Molecular weight distribution effects on craze micromechanics

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Quantitative transmission electron microscopy has been used to investigate the micromechanics of crazes in monodisperse and polydisperse polystyrene (PS). In the monodisperse PS, a large stress is observed at the craze tip, but this stress falls rapidly with distance behind the tip. In the polydisperse PS (or in blends in which a small percentage of monodisperse low molecular weight PS has been added to monodisperse high molecular weight PS) the stress at the craze tip is lower and falls much less rapidly with distance behind the craze tip. These changes are attributed to the effects of diluting the network of entangled high molecular weight chains with molecules that are too short to entangle. This dilution increases the molecular stress on the load bearing chains of the network, thus increasing the ease of craze fibrillation.

Keywords Craze; micromechanics; molecular weight distribution; surface stress; molecular stress; entanglements

INTRODUCTION

Crazes are an important toughening mechanism in glassy polymers, but are also a source of weakness because they are the precursors of cracks. Because of this potential weakness, craze micromechanical properties are crucial in determining the strength of glassy polymers such as polystyrene (PS).

There have been many studies of craze micromechanical properties, notably using optical[1-4] or transmission electron microscopy[5-8] to measure the craze displacement profile $w(x)$ from which a stress profile $S(x)$ can be calculated. The simplest model for a craze grown from a crack tip is that due to Dugdale[9] and Goodier and Field[10], the so-called Dugdale model in which the stress is assumed to be a constant S_c throughout the plastic zone defined by the craze. Although some workers have claimed experimentally determined craze profiles to be in good agreement with the model[1-4], recent work[8] indicates that for certain polymers, such as poly(phenylene oxide)(PPO) and poly(styrene–acrylonitrile)(PSAN), S_c is far from constant along the craze.

Methods for analysing craze micromechanics based on optical techniques alone lack spatial resolution: this problem is overcome by the use of quantitative transmission electron microscopy[5-8]. The improved spatial resolution permits local variations in the surface stress $S(x)$ on the scale of $\sim 1\,\mu$m to be measured.

The first crazes to be studied by this technique were grown in polystyrene with a $M_w/M_n \sim 2$ (the ratio of weight average molecular weight M_w to number average molecular weight M_n)[5,6]. The effect of molecular weight on craze micromechanics has been considered in earlier studies[4,11-13]. In general, for a range of glassy polymers, it has been shown that the overall craze dimensions increase with molecular weight. In particular this means that the 'critical crack opening displacement', at which the

craze breaks down to permit slow crack growth increases as M_w increases. However, this displacement appears also to be a function of the polydispersity of the system[13], so that crazes in poly(methyl methacrylate) (PMMA) prepared from oligomers have larger values for the displacement than crazes in polydisperse PMMA. Döll *et al.* concluded from this observation[13] that the low molecular weight chains in polydisperse PMMA act as a plasticizer for the longer chains.

In this paper results are presented for the surface stress profiles of crazes grown in polydisperse PS, and a series of blends of monodisperse PS of differing molecular weights. In this way, variations in the form of the surface stress profile arising from changes in the molecular weight distribution can be probed.

EXPERIMENTAL

Specimen preparation

Crazes in thin films (0.6 μm) of the following 4 types of polystyrene have been studied.

(1) Polydisperse PS with $M_w = 300\,000$ and $M_n = 113\,000$. This was free of mineral oil commonly added as a processing aid, and was kindly supplied by Dr R. A. Bubeck of the Dow Chemical Company.

(2) Monodisperse PS with $M_w = 200\,000$ and $M_w/M_n \leqslant 1.06$, produced by the Pressure Chemical Co.

(3) A blend of 95% monodisperse PS ($M_w = 200\,000$) with 5% monodisperse PS of $M_w = 4000$. The resulting blend had $M_w = 190\,000$ and $M_n = 58\,000$.

(4) A blend of 85% monodisperse PS with $M_w = 200\,000$ with 15% monodisperse PS with $M_w = 20\,400$. The resulting $M_w = 173\,000$ and $M_n = 86\,000$.

