Mechanism of craze thickening during craze growth in polycarbonate

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It has been shown previously that dry craze growth kinetics in bisphenol-A polycarbonate (PC) subjected to creep are compatible with a model in which craze growth occurs at constant aspect ratio, the rate-controlling process being craze thickening due to homogeneous creep of craze material. In the present work, craze thickening during growth was investigated by electron microscopy and by an optical interference method in order to check this hypothesis. Results indicate that thickening occurs by drawing in fresh material from the craze–matrix interface. The previous model is modified in order to take these findings into account.

INTRODUCTION

Brittle fracture of glassy polymers generally involves the preliminary initiation and growth of a number of crazes, followed by the fracture of one or more of them. From previous investigations on bisphenol-A polycarbonate (PC)[1], it appeared that various aspects of craze initiation and growth in this material when submitted to creep were incompatible with a process controlled by craze-tip yielding, but could be explained by a model in which the rate-controlling process is craze thickening, which is supposed to be due to homogneous creep of craze material[2]. This model received further confirmation from the insensitivity of craze growth kinetics to thermal pretreatment, which would be expected to affect craze tip conditions, but not the stress acting along the craze body, nor the mechanical behaviour of the craze material[3].

The hypothesis of simultaneous width-wise and lengthwise growth of crazes, keeping the aspect ratio constant, was not fully checked in the previous investigation; some doubt also subsisted as to whether thickening occurs by creep of a constant amount of craze material or by drawing in fresh material from the bulk polymer–craze interface. As discussed below, some observations found in the literature indicate thickening by propagation towards the bulk polymer, whereas others point to thickening by extension of craze material.

Since it was felt that the mechanism of craze thickening must have an influence on the fracture mechanism, the research reported here was undertaken in order to investigate this point further. Firstly, thickening of crazes during growth was followed by electron microscopy of replicas of crazed specimens under stress. Since this method gives no information as to the origin of craze thickening, separate experiments in which the thickness and density of the same craze could be measured simultaneously were undertaken, making use of the optical properties of thin layers less dense than the surrounding medium.

EXPERIMENTAL

Material

All experiments were carried out on specimens cut from a 2 mm thick sheet of commercially available Makrolon (Bayer) bisphenol-A polycarbonate.

Electron microscopy

Preliminary experiments were conducted on specimens with a variable cross-section, in order to obtain results at several stresses simultaneously. However, it was found that results were irreproducible at low stresses, due to the very small number of crazes and difficulties in obtaining replicas, and finally it was decided to use specimens with a straight gauge section.

Three specimens having a gauge section 8 x 2 x 40 mm were used. Two were annealed at 120°C for 40 h (B), the third was used as received (A). The machined edges of all specimens were polished in order to avoid spurious crazing. Specimens were set in a horizontal strain frame and submitted to a stress of 49 MPa. This stress was chosen since at lower stresses there were so few crazes that on several replicas no crazes could be found, and at higher stresses as received specimens yielded before completion of the experiment.

A water-soluble replicating agent was needed in order to avoid solvent crazing or cracking. Of the commonly used materials, poly(vinyl alcohol) was chosen, since it has better dimensional stability on redissolving then gelatin, and it is more readily soluble than poly(acrylic acid). The upper surface of the specimen was coated with a saturated solution of poly(vinyl alcohol) which was then left to dry. The replica was stripped from the specimen and a strip 1 mm wide was cut from each edge to eliminate the possibility of observing spurious crazing from the edges. The replica was carbon coated, shadowed with chromium at an angle of approxi-

