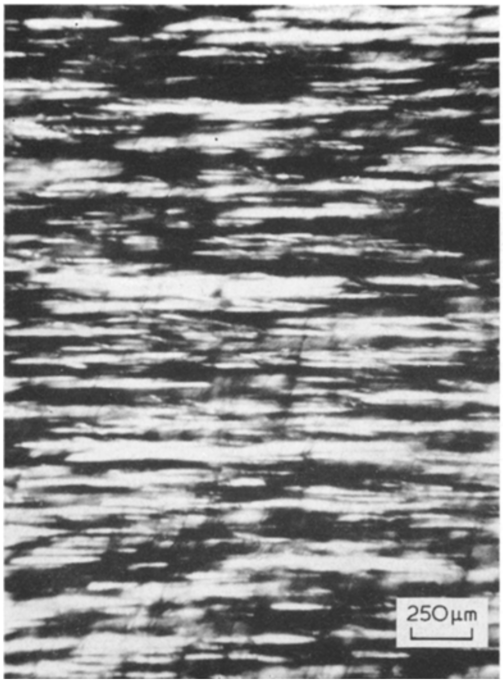

Figure 6 Concentrated shear crazing in 2:1 drawn PET for $\theta = 90°$.

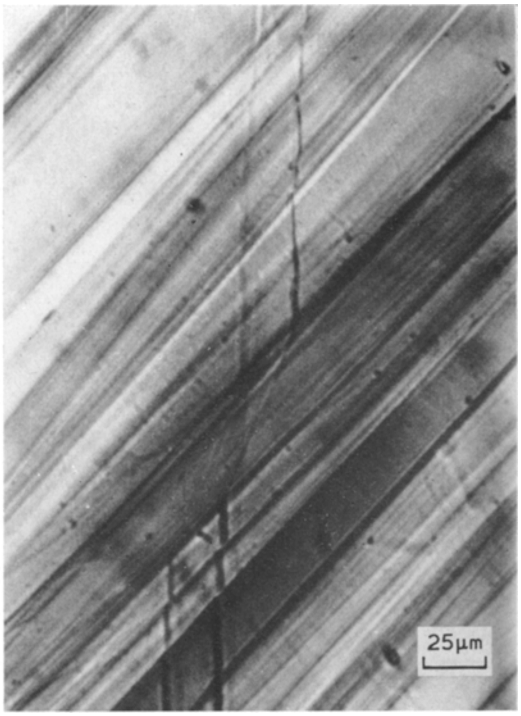

Figure 7 Scratch sheared by shear crazes in 2:1 drawn PET for $\vartheta = 45°$ (transmitted light).

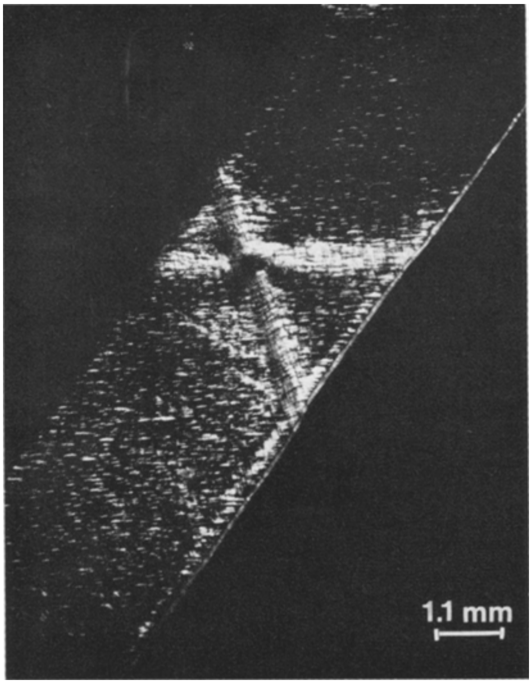

Figure 8 Shear crazes themselves sheared by a deformation band in 2:1 drawn PET for $\theta = 90°$.

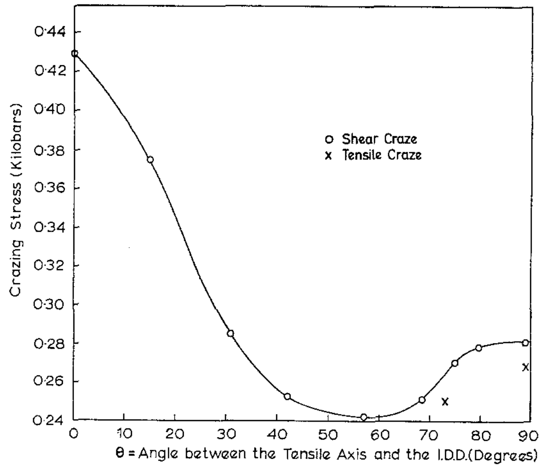

Figure 9 Crazing stress plotted against θ (angle between the tensile axis and the IDD) for 2:1 drawn PET.

