JOURNAL OF MATERIALS SCIENCE 24 (1989) 1399–1405

Crazing mechanisms and craze healing in glassy polymers

C. J. G. PLUMMER, A. M. DONALD
Cavendish Laboratory, University of Cambridge, CB3 OHE, UK

When held at temperatures above the glass transition temperature, crazes in certain polymers may be made to heal; that is, the crazed material may be made to recover the mechanical properties it had prior to crazing. Using thin films of a variety of polymers, we have investigated whether the mechanism of entanglement loss during crazing influences the heat treatment time necessary for healing. We find that under experimental conditions for which there is evidence of disentanglement during crazing, and if the crazes do not break down, healing occurs after heat treatment times of the order of those necessary to make the craze disappear optically. Similar heat treatments applied to scission mediated crazes however, do not result in healing. We argue that scission crazing results in a high proportion of chain fragments which are unable to contribute to the entanglement network. Since the heat treatments are not sufficiently long to disperse these fragments, and hence to restore the original local entanglement density, healing does not take place. Disentanglement should not result in such damage, so, consistent with our observations, healing times should be relatively short. Hence, these results provide independent evidence for disentanglement during crazing.

1. Introduction

The purpose of this work has been to investigate the possibility that the mechanisms by which entanglements are lost during crazing determines whether the craze material is able to heal, that is, recover the mechanical properties it had prior to crazing, when held at a temperature above T_g for a given length of time. Subsequent to shear deformation ductile glassy polymers generally maintain a memory of their initial (equilibrium) configuration and when held at high temperature are able to recover this configuration, even in the absence of a permanently cross-linked network [1]. This can be explained in terms of the entanglement network concept. Entanglement is a measure of the extent to which relative motion of polymer chains is subject to topological constraint. In the network model, entanglements are idealized as point constraints and are assumed to remain immutable during shear deformation, which may be visualized as the stretching of the polymer strands linking entanglement points. This leads to the concept of a natural draw ratio λ_{max}, approximately equal to l_e/d_e where l_e is the chain contour length between entanglement points and d_e is the spatial separation of topologically linked entanglement points. Indeed, there is good correlation between λ_{max} and λ_{DZ}, the draw ratio observed in localized shear deformation zones (DZs) in a variety of materials [2]. During recovery (i.e. when held above T_g), entropic forces lead to chain retraction and the entanglements are drawn back to their equilibrium positions relative to one another.

However, this view is not sufficient to describe what happens when a craze is held at temperatures above T_g. It is now well established that crazing in glassy polymers is not purely a yielding process. Forming the characteristic open voided structure of a craze involves a "geometrically necessary" entanglement loss [3, 4], and so it can no longer be assumed that the entanglement network remains intact subsequent to crazing. This entanglement loss is reflected by the observation that λ_{craze} is generally larger than λ_{DZ} [3, 4]. For the craze material to heal, there must be some degree of re-entanglement. That a craze is no longer within the resolution of an optical microscope is not a sufficient criterion for craze healing as we defined it in the opening paragraph. Wool and O'Connor [5] found that polystyrene crazes grown at room temperature could be made to reappear at significantly lower strains than those at which they were formed prior to heat treatment, even though the heat treatment time had been sufficient to make them disappear optically. In this particular case very much longer times were needed for the crazing strain to recover its initial value, or effectively, for the craze to heal.

Two mechanisms are available for entanglement loss during crazing. Chain scission [4] is favoured in high molecular weight, low entanglement density polymers such as polystyrene (PS) and disentanglement [4, 6] is favoured in low molecular weight, high entanglement density polymers such as polycarbonate (PC) and polyethersulphone (PES). In polymers such as low molecular weight PS, scission dominates at high strain rates and relatively low temperatures [4] but disentanglement has also been shown to occur close to T_g and at low strain rates [7, 8]. The important distinction between these mechanisms is that whereas disentanglement leaves the polymer chains chemically

0022–2461/89 $03.00 + .12

intact, scission results in substantial damage to the chains. If this damage can be shown to affect whether the craze material is able to heal during a given heat treatment, then one has a way of determining whether scission or disentanglement is taking place during crazing under a given set of experimental conditions.

2. Experimental details

Three different molecular weights (127 000, 260 000 and 1150 000; $M_W/M_n < 1.09$) of monodisperse PS (supplied by Polymer Laboratories Ltd) were used for the main part of the experimental work. Additional investigations were carried out using polydisperse PC (Lexan reactor powder, supplied by Dr Kambour of General Electric) of two different molecular weight averages (30 000 and 150 000) and polydisperse PES (Victrex, supplied by ICI plc) of two molecular weight averages (47 000 and 69 000). Uniform thin films were produced by drawing glass slides at a constant rate from solutions of the various polymers (the solvents were toluene at room temperature for PS, dichloromethane at room temperature for PC and cyclohexanone at 40° C for PES). The film thickness was held constant at 0.6 μm by regulating the concentration of the solutions. Following the method of Lauterwasser [9], the films were floated off on the surface of a water bath and picked up on annealed copper grids which had previously been coated with the same polymer. A short exposure to appropriate solvent vapour served to remove any slack from the films and to bond them to the copper grids. The films were then placed in a vacuum oven at approximately $T_g - 10°$ C for a minimum of 48 h in order to dry them and suppress the formation of DZs [11].