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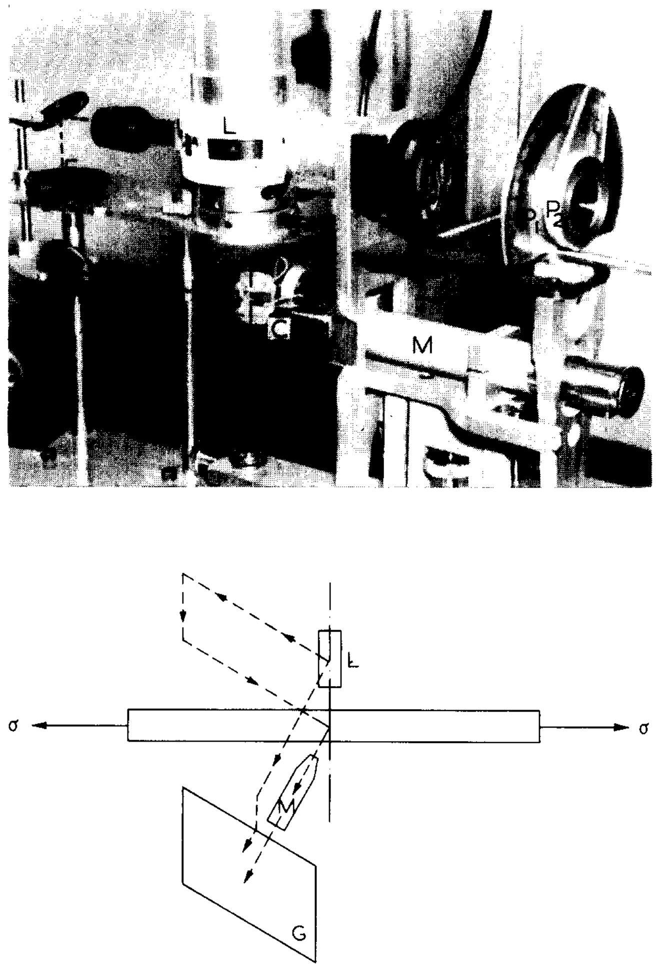

Figure 1 Strain frame and apparatus for measurement of optical properties of crazes

mately 15° in a direction parallel to applied stress, and backed with paraffin to avoid disintegration of the carbon replica on dissolving the poly(vinyl alcohol). After dissolving the poly(vinyl alcohol) in warm water, the replicas were cut into squares and the paraffin backing was dissolved in hot acetone. Finally, the replicas were floated onto grids for observation in the transmission electron microscope. Curling of replicas was a common problem, and was overcome to some degree by transferring replicas to a water bath before floating them onto grids. Replicas were taken following a logarithmic timescale with a ratio approximately equal to two, the first replica being taken a day after loading.

Optical interference method

A consequence of the lowered density of craze material is a decrease in refractive index, causing total internal reflection of light impinging on the craze at incidence angles larger than the critical angle. Use has been made of this property to determine the void content of craze material[4–6]. As pointed out by Kambour[4,5] frustration of total reflection occurs if the craze thickness is of the order of, or smaller than, the wavelength of the light; in this case, reflectance varies continuously over a wide range of incidence angles. Also, for slightly thicker crazes, interference fringes appear at incidence angles lower than critical incidence. It was thought that use could be made of these properties in order to determine not only the void content of the crazes, and hence their strain, but also their thickness.

A goniometer stage combined with a strain frame was specially designed for this work, and is shown in *Figure 1*. A mercury lamp L is centred above the specimen to enable use both as the reference beam R and as the illuminating beam I. Intensity fluctuations thus have no influence on reflectance measurements. An orange filter F is used, corresponding to a wavelength of 577 nm. Light is polarized perpendicularly to the plane of incidence.

The specimen is put under stress by means of a rod at one end, and at the other end by a strap passing round a wheel concentric with a larger wheel, thus multiplying the applied load by ten. Specially long specimens are used, since the grips would otherwise hinder rotation of the microscope at low craze incidence angles. The gauge section is 2 x 8 x 40 mm. Stresses range from 42 to 48 MPa; at lower stresses crazing could not be observed during a reasonable time and at higher stresses crazing was so profuse that identification of individual crazes became problematical.

The specimen is observed through a low-power microscope M, which can rotate about the same axis as the incident beam. The entire goniometer stage is set on roller bearings and can be moved in two perpendicular directions to centre the axis of rotation on the craze to be observed. The microscope can independently be shifted vertically.

In preliminary experiments, prisms such as used both by Kambour[4,5] and by Krenz and coworkers[6] were attached to the specimens to avoid total reflection from the specimen surface. However, prisms gave unsatisfactory results, since at glancing incidence on the specimen surface, the deviation of the incident beam at the front surface of the specimen, due to refraction in the prism and specimen, was frequently larger than the beam width. Therefore, half-cylinders cut from a rod of PMMA are used. As these are centred on the craze under observation, refraction only occurs at the interface between the specimen and the half-cylinder. The half-cylinder on the back surface of the specimen is cut back 2 mm in order that it can be centred on the front surface.

The half-cylinders C were first attached to the specimen using silicone grease, but this was abandoned since it caused extensive crazing and premature brittle fracture. Paraffin and glycerine were unsatisfactory for the same reason. Finally the cylinders were gripped to the specimen using rubber bands, and were previously wetted with distilled water to ensure optical continuity. Because of the low refractive index of water, this limits observations to angles of incidence on the craze larger than 33°.

