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Craze formation and growth in anisotropic polymers

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Craze formation and craze growth in anisotropic polymers has been studied as a function of the degree of anisotropy and the relation between the testing direction and the primary orientation direction. Tests on PMMA and PC indicate that both the morphology and orientation of the crazes are senstivie functions of testing direction. Crazes form in directions which are *not* orthogonal to the principal tensile stress, and the data clearly show that craze growth occurs in directions governed by the major principal strain. The fracture process is identical in nature to that in isotropic polymers, i.e. craze formation, crack nucleation within the craze and subsequent crack propagation through the craze. Thus, the angle of fracture coincides with the craze angle rather than occurring perpendicular to the principal tensile stress.

1. Introduction

The phenomenon of crazing has been the single most studied aspect of deformation and fracture in isotropic amorphous polymers. Several criteria have been proposed to describe both craze formation and the orientation of craze growth with respect to the applied stress field [1–3] and these are summarized in a recent review [4]. The question of craze initiation in isotropic polymers has been further discussed by Wang *et al.* [5]. Their experiments indicate that such factors as the local dilation and the major principal tensile stress are unlikely to control craze nucleation, whereas parameters such as the local strain-energy density and the major principal strain appear to be critical. Areal craze growth in isotropic glassy polymers has been reported to obey an orientation criterion such that the crazes always grow with the major principal stress perpendicular to the craze plane.

The criteria for craze appearance and craze growth mentioned above have all been formulated with respect to structurally isotropic glassy polymers. In such isotropic materials, the axes of principal stress and principal strain are always coincident and a clear distinction between the relative influences of stresses and strains on the crazing process cannot be made. On the other hand, in an anisotropic polymer the axes of principal stress and principal strain do not generally coincide. Thus, a study of crazing in oriented materials should allow a clear distinction between stress-based and strain-based criteria. In addition, information relevant to the molecular processes involved in crazing may well result from such studies because of the generally better defined initial molecular state. The present paper reports an investigation of the effect of anisotropy in polycarbonate (PC) and poly(methylmethacrylate) (PMMA) on the crazing and fracture behaviour.

2. Experimental procedure

Sheets of PC and PMMA were hot-stretched above their respective glass transition temperatures to varying degrees and cooled slowly at constant length to room temperature. The degree of orientation was determined by a measurement of birefringence. Tensile specimens were cut at various angles θ to the original stretching direction (the anisotropy axis) and all tests were carried out at 77 K in liquid nitrogen in order to enhance the propensity for crazing [6].

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3. Results and discussion

In both PC and PMMA, crazes always developed prior to fracture, irrespective of the angular relationship between the tensile axis and the original orientation direction. An example of the crazes produced is shown in Fig. 1, which also illustrates the definitions of θ (the angle between the original orientation direction and the tensile axis) and α (the orientation of the craze with respect to the applied tensile stress – for an isotropic polymer, $\alpha = 90^\circ$). In Fig. 1, $\theta = 45^\circ$ and it is clear that α is *not* 90°. The primary variable in the testing was the angle θ and associated with varying θ were the following observed variations in: (1) the general morphology and distribution of the crazes; (2) the craze appearance stress σ_c and the fracture stress σ_F; (3) the craze orientation, i.e. α; (4) the fracture orientation.It is convenient to divide the results and discussion under these four headings.