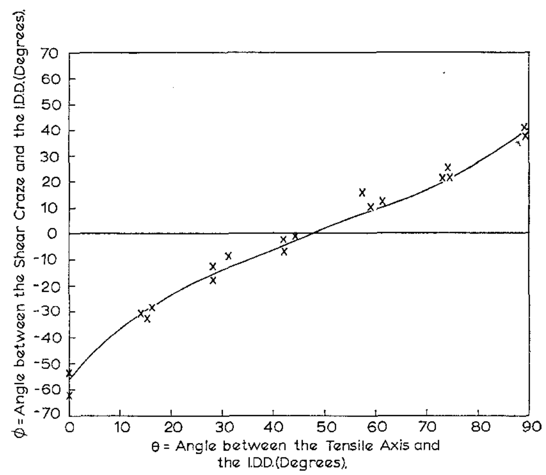

Figure 10 ϕ (angle between the shear craze and the IDD) plotted against θ (angle between the tensile axis and the IDD) for 2:1 drawn PET.

deformation band formed in the region of most concentrated crazing. Fig. 6 shows some dense shear crazing. The crazing is so concentrated that many of the crazes are merging together.

Light scratches made on the surface of some of the specimens confirmed that there is appreciable shear associated with shear crazing (fig. 7). The shear strain is unity at one point. Fig. 8 shows some shear crazes being themselves sheared by a subsequent deformation band. It can be seen that apart from the shear displacement, the crazes appear to be undisturbed by the formation of the deformation band.

The shear crazes appeared to initiate near the edges of the specimens, presumably owing to the presence of rough edges formed during the cutting of the specimens, acting as centres of stress concentration.

Measurements of the crazing stress and the craze angle (angle between the crazes and the IDD) were made, and are shown in figs. 9 and 10. The tensile crazing stress measurements are also shown for comparison in fig. 9. There is a marked resemblance between these results and the corresponding yield stress and band angle curves for deformation bands [5]. One marked difference is that fig. 9 shows a broad minimum which is absent in the yield stress curves. In addition, two branches to the band angle curve have previously been observed, and these have been referred to in the deformation band case as "slippy" and "kinky" bands [6].

Experiments did show that a second branch of craze angles did appear in a few specimens although detailed measurements of these were not made, and they are therefore not shown in fig. 10. This second branch would correspond to the "kinky" branch of solutions for the deformation bands.

There being so many points common to shear crazing and yielding, the search for a shear crazing criterion should clearly start with the yield criterion, and attempts should be made to see if it can be applied directly to shear crazing, and if not, what modifications would be necessary in order that it can.

3.3. Shear Craze Criterion

Brown, Duckett and Ward [5] have shown that a modified Hill theory can be used to describe the yielding process in oriented PET. In order to account for the difference between the tensile and compressive yield stresses, it was proposed that there is an internal compressive Bauschinger stress, σ_i, which is a function of the anisotropy of the material.

The criterion on Hill's theory [7] is

$$F(\sigma_y - \sigma_z)^2 + G(\sigma_z - \sigma_x)^2 + H(\sigma_x - \sigma_y)^2 + 2L\,\tau_{yz}^2 + 2M\,\tau_{zx}^2 + 2N\,\tau_{xy}^2 = 1 \quad (1)$$

where 0_x, 0_y, 0_z are mutually orthogonal axes drawn in the material, 0_x parallel to the IDD, and 0_y in the plane of the sheet. F, G, H, L, M, N, are unknown constants.

For a uniaxial stress σ applied at an angle θ to the IDD,

$$\begin{aligned}\sigma_x &= \sigma\cos^2\theta - \sigma_i\\ \sigma_y &= \sigma\sin^2\theta\\ \tau_{xy} &= \sigma\sin\theta\cos\theta\\ \sigma_z &= \tau_{xz} = \tau_{yz} = 0\ .\end{aligned}$$

The criterion becomes

$$\sigma^2[(G+H)\cos^4\theta + (F+H)\sin^4\theta + 2(N-H)\sin^2\theta\cos^2\theta] + 2\sigma\,\sigma_i[H\sin^2\theta - (G+H)\cos^2\theta] + (G+H)\,\sigma_i^2 = 1\ . \quad (2)$$

The direction of the deformation band is that direction in the material which is neither extended, contracted, nor rotated during the deformation. Using the anisotropic equivalent of the Lévy-Mises equation, the direction of the deformation band [5] is given by

$$[(F+H)\,\sigma\sin^2\theta - H\,\sigma\cos^2\theta + H\,\sigma_i]\tan^2\beta + 2N\,\sigma\sin\theta\cos\theta\tan\beta + [(G+H)\,\sigma\cos^2\theta - (G+H)\,\sigma_i - H\,\sigma\sin^2\theta] = 0 \quad (3)$$

where β is the angle between the deformation band and the IDD.