The angle of incidence at which each dark fringe appeared at the thickest part of the craze was measured for various crazes. Due to difficulties in judging when the darkest part of the fringe appeared at this thickest point, the uncertainty in these measurements was taken to be 0.5°. This angle of incidence was corrected for refraction at the specimen surface to obtain the angle of incidence on the craze.

For reflectance measurements, the image is formed on a translucent glass plate G for comparison with the reference beam. In this case the reference beam illuminates half the plate, the image being formed on the other half. The reference beam passes through polarizers P_1 and P_2 which are set so that the brightness of the image is equal to that of the reference beam; the intensity of the image is thus determined by the angle between the polarizers.

Reflectance measurements are limited to incidence angles on the craze lower than 80° to avoid the influence of light diffused from the incident beam.

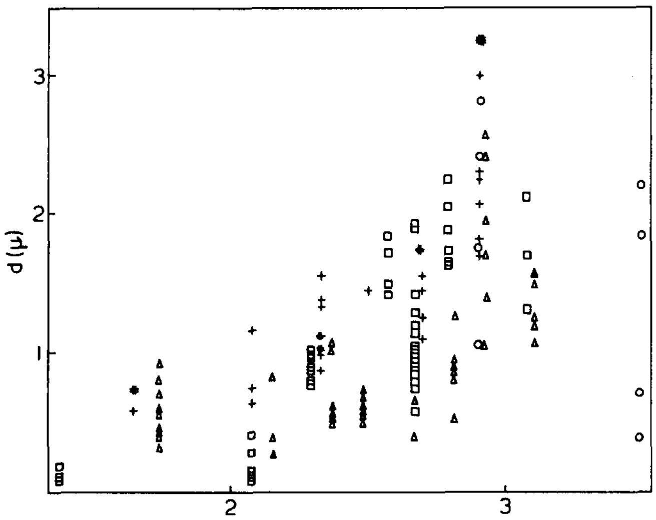

Figure 2 **Variation of thickness of crazes during growth, at a stress of 49 MPa. +, As-received specimen: △, annealed specimens; ○, thicknesses after unloading and recovery for as-received specimen**

RESULTS

Electron microscopy

A plot of thickness of various crazes *versus* log(time) is given in *Figure 2.*

Since there is no possibility of identifying crazes, it is difficult to draw quantitative conclusions from these results. However, it is probable that most thin crazes observed at long times are crazes that initiated after a long time rather than crazes which did not thicken during growth. This interpretation is suggested by the fact that the longer the time, the more crazes could be found on the replicas. Comparisons were therefore based on the thickest crazes rather than on average thickness, which would be biased towards low values as a consequence of the continuous initiation of fresh crazes. When compared in this manner, no significant difference can be found between the heat-treated and the untreated specimen, in agreement with previous results[3]. There is, however, an up-turn at long times in the as-received specimen, which is not observed in annealed specimens, but this was attributed to approaching general yield since deformation bands were observed at the tips of crazes on these replicas.

The variation of craze thickness must now be compared with the rate of length-wise growth. Due to the experimental difficulties, these measurements could not be conducted on the specimens used for electron microscopy, and growth-rates were taken from previous results[7], given in *Figure 3.* From a comparison of *Figures 2* and *3,* it can be seen that craze growth occurs at an approximately constant aspect ratio since extrapolation of growth to either zero length or to zero thickness lead to the same value of time (approximately 10 h). The ratio of thickness to length was approximately 5×10^{-3}; if craze strain was 100%, the ratio $2\delta/l$ of relative displacement to craze length was 2.5×10^{-3}.

It was observed that some retraction occurred on removal of the stress, followed by significant recovery. This can be seen as the circles in *Figure 2.*

Interference method

Optical thickness and refractive indices of crazes were determined both from reflectance measurements and from interference fringe measurements using the following equation, which is valid for light polarized perpendicularly to the plane of incidence, and which accounts both for interference effects and for multiple reflections (e.g. ref 8):

$$R = \frac{(n_p^2 - n_c^2)^2 \sin^2\alpha}{(n_p^2 - n_c^2)^2 \sin^2\alpha + 4\cos^2 i(n_p^2 \sin^2 i - n_c^2)} \qquad (1)$$

where n_p is the bulk polymer index, taken as $n_p = 1.585$; n_c is the craze refractive index; i is the angle of incidence on the craze;

$$\alpha = (2\pi d/\lambda_0)(n_c^2 - n_p^2 \sin^2 i)^{1/2};$$

d is the total thickness of the craze layer; λ_0 is the wavelength of incidence light in a vacuum ($\lambda_0 = 577$ nm). Equation (1) is valid at all angles of incidence; beyond critical incidence α is imaginary and $\sin\alpha$ should be replaced by $\sinh(j\alpha)$, where $j = (-1)^{1/2}$.