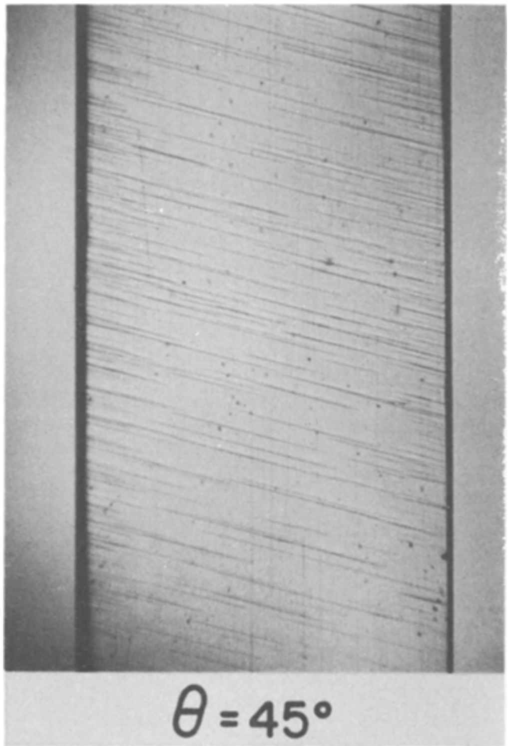
3.1. Craze morphology and distribution

Examples of the crazes formed in PMMA at various values of θ are shown in Fig. 2. The morphology of the crazes, i.e. their thickness and areal extent, and the density (number per unit area) of the crazes both vary between the two orientation extremes. When the tensile axis is parallel to the orientation direction ($\theta = 0^\circ$), a very high density of short crazes develops. In this orientation, the crazes are perpendicular to the applied stress axis as in isotropic polymers. Thus, the craze thickness strain, which is roughly normal to the craze plane [4], is parallel to the molecular orientation – a configuration generally thought to be prohibited.

At $\theta = 90^\circ$, the crazes are thick and large in area but the density of crazes is relatively low. In this orientation, the craze plane is also normal to the tensile axis, confirming previous observations [4]. The craze thickness direction is perpendicular to the molecular orientation providing a relatively easy configuration for the development of the thickness strain, i.e. primarily dispersion forces resist the deformation. The relative ease of crazing at $\theta = 90^\circ$ compared to $\theta = 0^\circ$ is reflected in a difference of a factor of 3 in the craze initiation stress for the samples in Fig. 2.

At testing angles between $\theta = 0^\circ$ and $\theta = 90^\circ$, crazes developed in orientations other than perpendicular to the tensile axis. Certain trends are obvious. Using $\theta = 90^\circ$ as the starting condition, as θ is decreased (i.e. the applied tensile stress moves towards the anisotropy axis) the crazes move away from perpendicular with respect to the applied stress and two changes develop: (a) the craze area decreases as θ decreases, and (b) the density of crazes increases as θ decreases.

All the angular measurements and observations are made on the face of the specimens. The molecular anisotropy is always manifest in this two dimensional face. However, on the thin edge of the samples, the resolved component of the molecular orientation direction onto the edge face is always in the applied stress direction. Thus, the inward growth of the crazes is always at 90° to the



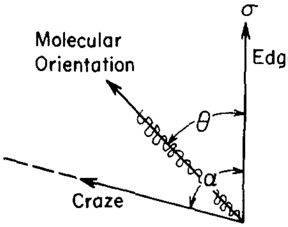


Figure 1 Example of crazed sample showing the relationship between craze orientation, molecular orientation and the applied stress. Note the definitions of the angles α and θ.

