

The competition between shear deformation and crazing in glassy polymers

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Whereas thin films of some polymers such as polystyrene readily form crazes when strained in tension, thin films of other polymers such as polycarbonate rarely exhibit crazing under the same testing conditions; the polymers that rarely craze tend to form regions of shear deformation instead. Polymers such as polystyrene–acrylonitrile which lie between these two extremes of behaviour may exhibit both modes of deformation. Thin films suitable for optical and transmission electron microscopy (TEM) of six such co-polymers and polymer blends have been prepared. After straining, the nature of the competition between shear deformation and crazing is examined by TEM. It is found that in these polymers many crazes have tips which are blunted by shear deformation. This process leads to stress relaxation at the craze tip, preventing further tip advance. In this way short, but broad, cigar-shaped crazes are formed. Examination of the deformation at crack tips in the same polymers shows more complex structures, the initial high stress levels lead to chain scission and fibrillation but as the stress drops, shear becomes the dominant mechanism of deformation and the stress is relieved further. Finally, at long times under stress, chain disentanglement may become important leading to fibrillation and craze formation again. The nature of the competition is thus seen to be both stress and time dependent. Physical ageing of these polymers, via annealing below T_g , suppresses shear leading to the generation of more simple craze structures.

1. Introduction

Glassy polymers may deform either by shear or crazing. Crazes are localized planar defects which contain a network of interconnected voids and fibrils. Typical values for the fibril extension ratio within crazes, λ_{craze} , lie in the range 2–7 [1]. Despite the possibility of high values of strain within the craze, the total plastic deformation caused by crazing in homogeneous glassy polymers prior to fracture tends to be small because the total crazed volume is small.

Shear processes, in contrast, may be localized or diffuse [2–4]; for a given polymer, the degree of localization increases with decreasing temperature and with physical ageing below T_g , the glass transition temperature [2, 4–6]. A “shear to craze” transition may be observed as a function of tem-

perature [4], crazing being favoured at elevated temperatures. A similar transition occurs as a function of annealing time below T_g [6], the propensity for crazing increasing with the length and temperature of the ageing treatment.

The molecular processes involved in the increased tendency for strain localization following physical ageing are not well understood. A slight increase in density is known to occur [2, 7–8] and Struik [9] has proposed that the strain localization and consequent embrittlement are linked to the decrease in free volume. More phenomenologically, one can relate the embrittlement upon annealing to an increase in the yield stress and subsequent yield drop of the polymer [10–12].

The microstructure of deformation in thin films of many glassy polymers can readily be

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studied by transmission electron microscopy (TEM) [1, 4–6, 13]. From such TEM studies it has been possible to show that the microstructure of crazes, represented quantitatively by the parameter λ_{craze} , is primarily governed by the entanglement network of the glass [1, 14]. This network can be characterized in terms of the chain contour length between entanglements l_e , and the entanglement mesh size d , given as the root-mean-square end to end distance of a chain of molecular weight M_e , the entanglement molecular weight determined from melt elasticity measurements. A maximum theoretical extension ratio for the craze, λ_{max} , is predicted by a model in which the entanglement points are treated as permanent crosslinks (i.e., no slippage), and chain scission is neglected. In this model

$$\lambda_{\text{max}} = l_e/d. \quad (1)$$

Good agreement is obtained between λ_{max} and experimental determinations of λ_{craze} for a wide range of homopolymers and co-polymers [1] and polymer blends [14].

For polymers of high l_e such as poly(styrene) (PS) and poly(tertbutylstyrene) (PTBS) crazes form readily when these polymers are strained in air at room temperature. However, polymers of low l_e , such as polycarbonate (PC) and poly(1,4-dimethyl-2,6-phenylene oxide) (PPO) show a marked tendency for diffuse shear deformation which becomes localized upon annealing below T_g . Polymers and polymer blends of intermediate l_e may show both crazes and localized deformation zones (DZs) in thin films. The latter tend to grow rapidly from crack tips, whereas the former grow over longer periods of time.