Strictly speaking, equation (1) is only valid if the less dense medium is limited by parallel plane surfaces. This is not the case for crazes, which are wedge-shaped; however, craze lengths are generally about 200 times longer than their thicknesses and it is to be expected in this case that equation (1) should give a fair approximation. It can be shown that the difference of phase between interfering rays at the surface of a wedge-shaped craze is given by:

$$\alpha = \pi\frac{2d}{\lambda_0}(n_c^2 - n_p^2\sin^2 i)^{1/2}\left\{1 - \frac{\gamma}{2}\frac{n_p \sin i}{(n_c^2 - n_p^2\sin^2 i)^{1/2}}\left[2 + \frac{n_c \cos i}{(n_c^2 - n_p^2\sin^2 i)^{1/2}}\right]\right\}$$

where γ is the angle between the craze faces. For small values of γ, such as are of application to crazes (of order 1/200) the above expression reduces to the former expression for α, except at angles of incidence close to critical incidence. If the first dark fringe appears close to critical incidence, its position is then affected by the shape of the craze. This only occurs for relatively thick crazes, on which several

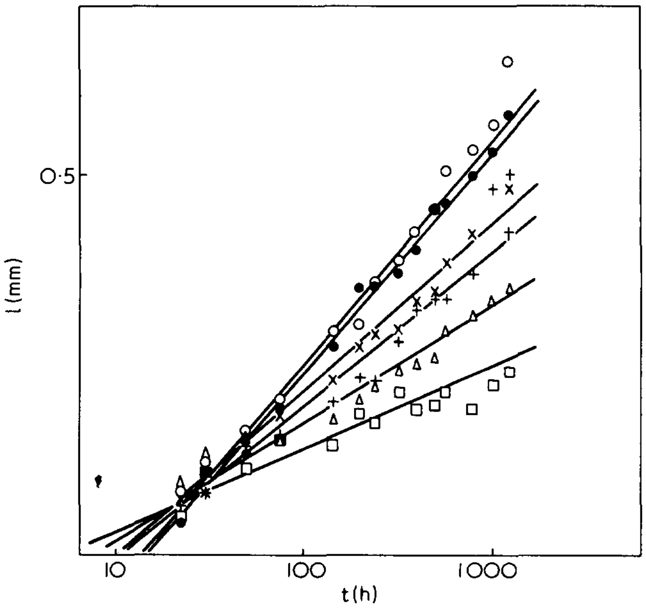

Figure 3 **Craze lengths *versus* log (time) at an applied stress of 50 MPa**

more fringes can be observed, and thus has very little influence on the precision of results.

Dark fringes appear when $\sin\alpha = 0$, that is when:

$$\frac{2d}{\lambda_0}(n_c^2 - n_p^2 \sin^2 i)^{1/2} = k \qquad (2)$$

where k is an integer, and i_k is the angle of incidence at which the kth fringe appears at the thickest part of the craze.

When at least three fringes could be obtained, $\sin^2 i_k$ was plotted *versus* k^2 to obtain a straight line. The ordinate intercept gave n_c^2/n_p^2 and d was obtained from the slope of the line. When only two fringes were obtained, these values were calculated directly from equation (2). In these cases practically no variation of reflected intensity could be observed above critical incidence, and therefore no use could be made of reflectance measurements.

The draw ratio $(1 + \epsilon)$ of craze material was determined from the craze refractive index using the Lorenz–Lorentz equation, written as:

$$\left(\frac{n_c}{n_p}\right)^2 = \frac{3 + \epsilon + \dfrac{2\epsilon}{n_p^2}}{\epsilon n_p^2 + 3 + 2\epsilon} \qquad (3)$$

The validity of the Lorenz–Lorentz equation in the case of an anisotropic material such as a craze has been questioned by Doyle[9], who used the Rayleigh equation for parallel rods. However, the Rayleigh equation does not appear to account for interaction between the external field and the internal field, and for this reason it was preferred to use the Lorenz–Lorentz equation.

