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The effect of cross-linking on crazing in polyethersulphone

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Cross-links have been introduced into thin films of PES (polyethersulphone)/1 wt% sulphur by heating them in air at 350 °C. The effect of this is to suppress crazing in favour of shear deformation in high-temperature regimes where disentanglement crazing dominates for uncross-linked films of the same composition. We argue that light cross-linking (one or two cross-links per chain) is sufficient to give rise to a finite gel fraction in the films which, because it effectively forms an infinite network, cannot disentangle. Thus for crazing to occur, chains which form part of the gel fraction must always break rather than disentangle. This has the effect of raising the crazing stress relative to the yield stress in the weakly temperature-dependent regime of crazing at high temperature, where disentanglement is normally considered sufficiently rapid for entanglement loss not to contribute to the crazing stress. Hence as the gel fraction is increased by increasing the heat-treatment time, crazing is suppressed at the highest temperatures with respect to shear deformation, leading to a second transition, this time from crazing back to shear.

1. Introduction

It is now firmly established that entanglement, the topological constraint on relative chain motion, plays an important role in the crazing behaviour of glassy polymers [1, 2]. This is a consequence of the open voided structure of a craze; in order for voids to propagate into the bulk, entangled chains immediately in front of the advancing void tips must either break (chain scission) or be pulled apart (disentanglement). The forces required to achieve this entanglement loss are crucial in determining the overall stress for crazing and the extent to which crazing is able to compete with simple shear deformation [1, 3–5] (and hence the extent to which nominally ductile polymers show embrittlement on a macroscopic scale).

The rate of craze propagation is governed by the craze widening rate and this in turn is controlled by a surface drawing mechanism [1, 6–8]. Polymer in a strain softened layer at the craze/bulk interface flows along the gradient in hydrostatic tension between the void tips and the fibril bases as illustrated in Fig. 1. By maximizing this gradient with respect to the fibril spacing, Kramer has shown that the crazing stress, S_c, is given by [1]

$$S_c \sim F(T,\dot{\varepsilon})\Gamma^{1/2} \tag{1}$$

where $F(T, \dot{\varepsilon})$ is a front factor related to the constitutive behaviour of the strain softened layer and is expected to be characterized by a relatively weak dependence on temperature, T, and the deformation rate, $\dot{\varepsilon}$, and Γ is the effective surface tension at the void tip. Γ consists both of a term Γ_0 representing the Van der Waals contribution to the surface energy, and an additional term representing the interchain tension required to overcome the entanglement constraint and thus accommodate the geometrically necessary entanglement loss, illustrated in Fig. 1.

In Kramer's original treatment, entanglement loss was assumed to be due to scission [1]. If the bond energy is U, then the force, f_b, required to initiate a scission event is given approximately by

$$f_b = \frac{U}{2a} \tag{2}$$

where a is the bond length associated with each scission event. Because the number of entangled strands crossing unit length of surface is approximately $\nu_e da/2$ [9] then the total contribution from scission to the surface energy is given by

$$\Gamma_s = \frac{\nu_e dU}{4} \tag{3}$$

so that

$$S_c \simeq F(T,\dot{\varepsilon})\left(\Gamma_0 + \frac{\nu_e dU}{4}\right)^{1/2} \tag{4}$$

Because neither $F(T, \dot{\varepsilon})$ nor U are expected to be strongly temperature dependent, this is consistent with the observation that in cases where this mechanism is known to operate, such as in PS (polystyrene) at ambient temperature, S_c falls slowly with temperature. However, as the temperature approaches T_g there is an increasing tendency for disentanglement to replace scission as the mechanism for entanglement loss during crazing [4, 5, 7, 8]. When the molecular weight is sufficiently high this disentanglement crazing is suppressed even at temperatures close to T_g and as the temperature is raised there is a transition from

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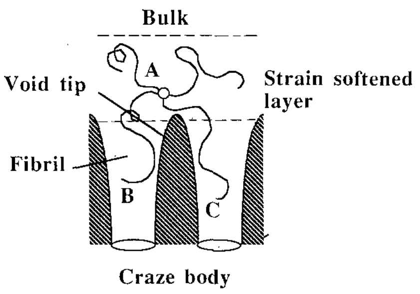

Figure 1 This figure illustrates the surface drawing mechanism for crazing and the reason for entanglement loss during crazing. Polymer in a strain softened layer of thickness *h* at the craze/bulk interface moves towards the fibril bases along the gradient in hydrostatic tension between the fibril bases and the void tips. However, in order for the void tip to advance into the bulk, entangled chains moving into adjacent fibrils such as those labelled B and C in the figure (an entanglement is depicted schematically at A) must either break or disentangle.

crazing to shear deformation. This is because although the shear stress in PS exceeds the crazing stress at room temperature, the yield stress drops more rapidly with temperature than does the scission crazing stress [4].