The DZs grow along a direction normal to the tensile axis, as do crazes, but are distinguished from crazes by the absence of voiding and fibrillation. The deformed polymer within the zone is highly oriented [5] and the extension ratio characteristic of the localized deformation, λ_{DZ} , can be measured by the same methods used to measure λ_{craze} [6]. Such measurements show that λ_{DZ} correlates strongly with λ_{max} , indicating the importance of the entanglement network for this type of deformation. However, whereas $\lambda_{\text{craze}} \approx 0.8\lambda_{\text{max}}$, for the polymers studied, the corresponding λ_{DZ} values are lower, clustering around the line $\lambda_{\text{DZ}} \approx 0.6\lambda_{\text{max}}$. Since the process of crazing must involve chain scission or disentanglement (via reptation) to generate the void–fibril network, whereas the

unvoided DZ structure can be formed with no such breakdown of the entanglement network, the lower value of λ_{DZ} is to be expected. That crazes form over longer time scales than DZs also indicates the importance of the extra kinetic step of scission/disentanglement for crazing.

The formation of plane stress deformation zones can occur in the thin films suitable for study by TEM because shear through the thickness of the film may take place. In bulk specimens, where a state of plane strain exists, shear occurs along directions inclined at 45 to 58° to the tensile axis. The degree of localization in these shear bands is affected by physical ageing in the same way as for DZs.

However, separation of crazing and shear processes into independent modes of deformation is an artificial oversimplification. In practice the two processes are seen to be closely linked, particularly for those polymers with intermediate l_e . In this paper TEM results on the nature of the competition between shear and crazing are presented for thin films of a range of polymers. For bulk specimens, plane stress deformation is no longer possible, but a similar interplay between plane strain shear bands and crazing is to be expected.

2. Experimental procedure

Thin films ($\sim 0.8\mu\text{m}$ thick) were prepared from solutions of the following polymers and polymer blends in an appropriate solvent. The polymer–solvent systems used were:

(1) Polycarbonate (PC) Lexan[®] reactor powder with weight average molecular weight $\bar{M}_w = 39\,000$ and number average molecular weight $\bar{M}_n = 15\,700$, dissolved in methylene chloride.

(2) Two types of polystyrene–acrylonitrile, a random co-polymer: PSAN 1 contained 76 wt% styrene and 24 wt% acrylonitrile with $\bar{M}_w = 216\,000$ and $\bar{M}_n = 102\,000$, and PSAN 2 contained 34 wt% styrene with $\bar{M}_w = 106\,000$ and $\bar{M}_n = 56\,000$. Both were dissolved in methyl ethyl ketone.

(3) Poly(styrene–methylmethacrylate) (PSMMA), a random co-polymer consisting of 35% styrene and 65% methylmethacrylate, $\bar{M}_w = 140\,000$ and $\bar{M}_n = 74\,000$, dissolved in toluene.

Three blends of polystyrene (PS) with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO[®]) were also studied; two blends contained PS of $\bar{M}_w = 300\,000$ and $\bar{M}_n = 124\,000$ (which was free of mineral oil, commonly added as a processing aid) mixed with

PPO of $\bar{M}_w = 35\,000$ and $\bar{M}_n = 15\,000$, and the third contained the same PPO mixed with PS with very low molecular weight, $\bar{M}_w = 4000$ and $\bar{M}_w/\bar{M}_n \leq 1.06$. The blend compositions were as follows: PS:PPO 1—75 wt% high molecular weight PS; PS:PPO 2—50 wt% high molecular weight PS; PS:PPO 3—25 wt% low molecular weight PS. All these blends were dissolved in chloroform.

The method of specimen preparation was the same for all systems. The polymer films were prepared by drawing glass slides from each solution at a constant rate. When the film had dried it was floated off the slide onto a water bath from which it was picked up on an annealed copper grid which had previously been coated with a film of the same polymer. Bonding of the film to the grid was achieved by a short exposure to the vapour of the same solvent. When growth of plastic deformation at crack tips was examined, a crack of the required geometry could be introduced utilizing the intense beam of a JEOL 733 electron microscope to "burn" a thin slit of material. In this way, cracks typically 100 to 120 μm long by < 10 μm wide could be introduced into the centre of each grid square [5]. Deformation was examined both in films which had been annealed below T_g and unaged specimens. A typical ageing treatment for most of the polymers was 1 h at 100°C.