Equation (3) is valid for a dry craze, which at first sight may seem illogical since it could be expected that, during measurements, water would be pressed into the craze by pressure from the half-cylinders. It was found, however, that n_c was lower than the refractive index of water, and therefore the craze was considered to be dry. No explanation was found for the absence of water in the crazes. This might be due to surface tension, or to local small-scale lateral contraction at the specimen surface causing the craze structure to close up.

The displacement of one craze boundary with respect to the other was taken as:

$$2\delta = \frac{\epsilon}{1 + \epsilon} d \qquad (4)$$

and the original thickness of craze material, prior to craze formation, as:

$$e = \frac{d}{1 + \epsilon} \qquad (5)$$

The uncertainty in δ ranged from 4% for short crazes (two visible fringes) to 2% for long crazes; that in ϵ ranged from 8 to 4%.

For very thin crazes, no interference fringes were observed and reflectance varied continuously as a function of incidence angle. Measured values of reflectance were corrected for partial reflection at the interfaces between half-cylinders and water, and between water and specimen, and compared graphically with plots of R *versus* i calculated from equation (1) for various values of n_c and d. It was often found very difficult to obtain reproducible values of R at glancing incidence on the craze, since the craze image was then very narrow, making it difficult to estimate when the intensities of the reference beam and of the reflected beam were equal. In this case there was no way to determine even an approximate value of R_0, which would normally be needed to put reflectance on an absolute basis. However, this only occurred for extremely thin crazes, for which the shape of the plot of R *versus* i is sufficiently characteristic both of n_c and of d to make it possible to adjust the experimental plot to a calculated plot, using only values of reflected intensity measured at incidence angles between 40° and 65°. For these crazes, 2δ could be estimated within 0.02 μm and ϵ to within 0.1.

This method of adjustment is illustrated in *Figure 4* which gives theoretical plots for two different values of d, calculated from equation (1), taking account of partial reflection. Experimental values of reflected intensity were multiplied by a constant to give a good fit of the crosses to the full curve and of the circles to the broken curve, for incidence angles above 54°. It can be seen that the circles give a poor fit to the broken curve at low incidence angles, whereas the crosses give a good fit to the full curve.

For crazes of intermediate length, reflectance measurements could be carried out and one interference fringe could be observed. Since practically no variation of craze refractive index was found during growth, the average refractive index and the incidence angle at which the fringe appeared

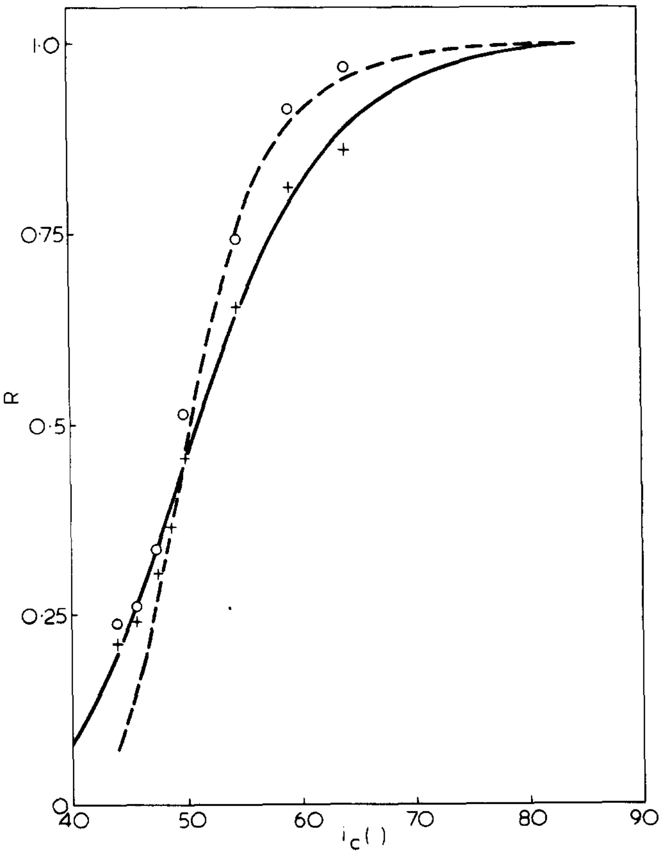

Figure 4 Plot of relative reflected intensity *versus* craze incidence angle. Calculated plots: ——, $2\delta = 0.22$ μm, $n_c = 1.28$; – – –, $2\delta = 0.29$ μm, $n_c = 1.28$. Crosses are fitted to the full curve, circles are fitted to the dashed curve