In polymers such as PES (polyethersulphone) where ν_e is large, and consequently so is the stress, S_c, for scission crazing, shear replaces crazing as the dominant deformation made at ambient temperature. In this case the onset of disentanglement may be clearly identified with a transition from shear to crazing as the temperature is increased [5, 8]. The temperature at which this transition occurs and the stress to craze at temperatures just above the transition temperature are strongly molecular weight dependent, consistent with a disentanglement mechanism. At temperatures very close to T_g, however, disentanglement may become sufficiently rapid that it no longer has a significant effect on crazing kinetics, and the molecular weight dependence is lost [5, 8, 9]. In this limit, for uncrosslinked polymers, Γ in Equation 1 is approximately equal to the Van der Waals surface energy, Γ_0, and so we term this the "Van der Waals" regime.

The first experiments to investigate the effect of cross-linking on crazing involved the irradiation of PS films (gamma or electron irradiation will induce cross-linking in PS films) [10, 11]. As cross-linking proceeds in PS there is initially little effect on the strain to craze at room temperature, but higher degrees of cross-linking lead to both an increase in the yield stress and the strain to craze at room temperature. Because the increase in the strain to craze is more marked, there is increasing competition between crazing and shear deformation as the cross-link density is increased, with shear deformation eventually replacing crazing. At very high cross-link densities, both deformation mechanisms are suppressed and the films become brittle [1, 10–12].

This behaviour may be rationalized in terms of the expression for scission crazing, which is the dominant mechanism for crazing in PS at room temperature. Thus we may use Equation 4 to describe crazing kinetics. Increasing the degree of chemical cross-linking will increase the effective value of the entanglement density, denoted ν_{eff}, such that $\nu_{eff} = \nu_e + \nu_x$ where ν_x is the cross-link density in the polymer [1]. Clearly for low degrees of cross-linking, ν_e will remain much larger than ν_x, so that the effect on the crazing stress of replacing ν_e by ν_{eff} in Equation 4 will be small. However, as ν_x approaches ν_e it may be seen that the scission crazing stress will begin to rise rapidly with increasing ν_x [1, 10–12]. It has been suggested that the effect of this cross-linking will be much less marked on the yield stress, and experiments seem to support this [12]. Thus for high molecular weight PS, increasing the cross-link density has the effect of lowering the temperature of the transition from crazing to shear [12].

Light degrees of cross-linking will also suppress the transition to disentanglement controlled crazing observed in low molecular weight PS [10]. One or two cross-links per chain will be sufficient to reach the percolation threshold and there will be an increasing proportion of chains effectively bonded to an infinite network and thus unable to disentangle at any temperature. The fact that such chains must always undergo scission during crazing means that one expects the existence of an infinite network to show up in what would otherwise be the Van der Waals regime of disentanglement crazing very close to T_g. As we have seen, for the uncross-linked case the chain mobility is sufficiently high in this regime for the work of disentanglement to be negligible and the surface energy term in Equation 1 to be approximately equal to the Van der Waals surface energy, Γ_0. The residual scission which must occur during crazing in the presence of a gel fraction, that is an infinite network, should result in an increase in Γ_0 by an amount $\varphi d \nu_e U/4$ where φ is the gel fraction. Because U does not vary strongly with temperature, this increase may be expected to be independent of temperature. However, in PS the extent of the Van der Waals regime is limited even at low strain rates and for low molecular weights [9, 13]. Thus the effect will be masked by the scission-to-disentanglement transition being forced to temperatures very close to T_g as the effective molecular weight increases with the degree of cross-linking. In low molecular weight PES, on the other hand, the transition to the disentanglement regime occurs more than 100 °C below T_g even at relatively high strain rates, and because the transition is steep, there is a correspondingly large Van der Waals regime [5]. This polymer therefore provides much greater scope to investigate the effect of cross-linking on disentanglement crazing in this regime.