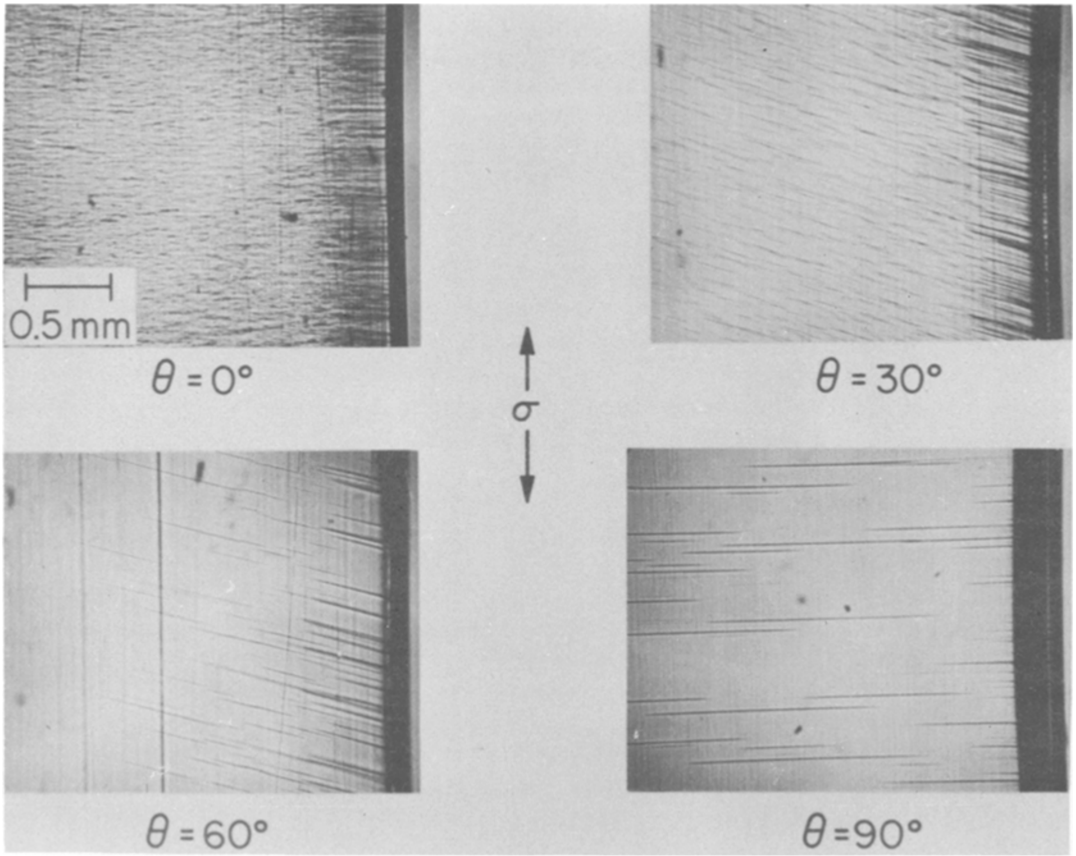


Figure 2 Examples of the variation in craze size, craze density and craze orientation as a function of θ in PMMA.

applied stress. An example of this effect is shown in Fig. 3 – note that the "area" effect on observing the edge in transmitted light occurs because the crazes are entering the bulk specimen at a distinct angle, resulting in a projected craze area on the surface.

No attempt has been made in the present work to examine the morphological variations in greater detail. In addition to these macroscopic variations, it might be expected that the microscopic structure would also vary as a function of the initial material condition and deformation angle. Recent progress in electron microscope procedures for studying crazes may well be used to further study this phenomenon.

Another aspect of craze growth in oriented polymers is illustrated in Fig. 4, where a double network of crazes is clearly visible in a PC sample deformed at $\theta = 0^\circ$. In the primary network, the crazes are oriented at $\alpha = 90^\circ$; crazes in the secondary network form at $\alpha = 19^\circ$. The secondary network has only been observed at angles $\theta < 30^\circ$. The angle α for the secondary network increases as θ increases from 0° – an opposite trend to the primary network; in addition, α increases with increasing birefringence. There is some indication, as seen in Fig. 4b, that the two craze networks intersect with concomitant interactive effects. The fact that two craze networks can develop simultaneously illustrates the complexity (and diversity) of craze formation and growth criteria.

Harris and Ward [7] reported some observations on crazing in oriented poly (ethylene terephthalate) (PET). They also noted two distinct types of crazing which they termed "tensile crazes" (formed at $\alpha = 90^\circ$, independent of the angle θ) and "shear crazes"; the plane of the shear crazes developed at approximately 50° ($\pm 5^\circ$) to the tensile axis at all angles θ. The angular relationships between the craze growth direction and the axes of tension and anisotropy in PET are quite different from those in the present work on PMMA and PC (see later), and add to the com-