For both the growth of isolated crazes and crazes at crack tips, straining was performed by mounting the grids in a strain frame and straining in air while observing them with an optical microscope. In this way growth of the deformation could be followed as a function of time. After straining, suitable grid squares were cut out and examined in the TEM (a Siemens 102 electron microscope operating at 125 keV); the copper grid deforms plastically during straining, and thus maintains the level of applied strain in the film. Further details of this specimen preparation technique are discussed by Lauterwasser and Kramer [15].

To characterize the local extension ratio of a craze/DZ, the method developed by Lauterwasser and Kramer [15] may be used. For a craze, v_f , the volume fraction of fibrils in the craze, is found from microdensitometry of the electron image plate to give values of the optical densities of the craze (ϕ_{craze}), the film (ϕ_{film}), and of a hole through the film (ϕ_{hole}). The value of v_f is then given by

$$v_f = 1 - \frac{\ln(\phi_{\text{craze}}/\phi_{\text{film}})}{\ln(\phi_{\text{hole}}/\phi_{\text{film}})} \quad (2)$$

TABLE I Values of various parameters of the polymer

Polymer	l_e (nm)	λ_{max}	λ_{craze}	λ_{DZ}
PS	40.0	4.2	4	—
PSAN 1	27.0	3.3	2.7	2
PSAN 2	18.0	2.7	2.0	1.8
PSMMA	19.0	3.1	2.0	1.7
PC	11.0	2.5	2.0	1.4
PPO	16.5	3.0	2.6	1.6
PS:PPO 1	27.0	3.1	3.2	2.1
PS:PPO 2	22.0	2.9	2.8	2.0
PS:PPO 3	22.0	2.9	3.4	1.6

For the case of unfibrillated regions, v_f is now the ratio of the thickness within the zone to the undeformed film thickness; the expression for v_f is identical to Equation 2, but with ϕ_{craze} replaced by ϕ_{DZ} , the optical density of the DZ image [8]. Since both crazing and DZ formation are plastic deformation processes which occur at constant polymer volume, the extension ratio λ is related to v_f by

$$\lambda = 1/v_f \quad (3)$$

Values of l_e and λ_{max} for the polymers are listed in Table I. The calculation of these parameters is described fully in previous papers [1, 6, 14].

3. Results

Optical microscopy and TEM both reveal the existence of short, cigar-shaped crazes (Fig. 1a, b and c) in PSAN 1, PSAN 2, PSMMA and the three blends of PS with PPO. At its tip the craze is blunted either by a pair of diffuse shear bands which lie at an angle of $\pm 32^\circ$ to the craze plane (Fig. 1a and b), or alternatively by a region of diffuse shear extending directly ahead of the craze tip (Fig. 1c).

The onset of shear deformation does not necessarily coincide with the craze tip, but may run alongside the craze for part of its length. This effect is clearly seen in Fig. 1b. In some cases the region of shear may also be punctuated by short segments of craze, where fibrillation has not occurred throughout the film thickness. An example of this type is shown in Fig. 2. Fig. 2 shows clearly that the extension ratio within the midrib increases towards the craze tip; this effect is seen more clearly in a craze in PSAN 1 in Fig. 3. This increase was commonly observed.

Crazes which are long and thin, as opposed to the short, wide crazes shown in the preceding

figures, also often have diffuse shear zones extending ahead of their tips (Fig. 4). The growth of these sheared regions which, in thin films correspond to a local thinning, could be observed in the reflection optical microscope by changes in the interference fringe colour. The extent of the zones grows slowly over a period of several hours, during which time the craze tip does not appear to advance; because of the limited resolution of the optical microscope it is not possible to measure if significant craze thickening occurred during this time.

For PSAN 1, PS:PPO 1 and PSMMA the formation of these diffuse zones ahead of the craze tips was suppressed by annealing below T_g . The crazes that formed in annealed films had low aspect ratios (i.e., were long and thin), and the tips exhibited no shear blunting. However, in PSAN 2 and PS:PPO 3 crazes were not observed to form at all without an ageing treatment, and following a short anneal, shear at the craze tip was still possible.