2. Experimental procedure

There are several ways of cross-linking PES, for example by exposure to gamma radiation and heating in oxygen [14]. Here systematic tests were carried out on VICTREX™ PES ($M_w = 47\,000$, supplied by ICI plc) to which was added 1 wt % sulphur. Thin films were made by drawing on to glass slides from a solution in cyclohexanone at 40 °C to an initial thickness of 0.5 μm. Still on the glass slides the films were held in air at 350 °C for various times between 1 and 12 h in order to cross-link them, and then floated off the glass slides on a water bath. This latter operation proved more difficult for cross-linked films than for untreated films, the cross-linked PES adhering strongly to the slides, and it was necessary to coax them off with tweezers. Following the method of Lauterwasser and Kramer [15], the films were picked up from the water bath on to copper grids which had been previously coated with PES, and dried. For the longest heating times, damage to the films during removal from the glass slides resulted in the appearance of numerous small diamond-shaped patches of shear deformation as shown in Fig. 2. However, it was found that by holding the films at 30 °C above T_g for approximately 10 min, these regions could be made to disappear. In this way we found that the presence or otherwise of these regions did not significantly affect the strain for the onset of shear deformation under tension, although they were found to provide suitable stress concentrations for the nucleation of crazes. However, although the cross-linked films were relatively stable during this heat treatment compared with uncross-linked films of PES [16], there remained a tendency for film breakdown to occur at these defects, and so for the purpose of systematic testing, unheat-treated films were used throughout.

For all the heat treatments at 350 °C the cross-linked films were found to be partially insoluble in dichloromethane at room temperature, indicating the presence of a gel fraction. As a crude measure of the gel fraction, films were weighed and then inserted into dichloromethane. The insoluble part of the film was then dried and reweighed and the difference between the weight before and after insertion into dichloromethane was assumed to be that of the sol fraction, leading to the estimates indicated in Table I.

In previous investigations we have used short exposures to solvent vapour to bond the films to the grids and to remove wrinkles and other defects [5, 16].

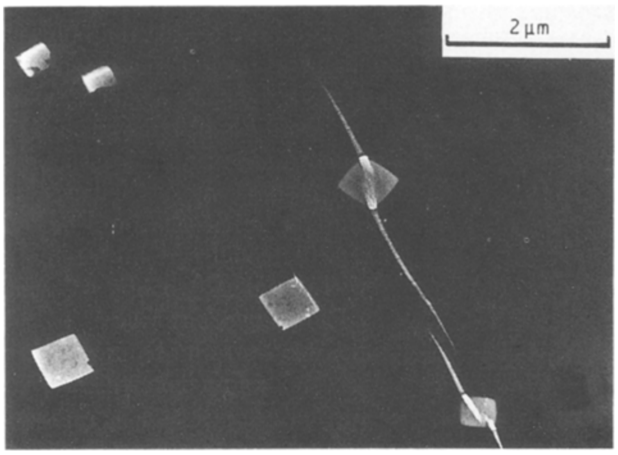

Figure 2 Diamond-shaped patches of shear deformation observed under TEM in a thin film of PES/1 wt % sulphur heat treated for 12 h at 350 °C. The orientation of these regions appears random, and it is believed they arise as a result of damage caused when the films are removed from the glass slides after the cross-linking treatment. Crazes have grown from the shear patches on the right-hand side of the figure.

TABLE I Gel fraction as a function of heat treatment time in air at 350 °C

Heat-treatment (h)	Gel fraction (± 0.05)
1.0	0.2
4.0	0.5
12.0	0.9

However, when this was tried with the cross-linked films, the films tended to trap solvent and swell. Hence it was necessary to heat the films to approximately 250 °C for a few seconds to achieve the desired effect (T_g for PES is approximately 220 °C). Having bonded the films to the grids, they were then held at 200 °C for 4 h under vacuum in order to suppress shear deformation, ageing having little effect on the crazing stress but raising the upper yield stress markedly [3, 5]. Once prepared the copper grids were strained at 10^{-2} sec^{-1} in a variable temperature straining rig, which could be mounted on the stage of a Carl–Zeiss Jenapol optical microscope. The strain at which either shear or crazing occurred was recorded, and after straining, individual squares could be cut from the grids and examined using TEM (transmission electron microscopy) in order to determine the precise nature of the deformation.

3. Results

Whereas the uncross-linked PES generally shows a transition from shear to crazing at roughly 100 °C at a strain rate of 10^{-2} sec^{-1}, the precise temperature depending on the ageing time [5], the samples cross-linked for the longest times at 350 °C were found to show predominantly shear deformation up to 200 °C, the highest test temperature used. This shear deformation was characterized by the appearance of deformation zones (DZs) which are regions of localized necking of the film, the localization resulting from instabilities associated with the yield drop observed in the stress–strain curve of aged films. The cross-linking also raises the yield stress (in contrast to the assumptions made in [12]) as suggested by the increase in the strain to form a DZ with φ at room temperature and above, as shown in Fig. 3. This figure gives results for various heat-treatment times at 350 °C, along with estimates of the gel fraction in each case. The longer the heat-treatment time the greater the increase in the strain to form a DZ. (The deformation behaviour of untreated films was found not to be significantly affected by the presence of the sulphur.) Eventually, for very long heat-treatment times, the films become brittle at low temperatures as indicated in Fig. 3.