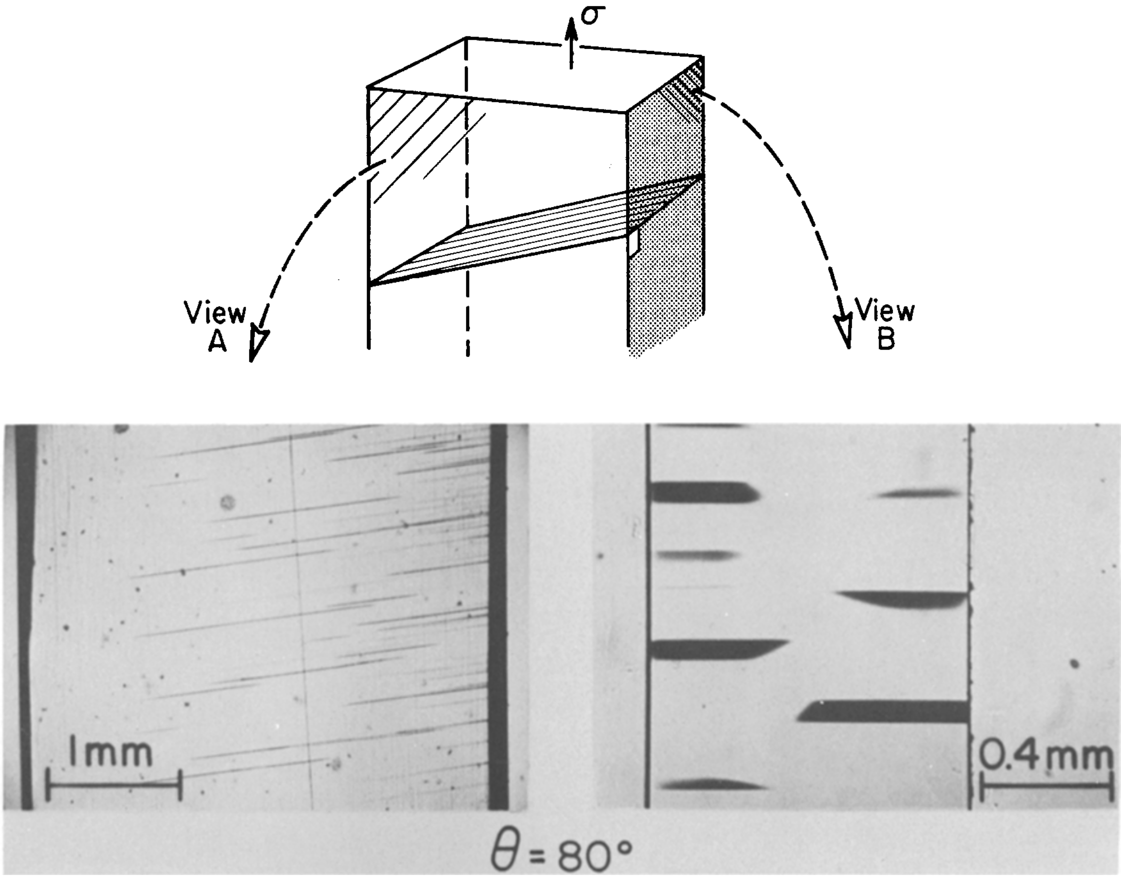


Figure 3 Illustration of the different appearance of the crazes on the surface and edge of the samples.

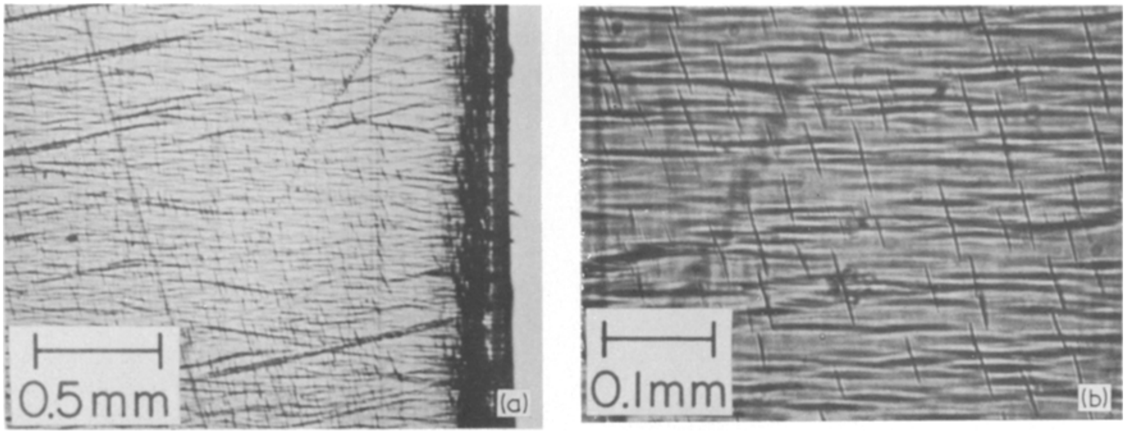


Figure 4 Double network of crazes in PC at $\theta = 0^\circ$.

plexity of any general criteria for craze formation and growth.