The unknown constants are found by solving four simultaneous equations. These equations are obtained by fitting equation 2 to the experimentally observed values at $\theta = 0°$, $45°$, and $90°$, and fitting equation 3 at $\theta = 45°$.

Values of σ_i can be determined by comparison of the yield stress in tension and compression. Measurements made by Rabinowitz (unpublished) showed that for 2:1 PET at 60° C, $\sigma_i = 0.08$ kbar.

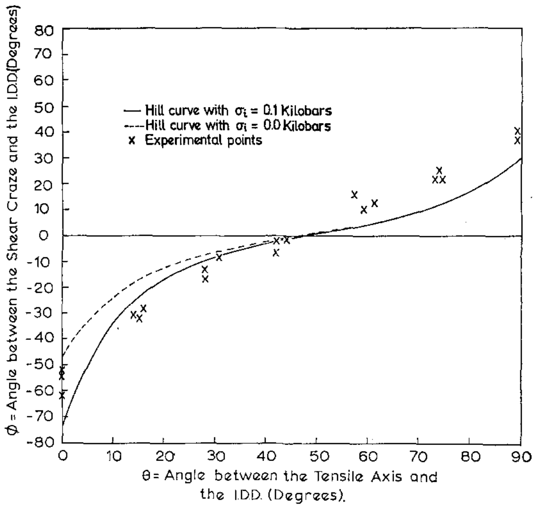

Figure 11 ϕ (angle between the shear craze and the IDD) plotted against θ (angle between the tensile axis and the IDD) for 2:1 drawn PET showing the theoretical predictions based on the Hill theory.

This yield criterion was applied directly to the crazing stress and craze angle data, for varying values of σ_i. For $\sigma_i > 0.1$ kbar, solutions of equation 3 became imaginary. With this restriction, fig. 11 shows that the best fit is obtained with $\sigma_i = 0.1$ kbar, although the fit is not as good as might have been hoped. Fig. 12 shows the corresponding crazing stress fit, which is very good.

By attempting to apply the yield criterion to shear craze formation we are implying that the formation of shear crazes is a form of yielding; however the constants calculated for crazing and

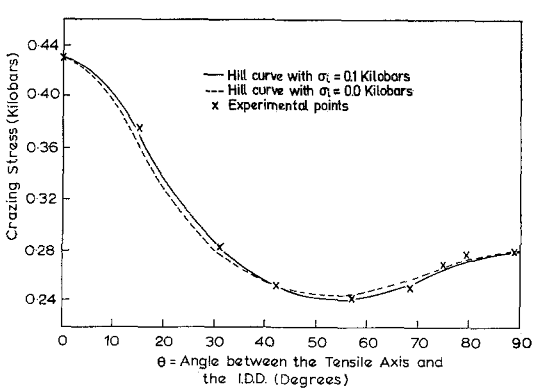

Figure 12 Crazing stress plotted against θ (angle between the tensile axis and the IDD) for 2:1 drawn PET showing the theoretical predictions based on the Hill theory.

yielding are different, and there is no simple scaling factor relating them.

The Hill theory assumes that hydrostatic pressure has no effect on yielding. Recent work has shown that this assumption is not justified for several polymers [8], including poly(ethylene terephthalate) [9]. It would also seem likely that the hydrostatic pressure component will be important in crazing. This can best be resolved by direct experiment under hydrostatic pressure. If there is an effect it will involve modifications to the equations 2 and 3.

4. Summary

Two types of crazing, tensile and shear crazing, have been observed in oriented PET. The tensile crazes form as would be expected on the basis of our present understanding of the nature of crazing, namely parallel to the IDD. The shear craze behaviour bears a strong resemblance to the yield behaviour of oriented PET, and it is tentatively suggested that the two phenomena may be closely related.

The conclusion is that the mechanisms responsible for the tensile and shear crazes are quite different, although there is still some doubt as to their exact nature.

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