It also appears that if the samples are aged in air at 200 °C (the standard ageing temperature used, when the samples are heated under vacuum), some degree of cross-linking ensues because the strain to form DZs in these samples is higher than that of films aged under vacuum for the same times (Fig. 4). However, the increase is not as marked as in samples heat treated in air at 350 °C. For example, the strain to form DZs after a 1 h annealing treatment in air at 350 °C is

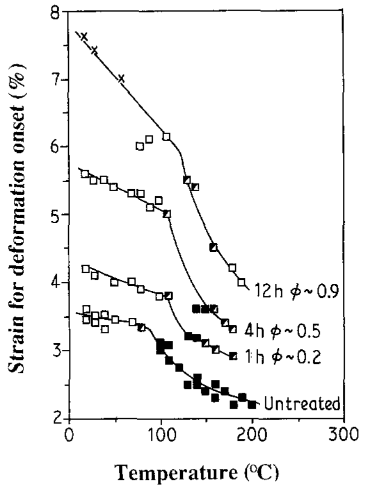

Figure 3 The strain for deformation onset as a function of temperature in thin films of PES/1 wt % sulphur heat treated for various times in air at 350 °C and then aged under vacuum for 4 h, and strained at strain rate of 10^{-2} sec^{-1}. (×) Brittle fracture, (□) shear deformation, (■) crazing, (▨) mixed regimes of shear and crazing. An estimate of the gel fraction, φ, of the films at each heat-treatment time is indicated.

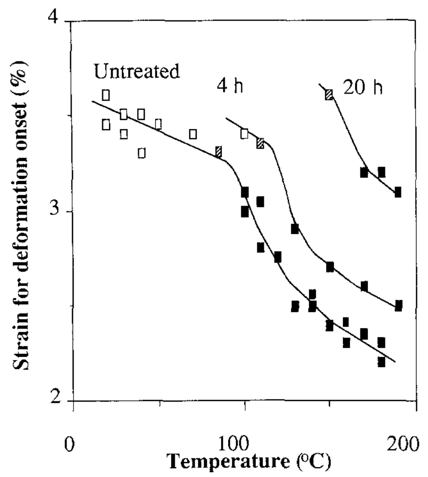

Figure 4 The strain for deformation onset as a function of temperature in thin films of PES/1 wt % sulphur heat treated for various times in air at 200 °C (the untreated films were aged under vacuum for 4 h), and strained at a strain rate of 10^{-2} sec^{-1}. (□) Shear deformation. (■) crazing. (▨) mixed regimes of shear and crazing.

significantly higher than that after a 4 h treatment in air at 200 °C (compare Figs 3 and 4).

Apart from the apparent rise in yield stress, the main feature of the present results is the suppression of crazing over almost the entire temperature range (i.e. up to 200 °C). It was found that in the films which have been heat treated in air at 350 °C, crazing is limited to a range of temperatures just above the transition from shear to crazing, this range becoming progressively narrower as the heat-treatment times are increased. Thus at the highest temperatures crazing is replaced once more by shear. Some suggestion of a transition from crazing back to shear deformation has been found in macroscopic tests on uncross-linked PES very close to T_g where the yield stress begins to drop rapidly towards zero with temperature [17]. Here brittle behaviour is replaced by homogeneous deformation rather than shear necking, and so is not detectable in thin film observations. However, in the present results for cross-linked films, the transition from crazing back to shear occurs at much lower temperatures, that is, well away from T_g, and is characterized by the reappearance of DZs rather than homogeneous deformation. In films cross-linked for 12 h or more, some crazing persists at temperatures close to the temperature of the transition from shear to crazing in uncross-linked PES, but only in association with the localized diamond-shaped regions of pre-deformation shown in Fig. 2, the bulk deformation mechanism being shear.

4. Discussion

These results show that in the regime of disentanglement-controlled crazing the effect of cross-linking is to suppress crazing by pushing up the crazing stress until it becomes comparable with the stress for DZ initiation. The net effect is that as the cross-link density and φ increase, crazing is restricted to a progressively narrower temperature range, with shear deformation dominating both at ambient temperature and at temperatures close to T_g.