3.2. Crazing stress and fracture stress

The two polymers, PC and PMMA, used in this study vary somewhat in behaviour. In general, the anisotropic PMMA is essentially completely brittle in the sense that little or no deviation from linearity of the stress–strain curve occurs prior to fracture. All the non-elastic strain is accommodated in the crazes formed – since this strain is very small, fracture can be classified as brittle. The only stress measurements to be made, therefore, are the fracture stress and the crazing stress. In the case of PC, in addition to non-elastic strain being accommodated by crazes, some large scale bulk flow does occur prior to fracture. Thus, large deviations from linearity in the stress–strain curve frequently occur prior to fracture in PC. Thus, for PC it is possible (in theory) to measure an offset flow stress, the fracture stress and the crazing stress.

In particular, the measurement of the crazing stress, σ_c is difficult if unambiguous data are to be determined. In the present work, it was decided to limit these precise measurements to (a) one series of PMMA samples as a function of orientation θ and to (b) a series of PMMA samples at $\theta = 0^\circ$ with varying degrees of anisotropy. The measurements were made by two techniques. First, specimens were loaded and then unloaded to successively higher stress levels, and the stress at which the smallest detectable craze formed was determined. Second, a set of tapered specimens were tested in tension – when crazes were clearly visible in the specimen, the specimen was sectioned and polished to reveal the spectrum of craze penetration depths as a function of the stress variation in the sample. Extrapolation of the depth spectrum to zero enabled a craze initiation stress to be calculated. Comparison of the data produced by the two techniques allowed a plot such as Fig. 5 to be made. Note that both the crazing stress σ_c and the fracture stress σ_F are included. When $\theta = 0^\circ$ (tensile direction parallel to molecular orientation), both σ_c and σ_F are extremely high – about twice the isotropic values. As θ increases, both σ_c and σ_F decrease smoothly to a minimum value at $\theta = 90^\circ$. For isotropic PMMA, σ_c is approximately 16×10^3 psi and σ_F is about 20×10^3 psi.

The orientation dependence of both σ_c and σ_F is essentially the same; the ratio σ_c/σ_F is constant within experimental error. The approximate constancy of this ratio may, however, be more fortuitous than meaningful since it is likely that the stress difference $\Delta\sigma$ (= $\sigma_F - \sigma_c$) is the most critical parameter. The stress difference $\Delta\sigma$ represents the increase in stress necessary to produce the critical craze *thickness* strain at which the craze structure breaks down to form a crack, leading to catastrophic failure. Complicating such an analysis of the data is the fact that this critical craze *thickness* strain probably is itself a function of the testing angle θ since the craze structure and breakdown kinetics are themselves probably a function of θ. For these reasons, the relationship between σ_c and σ_F is difficult to relate to specific mechanisms. There is no question that the fracture sequence observed in isotropic polymers – (a) craze nucleation, (b) craze growth/deformation, (c) craze breakdown/crack nucleation, (d) crack growth through craze, (e) failure – is followed in these anisotropic polymers. However, from the present study there is no way of determining the variability in craze structure with θ or the specific micromechanism of the craze breakdown process.

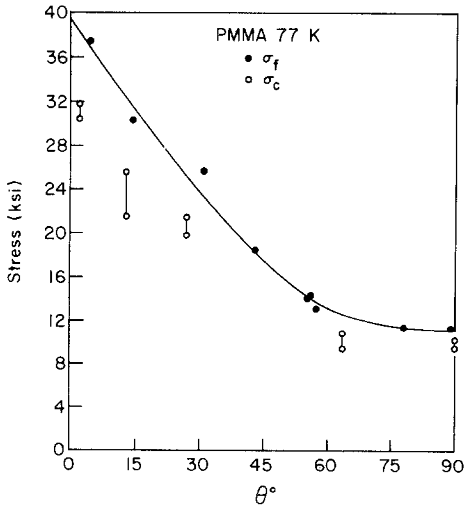


Figure 5 Fracture stress σ_F and crazing stress σ_c in PMMA as a function of θ. 1 ksi = 10^3 psi.