When films containing cracks were strained, more complex structures were nucleated in PSAN 1 and the blend PS:PPO 1 under certain conditions. An example is shown in Fig. 5 for PSAN 1. At the crack tip three distinct regions can be seen (see Fig. 5b). The outer edge resembles a typical fibrillated craze, and some indication of voiding can also be seen in the centre portion. The region lying between these two structures is less highly drawn and shows no such voiding. Measurements of the extension ratio within the three regions show the centre and outer structures both have a λ of 3.7, whereas λ for the unvoided portion is 2.0. Away from the crack tip progressively less shear occurs, and the craze structure dominates. The growth of these plastically deformed regions

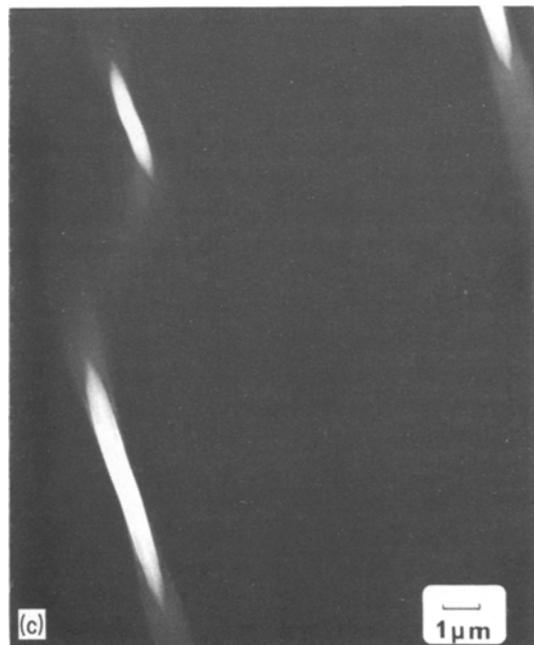
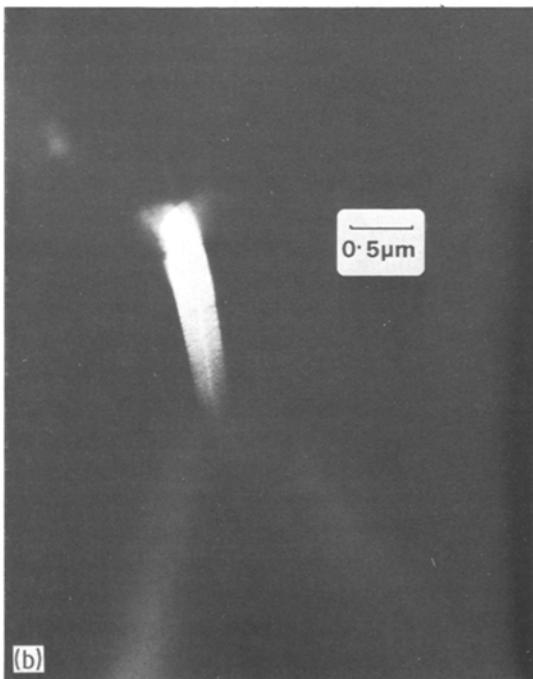
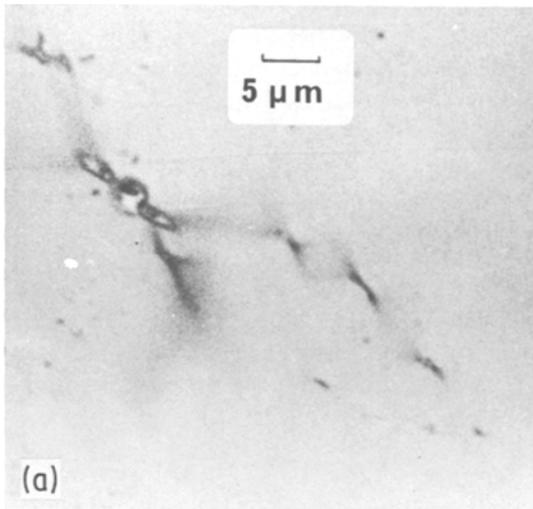
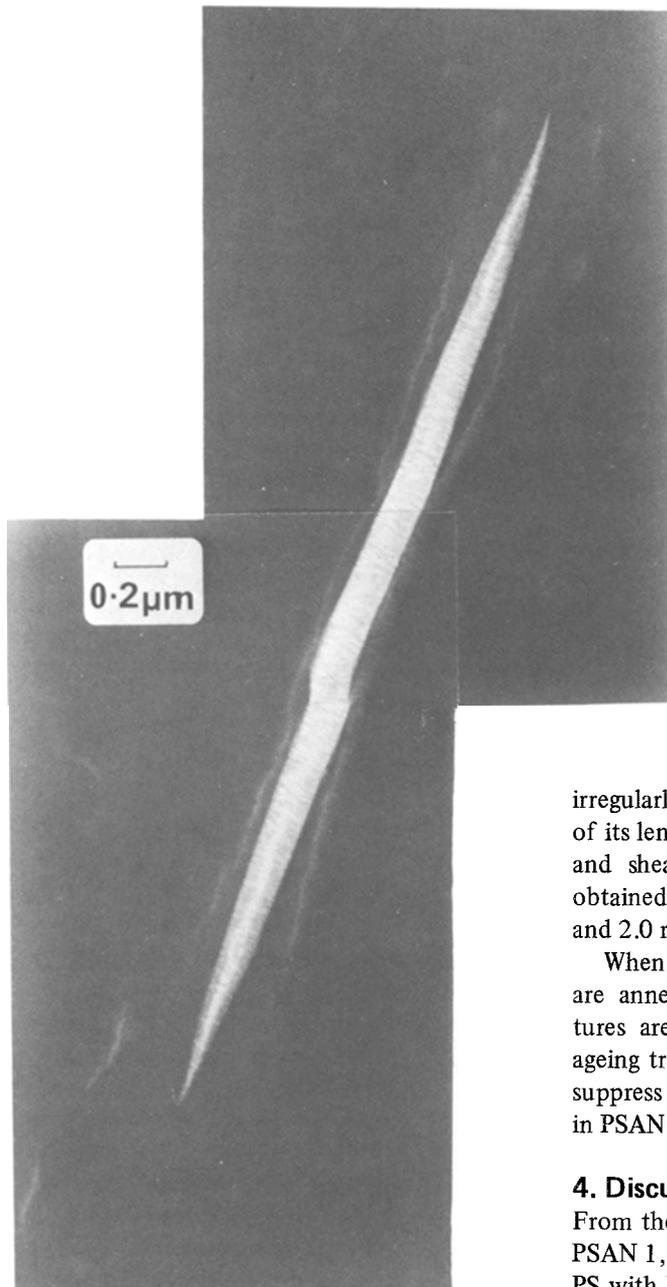