The films were strained at various temperatures in a constant temperature enclosure, the straining rig being connected to a variable speed motor, and observed using a Carl-Zeiss Jenapol optical microscope. Except where indicated, all the samples were strained at a constant rate of 6×10^{-5} sec^{-1} and the strain at which the crazes first appeared in each sample was recorded. In the first series of experiments the crazed samples were heated to various temperatures above T_g and the subsequent behaviour observed. The time it took to reach the point where the crazes could no longer be resolved using the optical microscope was recorded at each temperature (for which the craze did not break down). In a second series of experiments, measurements were made in order to compare the strain to craze before and after a given healing treatment. All heat treatments were carried out *in situ*, since removal from the strain rig was liable to damage the sample and alter the direction of principle stress in the films. After testing, individual grid squares were removed for examination using transmission electron microscopy (TEM). From electron micrographs it was possible via microdensitometry to determine λ_{craze} (the details of this method are given by Lauterwasser and Kramer [10]).

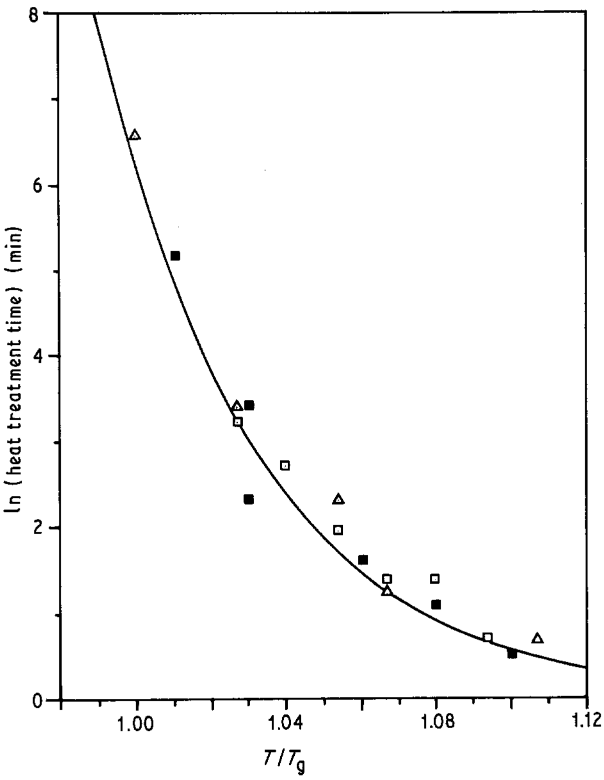

Figure 1 The time taken for crazes to disappear optically as a function of T/T_g. (□ PS 1150000, △ PS 260000, ■ PC 150000).

3. Results

The times for crazes to disappear optically are given as a function of T/T_g in Fig. 1 where T is the heat treatment temperature. For PS this time is independent of molecular weight. Craze breakdown was found to occur universally in PES and also in the lower molecular weight PC samples so the molecular weight dependence could not be determined for these materials. However, in the higher molecular weight PC (150 000) the crazes did remain stable and the times for these crazes to disappear showed a similar dependence on T/T_g to PS so that the points appear to lie on the same curve. The temperature at which the crazes were formed did not affect these results significantly. However, it was found that for the low molecular weight PS (127 000) there was a tendency for craze breakdown to occur at the tips of crazes formed at temperatures close to T_g as shown in Fig. 2. Even when the sample was initially strained at room temperature, the fact that the crazing strain drops markedly close to T_g at this molecular weight meant that additional crazes were often able to form as the temperature was being raised towards the healing temperature, these latter becoming sites for subsequent breakdown during healing.