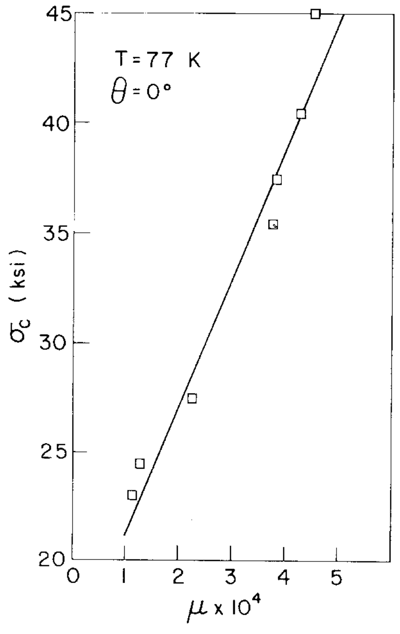


Figure 6 Effect of degree of anisotropy (measured as birefringence μ) on the crazing stress σ_c in PMMA. 1 ksi = 10^3 psi.

The effect of degree of anisotropy on the crazing stress σ_c is shown in Fig. 6. The relationship is approximately linear over the range of anisotropy (plotted as birefringence) studied. The data are all for $\theta = 0°$, that is the applied stress parallel to the orientation direction. This is the direction in which crazing is more difficult (high σ_c) and obviously the ease of craze formation is inversely proportional to the degree of molecular orientation. For the particular data in Fig. 6, the relation can be described as:

$$\sigma_c = \sigma_0 + (5.87 \times 10^4)\mu$$

where σ_0 is the isotropic crazing stress ($\sim 16 \times 10^3$ psi) and μ is the birefringence. The value of the slope (5.87×10^4 for $\theta = 0°$) could decrease continuously with increasing θ and would attain a negative value for orientations where $\theta > 50°$ (see Fig. 5). There is, of course, the possibility that the relationship between σ_c and μ is not linear for all values of θ.

3.3. Craze orientation

Fig. 7 is a plot of the angular relationship between test direction and craze orientation for anisotropic PMMA. At the two extremes, $\theta = 0°$ and $\theta = 90°$, the crazes form perpendicular to the applied stress, just as in isotropic material. At all angles between $\theta = 0°$ and $90°$, however, the craze orientation is not perpendicular to the stress axis. At angles between $\theta = 0$ and $\theta = 45°$ the craze orientation moves towards the applied stress axis, i.e. α decreases. At $\theta = 45°$, this deviation from the perpendicular reaches a maximum, and at greater values of θ the trend is reversed and the craze orientation moves back towards the perpendicular, i.e. α starts to increase again. The same general observations were made for PC as shown in Fig. 8. Note that the maximum deviation from the isotropic craze orientation again occurs at $\theta \sim 45°$.

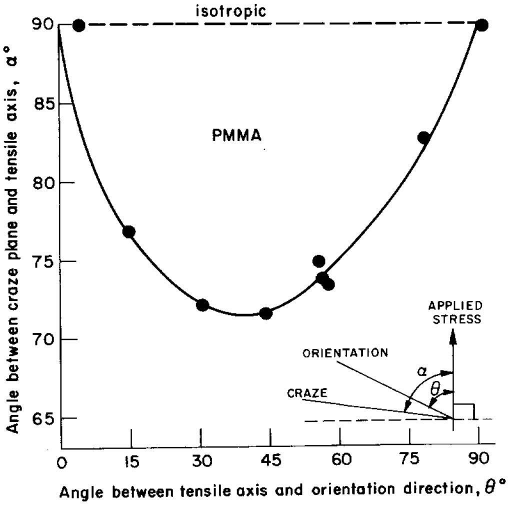


Figure 7 Angle between craze plane and tensile axis α as a function of θ in PMMA.