Figure 1 Showing (a) optical micrograph of shear bands growing from the tips of short crazes in PS:PPO 1, (b) micrograph of angled shear bands growing from the tips of a craze in PSAN 2 and (c) micrograph of shear ahead of craze tip in PS:PPO 3.

Figure 2 Shear and partial fibrillation outside a craze in PS:PPO 1.



can be followed optically before examination in the TEM. These growth experiments show that growth occurs slowly over 20 to 30 h, the highly fibrillated regions at the outer edges and tip forming at the longer times.

In contrast to this behaviour, some crack tips developed a more homogeneous structure which formed much more rapidly (Fig. 6). These zones resemble the DZs previously described except for a region of partially fibrillated polymer running

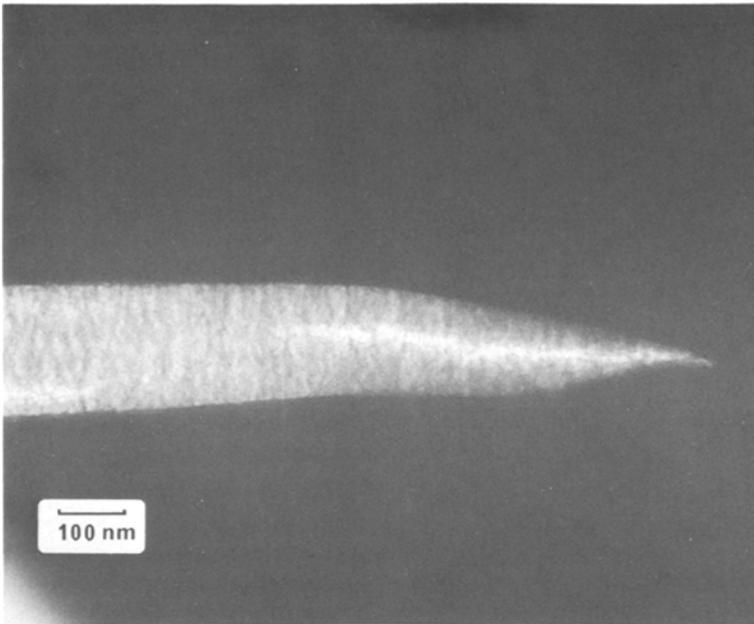
irregularly down the centre of the zone over part of its length. The extension ratios of the fibrillated and sheared regions were very similar to those obtained in the more complex structure, i.e., 3.7 and 2.0 respectively.