When there was no craze breakdown, the sample microstructure evolved as shown in Fig. 3, which shows successive optical micrographs of a room temperature craze in PS with a molecular weight of 260 000 being heat treated at 130° C (T_g + 30° C). Freshly formed crazes generally appear dark under reflected light owing to light scattering by the craze fibrils. During the intial stages of the heat treatment however, the craze body took on a uniform interference colour, indicating widespread fibril coalescence. As the heat treatment progressed the craze became less distinct from the surrounding material and the separation of the craze boundaries decreased, although in many cases a faint mark was visible at the site of the original craze a long time after the craze was judged to

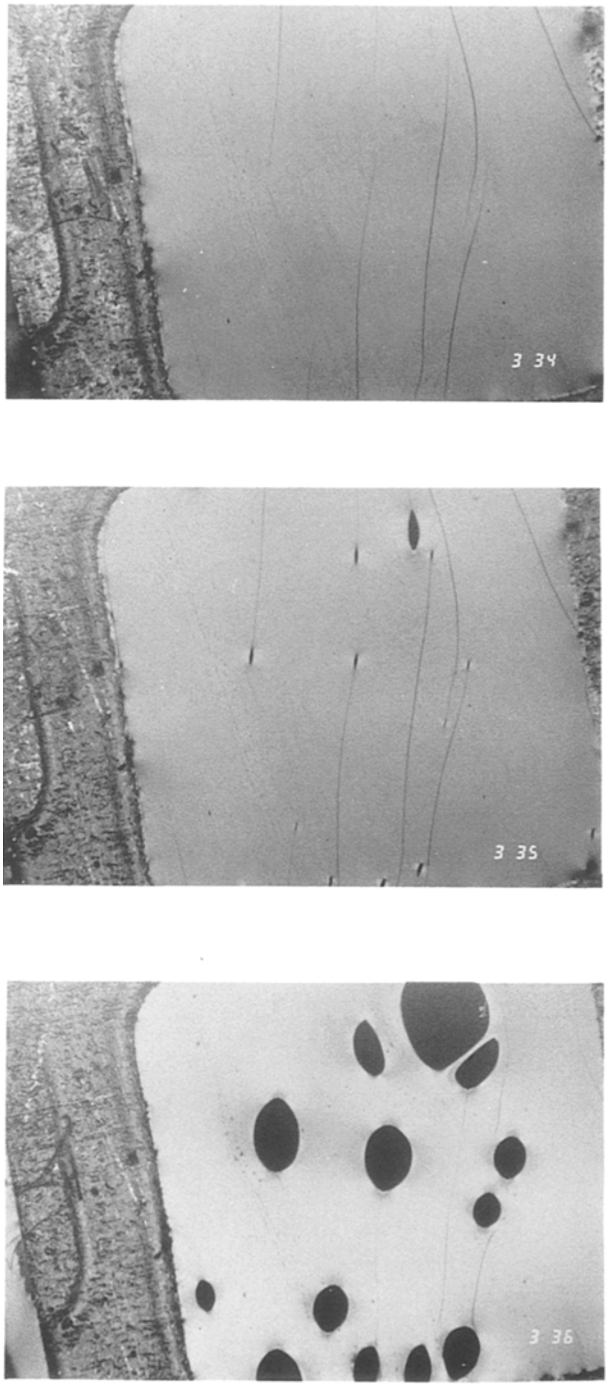

Figure 2 Craze breakdown at the tips of crazes formed at temperatures close to T_g.