A problem with more quantitative interpretation of these strain measurements in thin films is that whereas crazing will generally occur in the linear regions of the stress–strain curve and hence accurately reflect trends in the behaviour of the stress to craze, the appearance of a DZ is a post-yield phenomenon occurring beyond the yield drop in an aged sample [17]. Because the total strain to form a DZ is significantly greater than that at which the maximum stress in the film is reached (that is, the yield stress), interpreting the strain to form a DZ in terms of a linear stress–strain curve will result in considerable overestimates of the yield stress. This is also true of crazes at temperatures just above the transition from shear to crazing. Donald and Kramer have identified mixed regimes, where disentanglement crazes appear after the appearance of DZs in a given film, an observation rationalized with reference to the relatively long time constants associated with disentanglement [3]. It is expected, in general, that deformation mechanisms associated with disentanglement, such as disentanglement crazing, will be favoured over mechanisms with relatively short characteristic time constants, such as shear deformation, by low strain rates and long times. Certainly the crazing which is observed in the cross-linked films is limited in extent and in most cases occurs after longer times than the formation of DZs, which, whilst it suggests disentanglement may be contributing to crazing, also means that changes in the strain to craze can only be interpreted as qualitative indications of changes in the stress to craze. Furthermore, changes in the strain to craze will be affected by the tendency of the Young's modulus to increase with the degree of cross-linking.

In spite of these uncertainties it was felt worthwhile to compare the present results with the qualitative predictions of a model for disentanglement crazing modified to incorporate the effect of cross-linking. The underlying mechanism for disentanglement during crazing may be viewed in terms of the "tube" model, in which entanglement is represented as a nonlocal tube-like constraint and polymer chains are able to escape their confining tubes by moving along them, a process known as reptation [18, 19]. In particular, McLeish *et al.* have introduced the concept of "forced" reptation to account for crazing kinetics; here the force on the disentangling chain may be represented by the product of a dynamic friction coefficient, and the rate of disentanglement, which will in turn be proportional to the deformation rate [8]. This leads to

$$f_d \simeq 2\zeta_0 v(M/M_0)x \tag{5}$$

where x is the proportion of the chain entangled, M is the molecular weight, M_0 is the monomer molecular weight, ζ_0 is the monomeric friction coefficient of the polymer in question and v is the craze widening rate, which we take to be proportional to the strain rate $\dot{\varepsilon}$. Because ζ_0 is expected to show an exponential dependence on T, the kinetics of disentanglement crazing should also be strongly temperature dependent [5, 8]. This is reflected by the rapid drop in S_c with temperature which characterizes the transition from shear to crazing in materials such as PES [5].

As in the scission case, following Kramer and Berger, Equation 5 may be converted into a surface tension [9]. The quantity x will be statistically distributed over all possible values between 0 and $\frac{1}{2}$. Because it is reasonable to assume that at any given point in time the probability of a given value of x is independent of x, we assume that the probability density function for x is $\rho(x) = 2$. If we average over all possible values of x in Equation 5, $\langle f_d \rangle \simeq \frac{1}{2}\zeta_0 v(M/M_0)$. Again, because the strand density per unit length in the surface is $\nu_e da/2$, the overall contribution to Γ from disentanglement (in the absence of scission) is

$$\Gamma_d = \frac{\nu_e da}{2}\frac{\zeta_0 vM}{2M_0} \tag{6}$$

Because x does vary from chain to chain, however, in general it is to be expected that a transition from scission to disentanglement will be characterized by a mixed regime in which both scission and disentanglement are contributing to entanglement loss [9]. For any given chain in this regime if $x < x_c$ where

$$x_c = \frac{U}{4a}\frac{M_0}{\zeta_0 vM} \tag{7}$$

then from Equations 2 and 5 it may be seen that the force to disentangle the chain will be less than that for scission and so the chain will disentangle rather than break. Similarly, where $x > x_c$ scission is expected rather than disentanglement. Assuming the distribution in x to be independent of x the respective contributions to the overall surface tension at the void tip can be weighted accordingly, which results in the following expressions

$$\Gamma = \Gamma_0 + (1 - x_c)\frac{d\nu_e U}{4} \tag{8}$$

for $x_c < \frac{1}{2}$, and from Equation 6

$$\Gamma = \Gamma_0 + \frac{1}{4x_c}\frac{d\nu_e U}{4} \tag{9}$$

for $x_c \geqslant \frac{1}{2}$. (Values of $x_c > \frac{1}{2}$ have no physical meaning, but the substitution in Equation 9 may still be made when the quantity on the left-hand side of Equation 7 becomes greater than 1). Because the quantity ζ_0 decreases very rapidly with increasing temperature, it is clear from Equation 9 that in the regime of temperatures much higher than that in which the transition to disentanglement crazing occurs, as suggested in Section 1, Γ will be very close to Γ_0 (the Van der Waals regime).