When films of PSAN 1 or the PS:PPO 1 blend are annealed below T_g , only simple craze structures are formed at crack tips; for instance, an ageing treatment of 0.5 h at 100°C is sufficient to suppress shear completely and to promote crazing in PSAN 1.

4. Discussion

From the preceding micrographs, it is clear that in PSAN 1, PSAN 2, PSMMA and the three blends of PS with PPO examined, there is a strong interplay between crazing and shear yielding. These polymers have values of l_e and λ_{max} in the range of 18.0 to 27.0 nm and 2.7 to 3.3 respectively (Table I). PS, which has a much larger value of l_e shows no sign of shear, whereas PC, which has a lower value of l_e , rarely exhibits crazing under equivalent testing conditions, even after prolonged ageing treatments [5]. The six polymers discussed here can be divided into two groups, PSAN 2 and PS:PPO 3 and the remaining four. The polymers PSAN 2 and PS:PPO 3, are distinguished from the remainder by the lack of crazing without a prior anneal, and

Figure 3 Pronounced midrib at a craze tip in PSAN 1.



the occurrence of shear together with crazing following annealing. It might be anticipated that longer annealing times (than the 1 h at 100° C for PSAN 2 and 0.5 h at 100° C for PS:PPO 3) would ultimately suppress shear in these polymers also. The effect of such an annealing treatment has not been investigated. It is probably significant that these polymers both have values of l_e and λ_{max} at the low end of the series of polymers. The other four polymers show shear only when the film has not been physically aged by annealing.

From the observations presented here and in previous papers [5, 6] it is clear that the suppression of crazing and propensity for shear increases as l_e and λ_{max} decrease. It has been suggested [16] that for low l_e polymers there are three stages of deformation which occur as the stress drops. At

the highest stress levels scission may occur, permitting void formation. As the average stress falls below the level where rapid chain breakage may occur, shear processes start to dominate. Finally, over long times at a low level of stress, significant disentanglement may occur permitting fibrillation and void formation and the consequent reappearance of crazing. This three-stage process is in accord with the appearance of Fig. 5, recognizing that the central region corresponds to the earliest stage of growth. The different structure of Fig. 6 can also be rationalized in terms of this three-stage process. Although the DZ grew rapidly, the craze which is seen to merge with the DZ did not grow significantly until several hours had passed. As this craze (nucleated at an early time from a dust particle) grew, it may have relaxed the stress on the DZ so that the necessary stress conditions for fibrillation at the zone edge were not met.

Although the ease of shear deformation is decreased by annealing, the values of λ_{craze} and λ_{DZ} are comparable for the annealed and un-annealed films. Also the extension ratio within the central "quasifibrillated craze" region in both Figs 5a and 6 have similar values to λ_{craze} , indicating similar molecular processes are involved in all cases.

From these arguments it is now possible to understand the appearance of the isolated "cigar-shaped" crazes with tips which have been blunted by shear bands. The fibrillated region grows under the initial high level of stress. As the stress drops,



Figure 4 Blunting by shear at the tip of a long craze in PS:PPO 1.

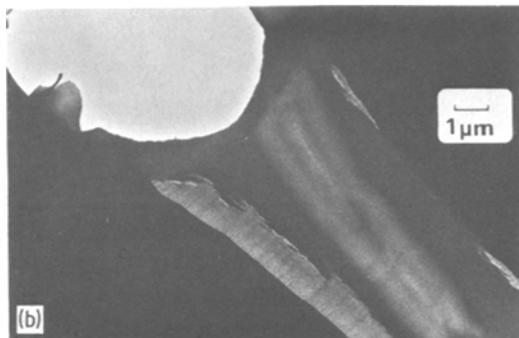
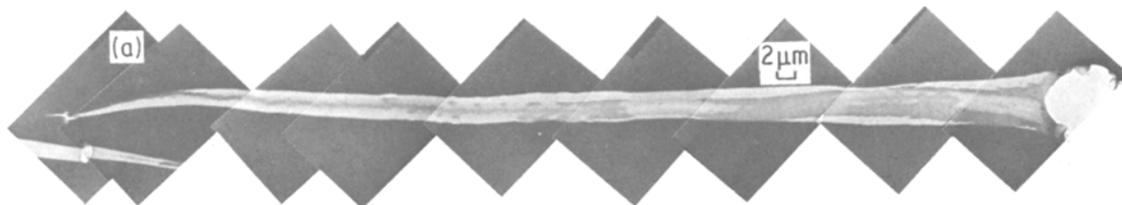