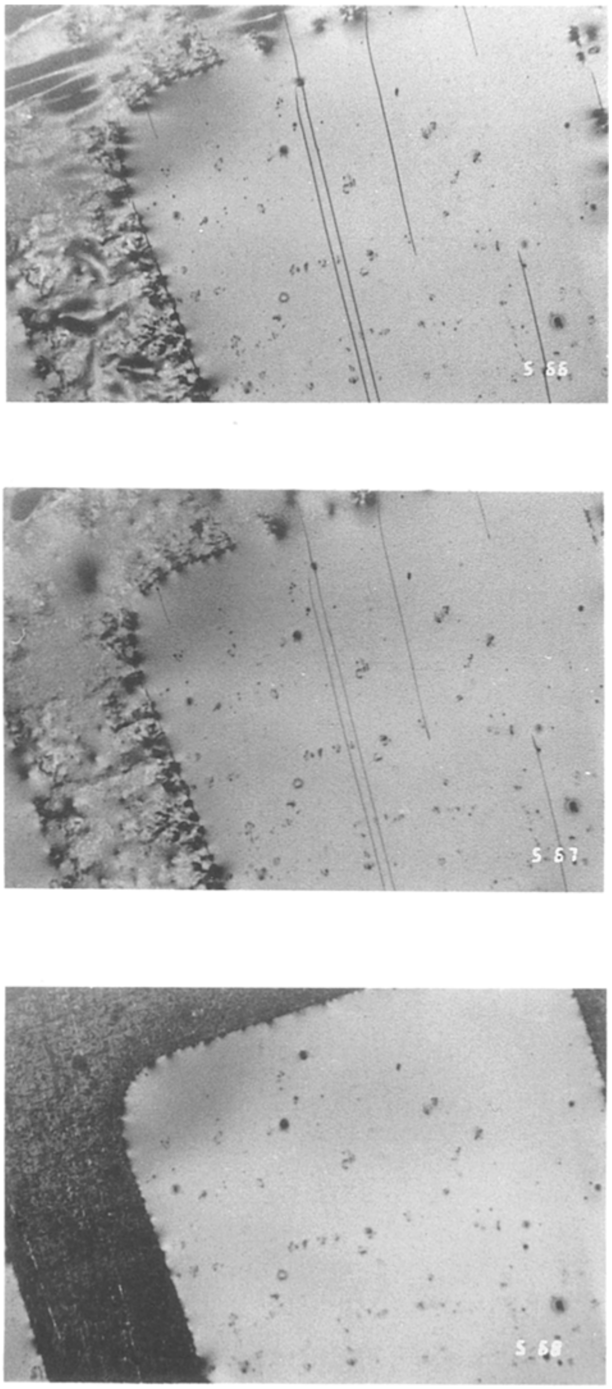

Figure 3 Optical micrographs of a room temperature craze in PS with a molecular weight of 260000 being heat treated at 130° C.

have disappeared. TEM showed this to be a shallow surface groove. The presence or otherwise of this groove did not affect the subsequent strain to craze.

Fig. 4 shows the strain to craze as a function of temperature at a strain rate of 5×10^{-5} sec^{-1} in the highest molecular weight PS (1150000) before and after a 10 minute healing treatment 130° C which was more than sufficient to make the craze disappear optically. It is clear from the figure that this treatment was inadequate to heal the crazes, in the sense of recovering the initial properties of the crazed material. Subsequent heat treatment and restraining did not lower the strain to craze further, and the lower curve in Fig. 4 could be reproduced by repeated cycles of heat treatment and crazing at different temperatures. The lower molecular weight samples showed similar behaviour when crazed at temperatures below 70° C as illustrated in Fig. 5. Comparison with Fig. 4 suggests that in this regime there is no molecular weight dependence in the strain to craze either before or after heat treatment. Above 70° C however, the results of Fig. 5 contrast markedly with those of Fig. 4. The initial strain to craze began to fall rapidly with increasing temperature, and it was found that after heat treatment for 10 minutes at 130° C there was no change in the strain to craze, even after several cycles of heat treatment and restraining. If on the other hand one followed a path such as indicated in Fig. 6, that is, crazing at 70° C, heat treatment, crazing at 50° C, heat treatment and finally crazing again at 70° C, it was possible to lower the strain to craze at 70° C and above in these samples.

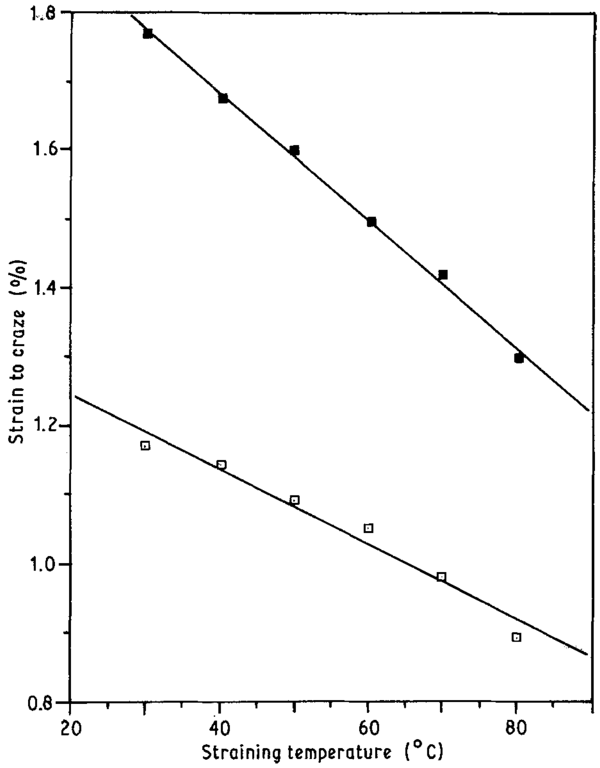

Figure 4 The strain to craze as a function of temperature at a strain rate of $5 \times 10^{-5}\,\mathrm{sec}^{-1}$ in the highest molecular weight PS (1150000) before (■) and after (□) a 10 minute healing treatment at 130° C.