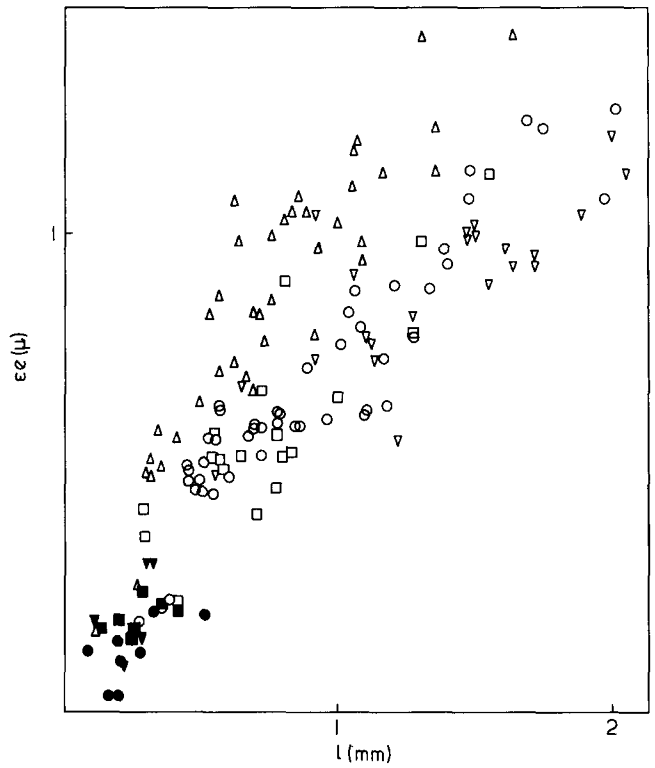

Figure 5 Variation of relative displacement of craze faces with craze length. ●, ○, 42 MPa; ■, □, 44 MPa; ▲, △, 46 MPa; ▲, △, 48 MPa. Open symbols are results from reflected intensity measurements, full symbols are from interference fringe measurements

were introduced into equation (2) to obtain a value of d. A value of d and of n_c was obtained independently from the variation of reflected intensity. The latter values both of craze thickness and of craze draw ratio were systematically lower than the former. This is to be expected since in measurements of reflected intensity the whole craze is compared with the reference beam, and this method would be expected to give average values of thickness and draw ratio, rather than those appropriate to the thickest part of the craze.

Figure 5 gives a plot of 2δ, i.e. the relative displacement of the craze boundaries, *versus* craze length l, for crazes grown under various experimental conditions. There is a good deal of experimental scatter, which is characteristic of all crazing phenomena. Full symbols indicate values from interference fringe measurements, and open symbols correspond to reflected intensity measurements. As pointed out above, the latter values fall systematically below extrapolation from the former.

During the first stages of growth, experimental data are compatible with a constant value of $2\delta/l$, equal to 0.78×10^{-3}. This value is significantly lower than that resulting from electron microscopic observations (2.6×10^{-3}); however, as pointed out by Kambour and Kopp[10], the surface groove associated with a craze is somewhat wider than the craze itself, and it is in fact the surface groove that is observed in electron microscopic observations. The latter value of $2\delta/l$ was estimated from comparison of *Figures 2* and *3* which were not obtained on the same specimen. The two values of $2\delta/l$ are therefore considered to be compatible.

For long crazes, $2\delta/l$ falls off. This occurs when the craze length is approximately half the specimen thickness, and is attributed to interference of the stress field of the craze with the opposite surface of the specimen, rather than to a change in the mechanism of craze growth.

No significant variation of $2\delta/l$ was found for stresses ranging from 41.8 to 46.0 MPa; nevertheless, values of $2\delta/l$ were significantly higher at 48.1 MPa (approximately 1.1×10^{-3}); this was thought to be due to approaching general yield.

Within experimental error, craze strain was independent of craze length, and was approximately 1.4. Residual craze strain on unloading was approximately 1.1, and decayed slowly. This confirms the viscoelastic nature of craze material, as observed previously[10–12].