Figure 5 A crack tip in PSAN 1 showing (a) mixed mode of deformation and (b) high magnification image of crazed region near the crack tip.

shear is favoured and fibrillation cannot proceed. Once this shear has occurred it prevents significant tip advance, even over long time scales, both because it relaxes the stress further, and because the shear will be accompanied by molecular orientation. The effect of this orientation is to increase the crazing stress [17]. However, thickening of the craze near its centre may continue, and hence the crazes are short but wide. Such thickening of the crazes will in turn change the stress concentration at the craze tip; ultimately this increase may permit further tip advance once again under high stresses. For the tip advance to take place a high degree of scission must occur, leading to an increased extension ratio in the midrib, as seen in Figs 2 and 3.

Blunting of craze tips by pairs of angled shear bands and by a single shear zone extending in the plane of the craze have been observed in these films. This variation in the appearance of the shear deformation is thought to be due to the degree of constraint through the thickness of the film, rather than any intrinsic property of the polymers

examined. If thick enough specimens could be examined by TEM, it is anticipated that angled shear bands would always be observed.

These observations on shear at craze tips indicate that shear bands will in a certain sense act as “craze stoppers” as has been suggested by Bucknall [18], and the micrographs presented here are consistent with scanning micrographs of an etched high impact polystyrene/PPO blend obtained by Bucknall *et al.* [19].

This role of shear bands growing to “blunt” a growing craze tip is distinct from the role of pre-existing shear bands as sites for preferential craze nucleation. In the latter case, the shear band having formed first, cannot relieve the stresses at the craze tip; indeed the pre-orientation in the shear band is such as to cause an increase in craze fibril extension ratio, leading to premature craze breakdown [20].

In contrast, when shear occurs together with craze thickening, or if a region of shear runs parallel to the craze as in Fig. 2, relief of stress may occur due to the shear deformation. This point is further demonstrated by Fig. 7 which shows a craze in a specimen of PS:PPO 3. Outside this craze, a region of shear and partial fibrillation through the film thickness has developed over much of the craze length. Where this region is absent (A) or less pronounced (B), the high stresses lead to further extension of the craze

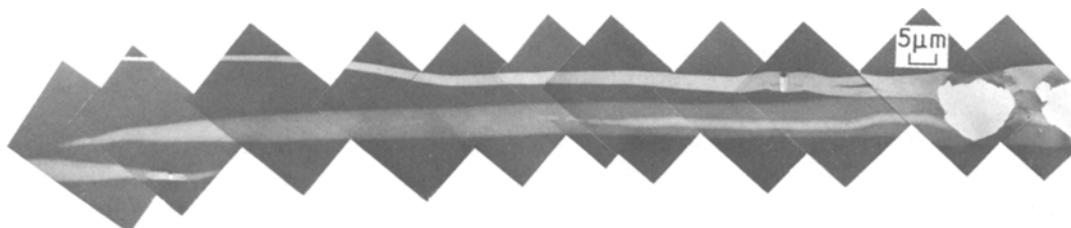


Figure 6 DZ with fibrillated centre growing from a crack tip in PSAN 1. The craze along side the DZ grew from the dust particle at A several hours after the growth of the DZ.