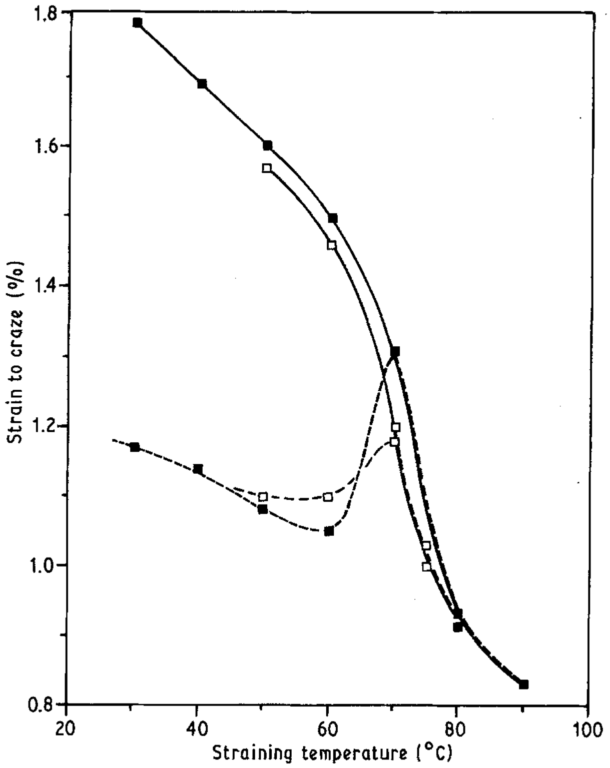

Figure 5 The strain to craze in low molecular weight PS as a function of temperature. (□ PS 127000, ■ PS 260000) before (——) and after (– – –) a 10 minute healing treatment at 130° C.

In Fig. 7 some results are also given for the high molecular weight PC samples, the strain rate in this case being $10^{-2}\,\mathrm{sec}^{-1}$ for convenience. Subsequent to a heat treatment of 10 minutes at 180° C (T_g + 35° C), an additional annealing treatment of 24 h at 130° C was used to suppress the formation of DZs during restraining [1] (the strain to craze in PC is unaffected by annealing below T_g [6]). The tendency for DZs to be favoured over crazing in thin films at relatively low temperatures in PC nevertheless limited the range of temperatures at which these experiments could be carried out. At all temperatures at which it was possible to obtain results, repeated crazing and healing treatment did not significantly affect the crazing strain, as with the low molecular weight PS crazed at temperatures above 70° C.

For crazes formed well below T_g there was a correlation between the position and sizes of the crazes before and after heat treatment at all molecular weights. For crazes formed in low molecular weight PS above 70° C there was still a tendency for the crazes to reappear in the same positions, but the correlation was often less marked than in the case of low temperature PS crazes.

4. Discussion

As pointed out in the introduction, it has been shown that scission will dominate crazing in high molecular weight PS at all temperatures, whereas in high entanglement density polymers such as PC one expects chain disentanglement to dominate [4, 6]. There is also evidence [7, 8] that disentanglement occurs during crazing in low molecular weight PS at low strain rates and temperatures close to T_g. From the results presented here, it appears that where crazing is expected to be mediated by disentanglement, the craze material is able to heal completely in times of the order of the time it takes the craze to disappear optically. Where there is chain scission however, the same heat treatment is not sufficient to restore the properties of the craze material, and the craze is subsequently able to reopen at a much reduced strain. In the present investigation we find that the ability of the crazes to heal coincides with a sharp drop in the strain to craze with temperature which is also suggestive of disentanglement since one expects disentanglement to be much more strongly temperature dependent than scission controlled crazing [6]. The temperature at which this occurs is consistent with the temperature range in which Berger and Kramer observed disentanglement [7].

Craze healing will proceed as follows; initially the highly oriented chains in the craze fibrils will retract, and at the same time the stress on the craze surface will decrease owing to viscoelastic relaxation of the bulk polymer. In some cases, where either the fibril extension ratio or the chain mobility is particularly high (for example for low molecular weight PS crazed close to T_g, where the extension ratio is known to be much higher than at room temperature [7], and PES, where disentanglement mediated crazing has been observed more than 100° C below T_g [6]), further disentanglement may cause fibril breakdown to occur as in Fig. 2. Analysis of typical craze displacement profiles [4] indicates a stress concentration at the craze tip which explains why fibril breakdown initiates at the craze tips in Fig. 2. However, if the craze remains stable, the craze material contracts and pulls the craze–bulk interface with it. At the same time fibril coalescence takes place. Our observations, and those