The type of data plotted in Figs. 7 and 8 allow an immediate conclusion to be made relative to the criticality of the principal stress in determining the craze orientation. While the principal stress axes are always determined by the applied stress, the orientation of the principal strain axes depend on both the angle θ and the state of anisotropy.

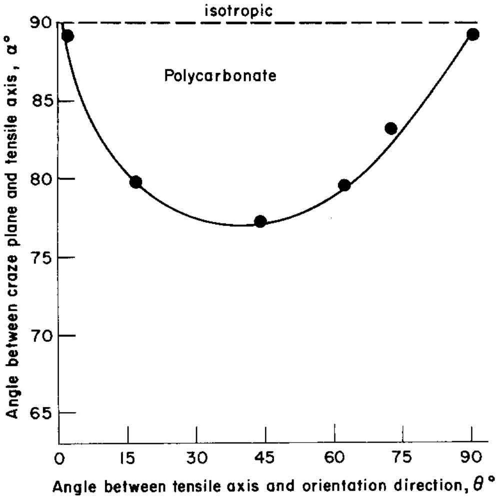


Figure 8 Angle between craze plane and tensile axis α as a function of θ in PC.

The principal axes of stress coincide with the principal axes of strain-increment *only* if the axes coincide with the axes of anisotropy. This is clearly the case at $\theta = 0°$ and $\theta = 90°$. At all angles between these two orientation extremes, the principal axes of stress and strain-increment do not coincide. It is clear from Figs. 7 and 8 that crazes do not grow perpendicular to the principal stress (applied stress) axis except at $\theta = 0°$ and $90°$ and thus the principal stress direction cannot be a governing criterion in craze growth.

The results on craze orientation indicate that molecular anisotropy, along with the applied stress field, is a critical parameter in determining craze growth direction. This can be seen quantitatively in Fig. 9 where the maximum angle α_{max} between the craze plane and the tensile axis ($\theta = 45°$) is plotted against birefringence for PMMA. The angle α_{max} increases approximately linearly with

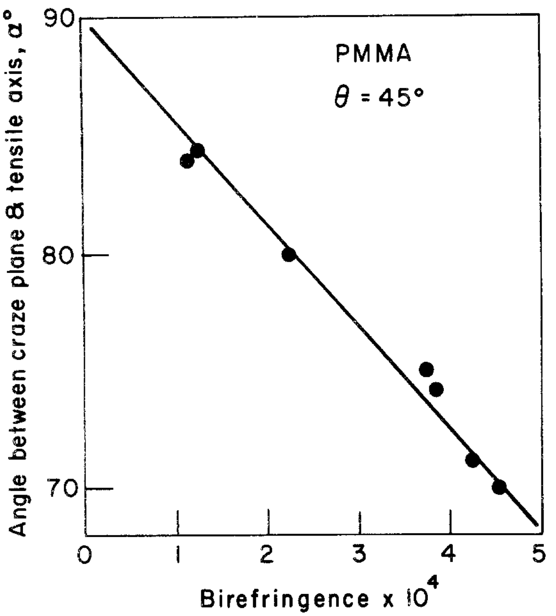


Figure 9 Maximum angle $\alpha_{\max}$ between craze plane and tensile axis ($\theta = 45°$) as a function of degree of anisotropy (birefringence) for PMMA.

birefringence, emphasizing the strong influence of the state of anisotropy on craze orientation. This same type of trend is observed at all values of the angle θ between 0° and 90°. The same general observations hold for PC.

The type of variation between α and θ here is very different than in the only previously reported case of craze orientation in an anisotropic polymer [7]. In that study, Harris and Ward noted two types of crazes developed in oriented poly(ethylene terephthalate) (PET): (a) crazes of the conventional angle of 90° to the tensile axis for $\theta = 90°$ and $\theta = 75°$, and (b) what they identified as "shear crazes" formed at a systematically varying angle to the tensile axis. In the present context, it is the orientation of the "shear crazes" which are of most interest. Examination of the Harris and Ward data indicates that the "shear crazes" formed at $\alpha \approx 50° \pm 5°$ at all values of the angle θ. Comparison with Figs. 7 and 8 indicates the markedly different character of the crazing they observed in PET. In essence, in PET the "shear crazes" form at approximately 50° to the applied tensile stress irrespective of the direction of the molecular orientation.