To summarize, craze refractive indices generally varied between 1.22 and 1.27, corresponding to craze strains between 1.28 and 1.65. (It must be stressed that this variation was largely scatter and that no systematic variation with craze length was found). The average ratio of relative displacement of craze face, 2δ, to craze length was 0.78×10^{-3}; the corresponding average ratio of total thickness to length was 1.34×10^{-3}, corresponding to an undeformed layer of thickness $0.56 \times 10^{-3} l$.

DISCUSSION

It was shown previously[2] that if the ratio of relative displacement at the centre of a craze to its length remains constant during growth, craze material is submitted to creep conditions as can be seen from the following equation (equation 16 from Reference 2):

$$\sigma_a - \sigma_c = \frac{E}{A}\frac{2\delta}{l} \qquad (6)$$

where σ_a is the applied stress: σ_c is the craze stress, that is, the stress acting along the craze body; E is the tensile modulus of the bulk polymer; $A = (1 + \nu)(1 - 2\nu)$ in plane strain or $(1 - \nu)$ in plane stress; ν is the bulk polymer Poisson's ratio; 2δ is the relative displacement of the two faces of the craze; and l is the craze length.

If craze thickening is the rate-controlling process for craze growth, the growth rate $\dot{l}$ is then proportinal to $\dot{\delta}$. This was presumed to be the case in materials where the yield stress is relatively insensitive to strain rate and in which the craze tips are much shorter than the craze body, since in this case even quite large variations in strain rate at the craze tip would have very little effect on the stress distribution along the body of the craze.

It was also assumed that σ_c would be sufficiently low for thickening to occur by an increase in the draw ratio of craze material, rather than by drawing in fresh material from the bulk. Information from the literature is not clear on this point. Kambour and Kopp[10], in their investigation on the stress–strain behaviour of a thick PC craze, state that 'at high stresses . . . the surface groove sometimes enlarges partly by drawing in more surrounding surface material'. Thickening in this manner is also suggested by Beahan *et al.*[13] and by Weidmann *et al.*[14], and is consistent with fractographic observations of fatigue specimens of glassy plastics[15–19], from which it appears that the craze generally fractures down the middle, as would be expected if this were the oldest part of the craze. This mechanism is also consistent with the occurrence of a midrib of large voids in crazes in PS[20,21] and in PC at high temperature[1]. Interference fringes of alternating intensity, which have been shown by Doyle[22] to be associated with this midrib, have also been frequently observed[16,23,24]. On the other hand, Brown and Ward observed craze extension ratios in PMMA of up to 3.6 at break with respect to the unstrained craze[25]. With a craze strain of 0.6, the total craze strain at break would be 4.8 and the ratio of craze strain at break to craze strain just after craze formation would be 8; this would be sufficient to account for observed craze growth at constant aspect ratio, even if no extra material were drawn from the bulk. This mechanism for craze thickening would be expected to be associated with fracture at the interface between the craze and the bulk, where orientation hardening would be smaller than in the middle of the craze. This mode of fracture has also been frequently observed[26–28], in particular in PC[29–31].

The present results from electron microscopic observations confirm the hypothesis that thickening is proportional to length-wise growth, but are inconclusive concerning which mechanism is operative; nevertheless, if thickening were due to creep of craze material, some difference in texture would be expected between replicas taken at different times, and this was not found to be the case.

Results from measurements of optical properties of crazes are far more conclusive. These clearly indicate, not only that the aspect ratio remains approximately constant during growth, but also that this ratio does not vary significantly with applied stress except at very high stresses, probably owing to approaching general yield. Large deviations from linearity are also observed when lateral dimensions of crazes approach specimen thickness.

The most significant observation, however, is that the craze refractive index, and therefore craze strain, is constant within experimental scatter during growth; this leaves no doubt that craze thickening occurs by drawing in material from the bulk and not significantly by creep of craze material. (This result is not in contradication with a mechanism for craze fracture based on viscoelastic processes such as disentanglement of craze filaments, as suggested by Hertzberg and co-authors[32]: such processes could conceivably result in variations of craze strain well below experimental scatter, which varied from 4 to 8%, especially if fresh material having a lower strain is constantly being drawn in from the bulk).

This last result raises fresh queries as to the mechanism of craze growth. Previous work on thermally pretreated PC clearly implied that craze tip conditions are not rate determining[3]. On the other hand, as shown by the results given above, $2\delta/l$ is constant during growth, and therefore, from equation (6), the craze stress σ_c is also constant. Since thickening occurs by propagation of the craze boundaries, it would be logical for σ_c to be equal to the lower yield stress; but in this case, according to Kramer's results on neck propagation[33], the propagation rate should be constant, and not proportional to reciprocal time, as observed in this work. An investigation on neck propagation in PC is currently in progress in order to check this point. Preliminary results indicate that, at intermediate stresses at least, neck propagation occurs at a continually decreasing rate, and not at a constant rate as observed by Kramer.