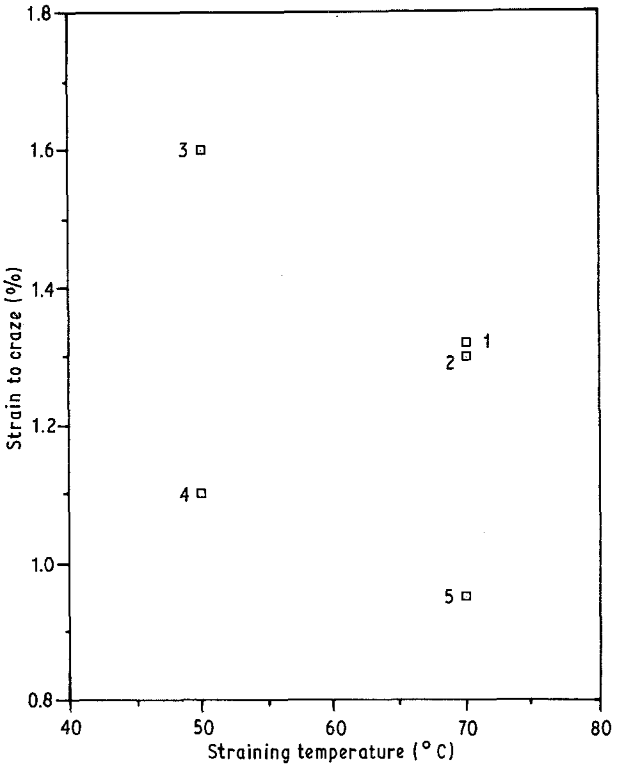

Figure 6 A path showing crazing at 70° C, heat treatment, crazing at 50° C, heat treatment and finally crazing again at 70° C for low molecular weight PS (127 000).

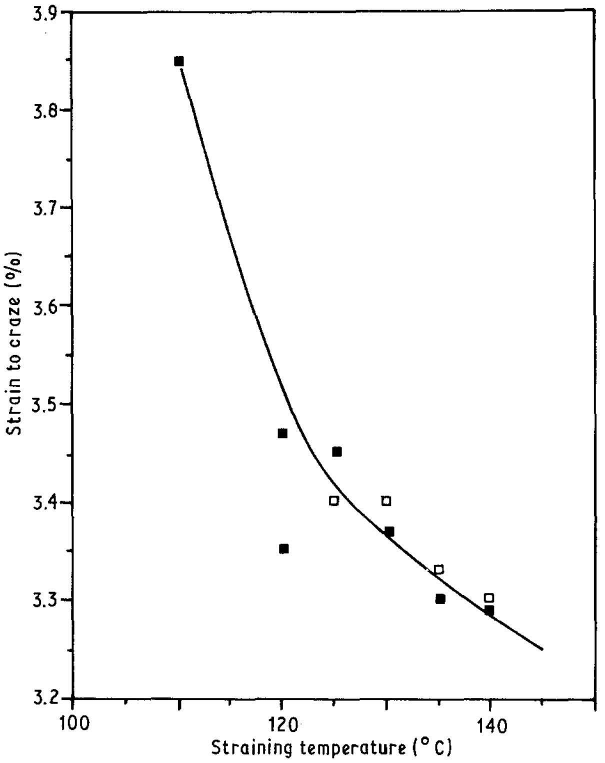

Figure 7 Results for the high molecular weight PC samples at a strain rate of 10^{-2} sec^{-1} before (■) and after (□) heat treatment.

of Yang and Kramer [12], suggest this to be a relatively rapid process and are therefore evidence of very high mobility of the polymer chains at the fibril surfaces. Hence it is reasonable to assume that these polymer chains are able to reach local equilibrium with each other within short times compared with the overall heat treatment time required to make the craze disappear optically. Hence, in the absence of permanent damage, they should reentangle to the same degree as they were entangled before crazing.

Clearly from our results, in the case of scission crazing in PS reentanglement cannot be complete after a 10 minute heat treatment at 130° C. We believe this to be a consequence of the damage caused to the chains themselves. Kramer has assessed the amount of damage occurring in PS from the geometrically necessary entanglement loss [4]. The number average molecular weight M_n' after crazing is given by him as

$$\frac{1}{M_n'} = \frac{1}{M_n} + \frac{1 - v_e'/v_e}{M_e} \qquad (1)$$

where v_e'/v_e is the ratio of the entanglement density after crazing to the entanglement density before crazing, M_e is the entanglement molecular weight and M_n is the number average molecular weight before crazing. The entanglement molecular weight of PS is 19 000 and v_e'/v_e is approximately 0.4 in PS at room temperature. For the high molecular weight PS used here, M_n' is approximately 1.7 M_e and for the lowest molecular weights it is closer to $1.5 M_e$. A calculation by Flory [13] suggests that for random scission the weight average molecular weight after scission M'_W will be approximately $2M_n'$ so that we expect the crazed material to have a broad molecular weight distribution with a standard deviation of the order of M_n' itself, and consequently a substantial number of chains with molecular weights of the order of M_e. Indeed, on the basis of Flory's calculation we estimate (see appendix) that as much as 24 wt % of the material present will have a molecular weight of the order of M_e and will not, therefore, be able to contribute to the entanglement network. If these short chains were distributed homogeneously within the crazed material this might not be expected to affect the crazing stress greatly; in Donald and Kramer's experiments with PPO diluted with short PS chains [14], upwards of 60 wt % of PS was needed substantially to affect the crazing properties. However, the scission is not random, but concentrated in the layer of material lying within one disentanglement separation of the surface of a primordial cylinder of diameter D_0, shown in Fig. 8. Chains whose centres of gravity lie well within this cylinder will suffer far less damage than ones whose centres of gravity lie close to its surface. Also, as the polymer is drawn into a fibril, the damage will be concentrated in the layer of polymer adjacent to the fibril surface as illustrated in Fig. 8b. Hence one expects very little chain entanglement at the fibril surfaces, and relatively long entangled chains deeper inside the fibril, acting to stabilize it. These latter chains will also provide the anchors by which chain retraction initiates the healing process.