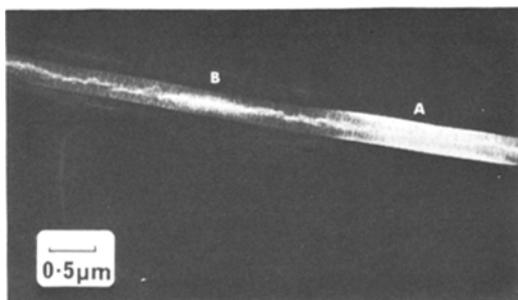


Figure 7 A craze flanked by region of shear deformation in PS:PPO 3. At positions A and B there is little stress relief via shear and craze fibril breakdown occurs leading to a high λ .

fibrils, and the midrib is no longer distinct from the outer portions of the craze. Elsewhere the stress relief by shear deformation prevents this incipient fibril breakdown. As has been previously discussed [14], fibril true stresses are very high in the PPO blends with low \bar{M}_w PS because the PS chains are not load bearing, and PS:PPO 3 is particularly prone to this type of craze breakdown. Such stress relief for a craze with a contiguous region of shear is likely to be of importance in the generation and stability of the “epsilon plastic zone” observed in fatigued specimens of PC [21]. In these epsilon zones a craze forms the central branch surrounded by two shear bands. As discussed by Takemori and Kambour [21], other polymers do not show the flanking shear bands but do show unstable discontinuous crack growth through a craze generated at the crack tip. Thus, if the primary role of the shear bands in the epsilon zone is to relax the stress on the craze fibrils, the higher resistance of PC to unstable discontinuous crack growth under fatigue is explicable.

The results presented here all indicate that as the chain contour length between entanglements is decreased, crazing becomes more difficult and plastic shear processes become increasingly important. On the other hand, increasing the rate of chain disentanglement (via reptation) by raising the temperature of deformation should promote crazing over shear deformation. Although straining thin films of PC at room temperature normally produces only shear deformation zones, even after ageing, one would expect straining such films at elevated temperatures to yield crazes similar in appearance to room temperature crazes in a polymer such as PS:PPO 1. Such an expectation is borne out by an examination of a PC film strained

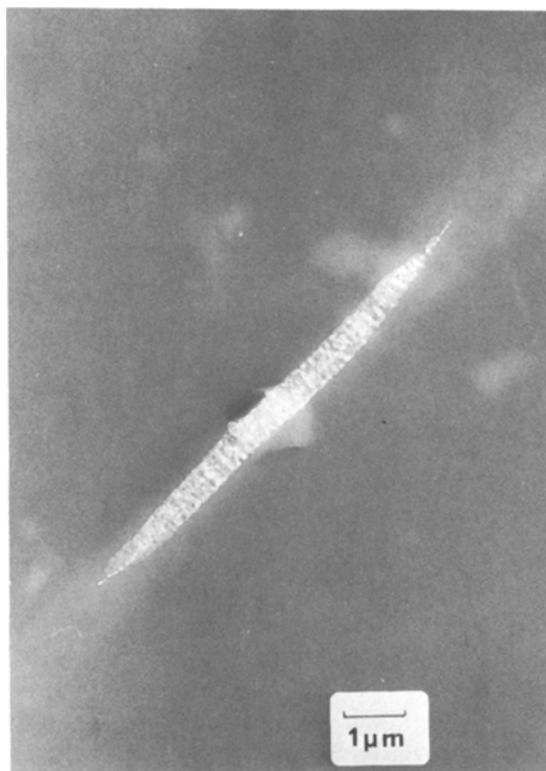


Figure 8 Short craze blunted by shear at its tips in PC strained at 132° C.

at 132° C, following an annealing treatment of 1 h at the same temperature. Crazes (Fig. 8) as well as DZs were produced in the film; the crazes were short and broad and exhibited tips blunted by a shear deformation zone.

From this study it is clear that the entanglement network governs many aspects of craze growth. Not only does it determine the extension ratio within crazes [1, 14] and deformation zones [6], but also the interplay between crazing and shear. Physical ageing and elevated temperatures clearly increase the contribution of crazing relative to shear. From knowledge of l_e alone, these ideas should permit predictions to be made about the ease of crazing, the nature of any crazes formed, and the importance of a physical ageing treatment for the polymer. One might also suspect that, if entanglements behave analogously to chemical crosslinks, radiation crosslinking of a large l_e polymer such as PS (which will lead to a reduction in the effective l_e) will lead to a similar transition from crazing to shear. Thus if PS were to be irradiated sufficiently to give a high crosslink density, with an effective l_e comparable to PC,

plane stress deformation zones should form in thin films. However, final clarification of the processes involved in the two modes of deformation will only be forthcoming when the molecular processes (scission and disentanglement) which modify the entanglement network during the crazing process are more completely understood.

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