The craze stress σ_c can be estimated from equation (6); from *Figure 5* an average value of $2\delta/l$ is found to be 0.78×10^{-3} for stresses between 42 and 46 MPa; in plane strain, taking $\upsilon = 0.3$ and $E = 2550$ MPa, $E/A = 4900$ MPa and $\sigma_a - \sigma_c = 3.8$ MPa. The craze stress in PC is therefore quite close to the applied stress, as is to be expected in a material in which crazes are known to be tough and load-bearing. The craze depth was approximately $0.6\,l$, and it was considered that at craze depths greater than 1 mm, corresponding to craze lengths greater than 1.67 mm, interference of the craze stress field with the opposite surface of the specimen occurred. In this case, equation (6), which is derived for an infinite plate, is no longer valid. This is probably the cause of the deviation from linearity of the plot of 2δ *versus* l for craze lengths greater than about 1.4 mm.

In view of the results given above, the previous model for craze growth is modified as follows: under conditions of constant applied stress, the craze stress and the aspect ratio of the craze remain constant during growth. The craze thickens by a mechanism similar to neck propagation in a bulk specimen, and this causes proportional lengthwise growth. This mechanism is capable of explaining craze growth in PC, which is linear on a log$t$ plot, if neck propagation is also linear on such a plot; this is apparently confirmed by preliminary experiments.

In other materials, craze growth has been observed to occur at a constant rate[34–36]. This behaviour is compatible with the model if neck propagation under a constant stress occurs at a constant rate; it could also be an indication that in these materials, the rate-controlling process is the behaviour of the craze tip rather than of the craze body. This would be expected in materials in which the yield stress is highly sensitive to strain rate, since in this case large modifications of the stress field would be needed to accommodate variations in the strain rate at the craze tip. It would also be expected in materials in which orientation hardening does not occur to any great extent, since the craze stress would then be very low and the craze would be crack-like in behaviour.

The model will now be compared with previous models for craze growth. Most previous models are concerned with environmental crazing; these will not be considered here.

The model proposed by Williams and Marshall[37] for crack-tip crazing, based on criteria of fracture mechanics, can be applied both to environmental crazing and to dry crazing. For dry crazing an average craze stress is estimated, considering that relaxation of the craze stress occurs from the tip to the base of the craze, and that stress relaxation is the rate-controlling process. This leads to a craze length proportional to t^{2m} where m is the exponent of the power law describing stress relaxation: $\sigma_c(t) = \sigma_0 t^{-m}$. This description of craze growth is apparently confirmed by experimental data not only on PC, but also on PMMA and on rubber-modified PS; however, the range of craze lengths investigated by Williams and Marshall is sufficiently narrow for their data to be compatible, within experimental error, with a linear plot of l *versus* log t, and therefore an unambiguous choice cannot be made between the two mechanisms.

Argon[38] first proposed a model for craze growth based on a repeated nucleation process; for various reasons, this model was later abandoned in favour of a process for craze growth which is entirely distinct from the nucleation process, and in which craze propagation occurs by repeated convolutions of the craze–bulk interface at the craze tip[36]. The theory leads to a constant growth rate which depends on the applied stress in a somewhat complicated manner. This is not at all borne out by our previous results on craze growth rates in PC. However, the theory is attractive in that the process leads to an open craze structure, and that the craze tuft diameter calculated from the theory is of the correct order of magnitude. The two points of view might be reconciled by supposing that craze matter is formed by interface convolutions at the craze tip, as proposed by Argon and Salama, but that the rate-controlling process is propagation of the deformation towards the bulk polymer at the interfaces along the craze body, as proposed here.

CONCLUSIONS

Use has been made of the optical properties of thin crazes to determine the variation of craze thickness and craze during growth of dry crazes in PC. Results clearly indicate the constancy of the craze aspect ratio, in partial confirmation of a previous model for craze growth. Another aspect of this model, namely that the craze thickens by viscoelastic creep, is not borne out by this work, and must be modified to take yield propagation phenomena into account.

In fact, it has been shown that crazes thicken primarily by drawing in fresh material from the bulk. This finding is thought to be of importance in connection with the fracture mechanism.

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