From the distribution of chain damage in Fig. 8, it is evident that for this model of scission dominated crazing, the heat treated craze would be able to reopen with little further entanglement loss since the entanglement density corresponding to the position of the original void fibril interfaces would be extremely low. Kramer's model for the craze widening stress [4] suggests a $\Gamma^{1/2}$ dependence, where Γ is the effective surface

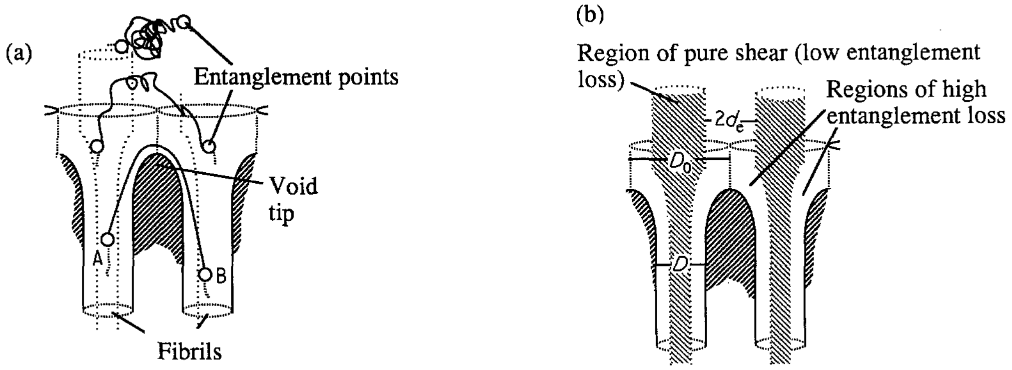

Figure 8 Schematic representation of the craze-matrix interface.

energy at the void tips. For scission crazing Γ may in turn be expressed as $\Gamma_0 + d_e v_e U/4$ where Γ_0 is the intrinsic surface energy of the polymer in question and U is the energy to break a single primary chain. Following Kramer [4] we take $d_e = 9.6\,\mathrm{nm}$, $v_e = 4 \times 10^{25}\,\mathrm{m}^{-3}$, $U = 6 \times 10^{-19}\,\mathrm{J}$ and $\Gamma_0 = 0.04\,\mathrm{J\,m}^{-2}$, giving a value of $0.098\,\mathrm{J\,m}^{-2}$ for Γ for PS crazes. Assuming the bulk polymer to be linear elastic the ratio of the initial crazing strain in PS to the crazing strain in PS in the absence of bond scission is given by $(\Gamma/\Gamma_0)^{1/2}$ or approximately 1.6. The results of Fig. 4 indicate that the ratio between the strain to craze before and after heat treatment are in the ratio of approximately 1.5 over the entire temperature range in which crazing was carried out, in good agreement with our estimate for $(\Gamma/\Gamma_0)^{1/2}$. These results are therefore consistent with the suggestion that minimal entanglement loss is needed for the reopening of scisson mediated crazes subsequent to relatively short heat treatments. As a further test we measured λ_{craze} for the crazes in Fig. 4 both before and after heat treatment and found no systematic change in λ_{craze} (in all cases λ_{craze} was approximately 4). As we pointed out in the introduction, that λ_{craze} is observed to be greater than λ_{DZ} is a consequence of entanglement loss during crazing and in general one would expect λ_{craze} to increase with the net entanglement loss in the craze material. Hence, the fact that λ_{craze} for the crazes in Fig. 4 does not change after heat treatment is again consistent with there being minimal further entanglement loss during craze reopening. In order for such crazes to heal, it would be necessary for the low molecular weight chain fragments to diffuse distances of the order of at least D_0, a process which would be substantially slower than reentanglement and so should require longer healing times than those for disentanglement mediated crazes.