We assume from Equation 1 that the strain to craze $\varepsilon_c = F_0(T)\Gamma^{1/2}E(T)^{-1} = F(T)\Gamma^{1/2}$ and that the Young's modulus $E(T)$ is independent of strain. Then the temperature dependence of F is obtained from the data for the strain to craze, ε_c, in the Van der Waals regime close to T_g for uncross-linked PES, as given in [5]. ε_c is found to vary approximately linearly with temperature over this temperature range, and it is assumed that this can be extrapolated back to lower temperatures. Γ_0 is taken to be equal to 0.04 J m^{-2} [1, 20] and independent of temperature and cross-link density [1]. By writing ζ_0 as $A \exp(-\Delta H/RT)$ where A is an empirical constant [8], $\Gamma(T)$ can be found from Equations 8 and 9. From this and the extrapolated form for $F(T)$ and substituting for x_c using Equation 7, a crude fit to the data may be obtained for the temperature dependence of the strain to craze in uncross-linked PES using a computed curve, and adjusting A. The values for the various parameters required are: $\Delta H = 115$ kJ mol^{-1} [20], $\nu_e = 50 \times 10^{25}$ m^{-3}, d = 3.2 nm [17] and $U = 6 \times 10^{-19}$ J [1]. Fig. 5a shows the experimental data for PES/1 wt % sulphur aged in vacuum for 4 h, and pure PES aged for 70 h, both strained at 10^{-2} sec^{-1}, together with a computed curve for uncross-linked PES. Although all the ageing treatments in the current investigation were limited to 4 h, because neither the sulphur content nor the ageing treatment affect the crazing stress, use of the data for pure PES aged for 70 h allows the temperature range in which the fit is made to be extended (the longer the ageing treatment, the lower the temperature of the transition from shear to crazing [5]).

Because it is found via transmission electron microscopy that the extension ratio in the DZs, which is 1.4 in uncross-linked PES [5], remains unchanged after cross-linking to within experimental error, it is known that the density of cross-linking, ν_x, is light compared with the entanglement density ν_e of the films. (The extension ratio λ scales approximately with $l_e|d$ where l_e is the chain contour length between entanglements [1], and hence assuming the strands between entanglements to be Gaussian, $\lambda \simeq l_e^{1/2} \simeq \nu_e^{-1/2}$; for the cross-linked case it is expected that $\lambda \simeq \nu_{eff}^{-1/2}$ where $\nu_{eff} = \nu_e + \nu_x$). However, because there are approximately 30 entanglement points per chain for the molecular weight of PES used here 47 000 [5]) it is possible to have two or three cross-links per chain and hence

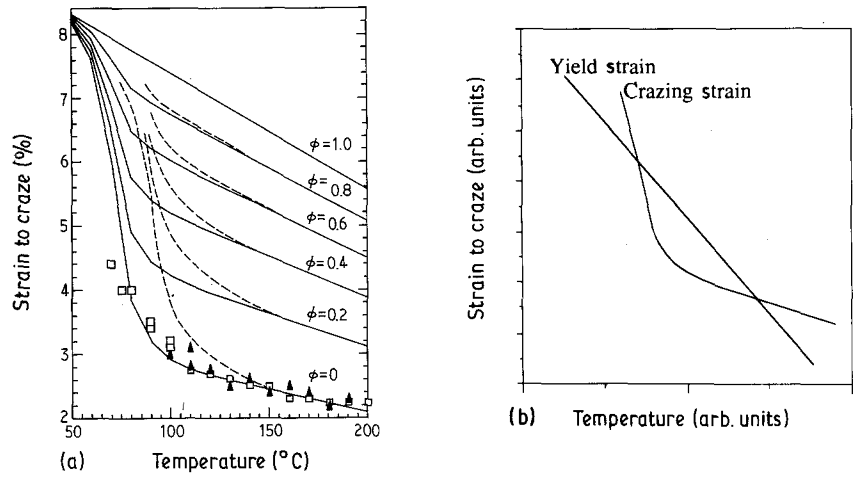

Figure 5 (a) Model curves for the strain to craze as a function of temperature in PES for different values of the gel fraction, φ, generated from a fit to data for uncross-linked PES aged under vacuum for 70 h at 200 °C shown in the figure [5]. The solid curves are obtained by assuming that the average molecular weight of the sol fraction remains constant during cross-linking, so for comparison curves are shown (– – –) where the average molecular weight of the sol fraction has undergone a ten-fold increase. (▲) PES 3600/1% S, aged *in vacuo* 4 h; (□) PES 3600, aged *in vacuo* 70 h. (b) A schematic illustration of how the model can explain the transition from shear to crazing and then back to yield in a cross-linked sample as the temperature is increased. It is assumed that there is linear decrease in yield stress with T, and that the mechanism with the lowest critical stress at a given T will dominate.

cross the percolation threshold, without affecting the extension ratios greatly.