As mentioned above, the dependence of craze orientation on θ (see Figs. 6 and 7) rules out the principal stress as the governing criterion for craze orientation. It is postulated, therefore, that the crazes form along trajectories defined by the principal strain axes – in other words, the strain analogue to Sternstein *et al.*'s observation in isotropic polymers. To check the validity of this postulate, the orientation of the principal strain axes for a given angle θ were calculated by the procedure outlined below.

Using the flow stress versus θ data for PC, the state of anisotropy was empirically characterized by application of Hill's anisotropic yield criterion [8]. The Levy-Mises criterion [9] was then applied to calculate the plastic strain increment-ratios and from these the orientation of the principal strain axes as a function of θ were determined. The results for a sample of PC are shown in Fig. 10. The experimental data are included for comparison with the theoretical line tracing the orientation of the major principal strain. It should be pointed out that this analysis does not work for PMMA due to the lack of yield stress data. Attempts to apply it using the crazing stress σ_c in place of a yield stress were not successful.

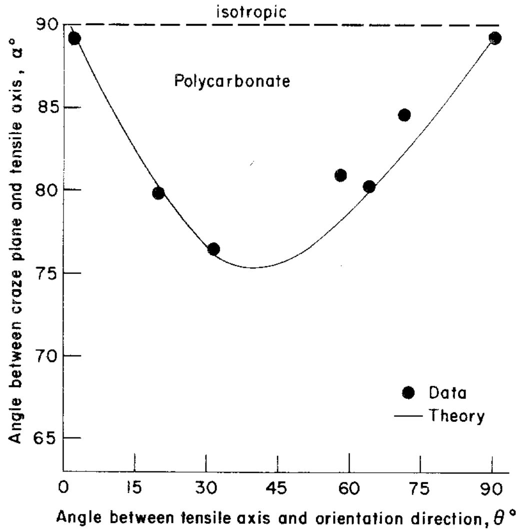


Figure 10 Comparison of data and theory for PC.

It is fairly clear that the inclusion of anisotropic polymers in studies of crazing can provide a sensitive and tractable analysis of the conditions required for craze formation in glassy polymers. In particular, these data show that craze formation is governed by the local dilatational strain and craze growth occurs along principal strain directions.

3.4. Fracture orientation

In general, fracture occurs through the pre-existing crazes and consequently follows the orientation of

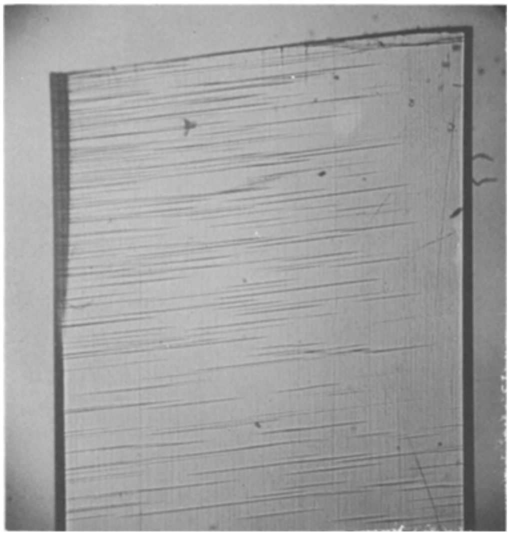


Figure 11 Example of fracture path following the craze orientation resulting in a fracture face which is not perpendicular to the applied tensile stress.

the crazes. An example is shown in Fig. 11 in which this trend is quite evident. As the fracture angle deviates from 90°, there is some tendency for the fracture path to become irregular due to the crack jumping from one craze plane to another. The overall relationship between fracture angle and θ would, of course, follow very closely to the type of curves shown in Figs. 7 to 9.

Acknowledgement

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