It is not clear why there sometimes remains a tendency for disentanglement mediated crazes to reappear at their original position after crazing, even though the original resistance of the material to craze growth has returned. However, one might argue that whereas the tip will generally follow the path of least resistance, the rate at which it does so is governed by the ability to the craze to widen [15, 16] and so whilst residual damage along the centre of the original craze may guide the craze tip, the rate of growth will be determined by the properties of material away from the centre of the original craze. This residual damage along the original craze centre line may be due to the occurrence of some chain scission at the craze tip during disentanglement controlled crazing, since the stress at the craze tip is higher than the stress along the craze body. Alternatively, it may simply be due to the fact that crazes tend to nucleate at local stress concentrations such as those associated with dust particles, and that these are largely unaffected by the heat treatment. The residual surface groove may also have a role in guiding the craze tip along its original path.

5. Conclusions

Our observations of the healing of crazes in thin films of glassy polymers show that in regimes where disentanglement mediated crazing occurs, the original resistance of the material to crazing returns after heat treatments of the order of the time necessary to make the craze disappear optically. Where scission is the dominant mechanism on the other hand, similar treatments do not result in true healing, since the craze is able to reappear at a much reduced strain. We believe this to be due to the severe damage to the chains during scission crazing, resulting in a concentration of very short chains in regions corresponding to the original void fibril interfaces. Since these chains cannot entangle, the craze is able to reopen on subsequent straining at a much reduced strain. It is speculated that relatively long healing times would be needed to reduce the effect of such damage on the strain to craze since the damaged chains must delocalize, that is, diffuse away from the site of the original void–fibril interface. These results provide good evidence in favour of our current view of disentanglement as a crazing mechanism in low molecular weight polymers at temperatures close to T_g.

Acknowledgement

We are grateful to ICI plc for funding.

Appendix

Consider the polymer chains to be made up of individual sub-units, each of molecular weight equal to M_e. Taking an arbitrarily chosen chain end as our starting point, the probability of the associated chain having a molecular weight $M = xM_e$ subsequent to a series of random scission events will be approximately

$$p(M = xM_e) = \frac{q(1-q)^{x-1}}{N_0} \qquad \text{(A1)}$$

where $1 - q$ is the ratio of the entanglement density after scission to the entanglement density before scission (such that q is the probability of a scission event being associated with any given chain sub-unit) and N_0 is a normalization constant such that

$$\sum_{1}^{x=x_0} \frac{q(1-q)^{x-1}}{N_0} = 1 \qquad \text{(A2)}$$

assuming all the chains to have a molecular weight $M_0 = x_0 M_e$ prior to scission. For a typical high molecular weight PS, M_0/M_e is of the order of 10^2 and for room temperature crazes q is approximately 0.6 [4] so that N_0 is close to unity. Hence approximately 60% of the chain ends present in the crazed material will be associated with chains with molecular weights of the order of M_e. The weight percent X of such chains may be estimated from

$$\frac{M_e q}{\sum_{1}^{x=x_0} x M_e q(1-q)^{x-1}} = X \qquad \text{(A3)}$$

For $x_0 = 10^2$ and $q = 0.6$, X is approximately 24 wt %.

References

1. R. SCHIRRER and C. GOETT, *Int. J. Fracture* **16** (1980) 133.
2. A. M. DONALD and E. J. KRAMER, *Polymer* **23** (1982) 1183.
3. *Idem, J. Polym. Sci., Polym. Phys. Edn* **20** (1982) 899.
4. E. J. KRAMER, *Adv. Polym. Sci.* **52/53** (1983) Ch. 1.
5. R. P. WOOL and K. M. O'CONNOR, *Polym. Eng. Sci.* **21** (1981) 970.
6. C. J. G. PLUMMER and A. M. DONALD, *J. Polym. Sci., Polym. Phys. Edn*, in press.
7. L. L. BERGER and E. J. KRAMER, *Macromolecules* **20** (1987) 1980.
8. A. M. DONALD, *J. Mater. Sci.* **20** (1985) 263.
9. B. D. LAUTERWASSER, PhD Thesis, Cornell University (1979).
10. B. D. LAUTERWASSER and E. J. KRAMER, *Phil. Mag.* **A39** (1979) 469.
11. A. M. DONALD and E. J. KRAMER, *J. Mater. Sci.* **17** (1982) 1871.
12. A. C.-M. YANG and E. J. KRAMER, *J. Polym. Sci., Polym. Phys. Edn* **23** (1985) 1353.
13. P. FLORY, in "Principles of Polymer Chemistry" (Cornell University Press, Ithaca, 1953) p. 317.
14. A. M. DONALD and E. J. KRAMER, *Polymer* **23** (1982) 461.
15. E. J. KRAMER, in "Environmental Cracking of Polymers", edited by E. H. Andrews (Applied Science, Barking, UK, 1979).
16. N. VERHEULPEN-HEYMANS and J. C. BAUWENS, *J. Mater. Sci.* **11** (1976) 7.

Received 24 February
and accepted 18 July 1988