For a finite gel fraction, φ, assuming all chains contained in the gel fraction to undergo scission during crazing, and ignoring the effect of cross-linking on the molecular weight of the chains in the sol fraction and on ν_{eff}, we have

$$\begin{aligned}\Gamma &= \Gamma_0 + (1 - \varphi)(1 - x_c)\frac{d\nu_e U}{4} + \varphi\frac{d\nu_e U}{4} \\ &= \Gamma_0 + [1 + x_c(\varphi - 1)]\frac{d\nu_e U}{4} \qquad (10)\end{aligned}$$

for $x_c < \frac{1}{2}$, and

$$\Gamma = \Gamma_0 + \left(\varphi + \frac{1 - \varphi}{4x_c}\right)\frac{d\nu_e U}{4} \qquad (11)$$

for $x_c \geqslant \frac{1}{2}$.

The effect of cross-linking predicted by these equations on the shape of the scission-to-disentanglement transition is indicated in Fig. 5a for various values of φ. Note these equations do not take shear into account and therefore one cannot expect to describe the behaviour at low temperature. In addition, no allowance has been made for any modification of the front factor due to cross-linking. However, Fig. 5a suggests that even for a relatively large gel fraction there will be a sharp drop in the stress to craze associated with the onset of disentanglement of the chains in the sol fraction. This in turn suggests that the transition from shear to crazing as the principal mode of deformation is likely to occur at this temperature, which is entirely consistent with the experimental observation, seen in Fig. 3, that there is a large drop in the strain for deformation onset coinciding with the appearance of crazing in the cross-linked films.

It is apparent that in a more complete treatment, any increase in the molecular weight of chains in the sol fraction must be taken into account, because this will affect disentanglement times in the transition region and change x_c. The cross-linked chains in the sol fraction may no longer be linear, but in the forced reptation model as opposed to "classical" reptation (where the disentanglement times increase exponentially with the molecular weight of the sidearm of a star polymer [21]), the relevant friction coefficient will depend only on the total molecular weight of the entangled part of the chain. Thus the fact that the chains in the sol fraction may be branched should not affect the total crazing stress by as much as that anticipated for linear chains of the same molecular weight. However, Fig. 3 shows that there is a shift of the transition to (disentanglement) crazing to higher temperatures as φ increases, which suggests a significant increase in the average force to disentangle chains in the sol fraction as cross-linking proceeds. This could be related to the branching.

As a qualitative indication of the effect an increase in molecular weight would have, the effect implied by the model of a ten-fold increase in molecular weight of these chains (still assumed to be linear) is shown in Fig. 5a. It should be kept in mind that although this implies a weak dependence of the transition temperature on molecular weight, a somewhat stronger dependence was deduced from measurements on different molecular weights of uncross-linked PES [5]. However, it might also be added that in these very polydisperse systems we expect the high molecular weight chains to be incorporated into the gel fraction first, so that in practice the average molecular weight of the sol fraction may even be less than that of the uncross-linked polymer for certain degrees of cross-linking. Regardless of these uncertainties, Fig. 5a does seem to demonstrate, qualitatively at least, the right type of behaviour. At higher temperatures, where disentanglement rates have increased to the point where disentanglement no longer contributes significantly to Γ, a much weaker dependence of the strain to craze on temperature is predicted. Although no quantitative information can be inferred about the dependence of the yield stress on temperature from the present data, it seems reasonable at assume (based on the behaviour of cross-linked PS [12]) that in this regime it is dropping more rapidly with temperature than the crazing stress. Thus as the temperature is raised a transition from crazing back to shear may occur, as shown schematically in Fig. 5b, where a linear decrease in yield stress with temperature over the whole temperature range is assumed. Furthermore, by analogy with the effect of increasing the cross-link density in PS [10, 11, 12] the rise in the crazing stress with φ in the high-temperature regime is expected to be stronger than that in the yield stress. As suggested in Fig. 5b, this means that the temperature for the transition from crazing back to shear will decrease as φ increases. This effect is also seen in the results in Fig. 3.

Further comparison of Figs 3 and 5a suggests that the contribution to the crazing stress from scission for a given value of φ is less than assumed on the basis of the estimates for the various parameters involved. This is suggested by the behaviour of samples with φ close to 1: crazes are seen, as shown in Fig. 6, and at strains very much less than that predicted for pure scission crazing in Fig. 5a. Whilst these crazes nucleate locally at the diamond-shaped regions of the sample which are already highly drawn prior to the tensile test as shown in Figs 2 and 6, and do not propagate far into the bulk owing to shear blunting, their existence suggests the possibility of a regime of cross-linking in which crazing by scission alone is competitive with shear deformation (clearly for very high degrees of cross-linking such that ν_x is comparable to ν_e, scission crazing will be suppressed as in highly cross-linked PS). In more recent experiments thin films have also been drawn on to KCl substrates which can then be dissolved away in water after the heat treatment, avoiding the localized damage of Fig. 2. The results of these experiments confirm that it is possible to observe isolated crazes in fully cross-linked films even in the absence of this damage, as shown in Fig. 7.

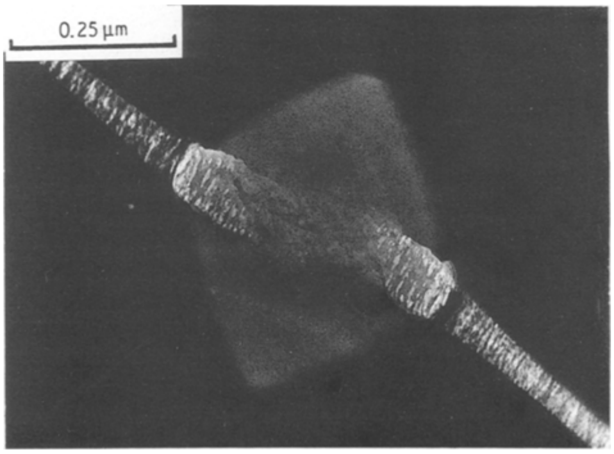

Figure 6 A craze associated with a region of shear deformation in a film of PES/1 wt% sulphur heat treated for 12 h at 350 °C and strained at 130 °C.

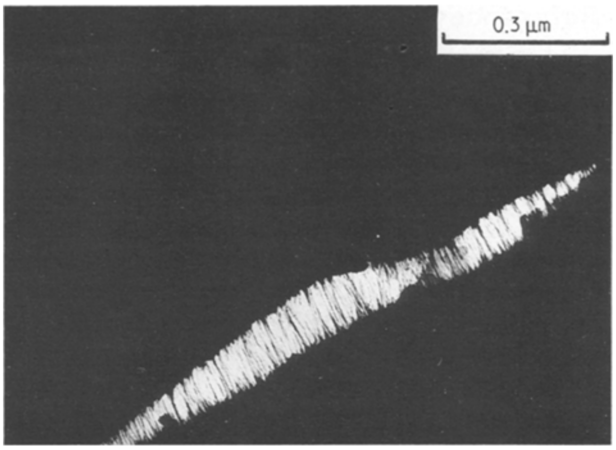

Figure 7 A craze in a film of PES/1 wt% sulphur drawn on to a KCl substrate, heat treated for 10 h at 350 °C and strained at 160 °C.

5. Conclusions

It has been shown that cross-linking thin films of PES has the effect of suppressing crazing in favour of shear deformation in regimes where crazing dominates for uncross-linked films. Because measurements of extension ratios suggest that the cross-link density remains small compared with the entanglement density, this suggests that disentanglement is the mechanism being affected by the cross-linking, because light cross-linking (one or two cross-links per chain) is sufficient to give rise to a finite gel fraction which, because it effectively forms an infinite network, cannot disentangle. Thus for crazing to occur, chains which form part of the gel fraction must always break rather than disentangle. This has the effect of raising the crazing stress in the weakly temperature-dependent regime of crazing at high temperature, where disentanglement is normally considered sufficiently rapid not to contribute to the crazing stress. Hence as the gel fraction is increased by increasing the heat-treatment time at 350 °C in air, crazing is suppressed at the highest temperatures with respect to shear deformation. Nevertheless, because chains belonging to the sol fraction are still able to disentangle, there may still be a transition from shear to crazing at lower temperatures when the disentanglement mechanism becomes activated. This is consistent with the observation of a transition from shear to crazing and then back to shear in the present cross-linked films. This then may be considered evidence in favour of the qualitative features of this model for disentanglement crazing in glassy polymers. In all cases crazing seems to be suppressed in spite of the increase in the yield strain, so it would appear that cross-linking inhibits crazing even more strongly than it does yield, in agreement with results for PS [16].

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