In each case the PS was dissolved in toluene, and glass slides were drawn from the resulting solution. After drying, the film coating on the glass slide was floated off on a water bath, from which it was picked up on a copper grid which had been precoated with a thin film of the same
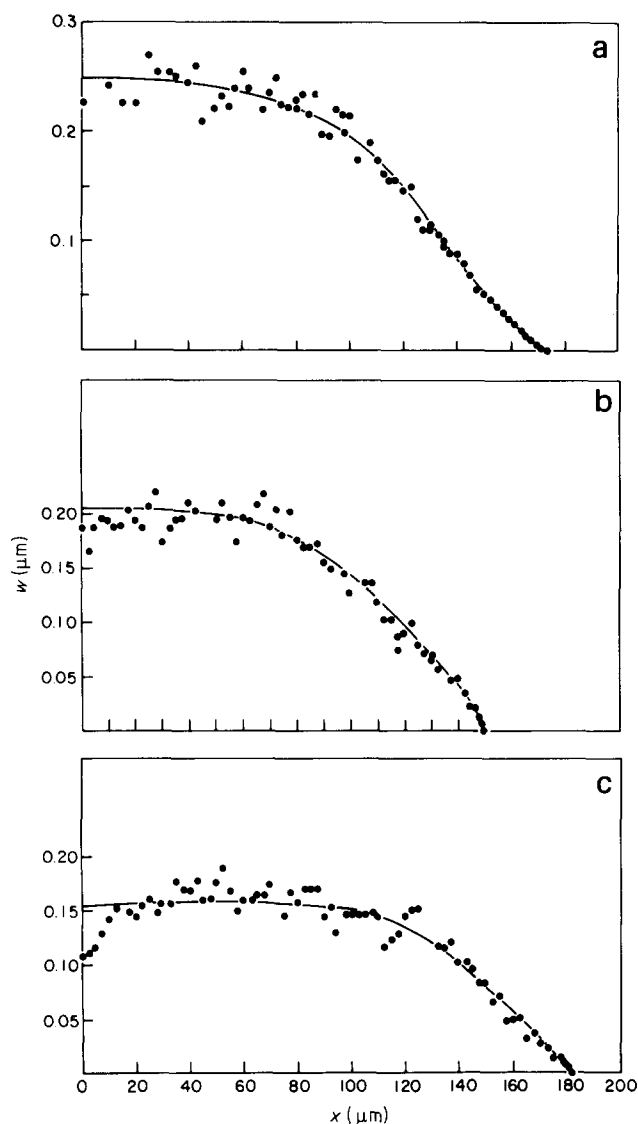
Figure 1 Displacement profiles $w(x)$ measured for (a) polydisperse PS, $M_w = 300\,000$; $M_n = 113\,00$ (b) monodisperse PS $M_w = 200\,000$; $M_w/M_n \leqslant 1.06$ and (c) Blend I containing 5% of monodisperse PS with $M_w = 4000$

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

The local value of the displacement $w(x)$ is then given by:

$$w(x) = \frac{T(x)}{2}(1 - v_f(x)) \qquad (2)$$

and thus the displacement profile of the craze can be determined with a high spatial resolution.

From knowledge of the form of $w(x)$, the surface stress profile $S(x)$ can be calculated using a double Fourier transform technique due to Sneddon[14]:

$$\Delta S(x) = -\frac{2}{\pi}\int_0^\infty \bar{P}(\xi)\cos(x\xi)\mathrm{d}\xi \qquad (3a)$$

where

$$\bar{P}(\xi) = \frac{\xi E^*}{2}\int_0^a w(x)\cos(x\xi)\mathrm{d}x \qquad (3b)$$

where

$$E^* = \begin{cases} E/(1-v^2) & \text{for plane strain} \\ E & \text{plane stress} \end{cases}$$

and where a is the half-craze length. The total craze surface stress is given by:

$$S(x) = \sigma_\infty + \Delta S(x)$$

where σ_∞ is the applied stress.

RESULTS

The form of the displacement profiles for the polydisperse PS, the monodisperse PS and the blend containing PS or $M_w = 4000$ (Blend I), are shown in *Figures 1a–c*, and the surface stress profiles calculated from these in *Figures 2a–c*. The form of the $w(x)$ and $S(x)$ profiles for the second blend, with 15% of $M_w = 20\,000$ PS, is similar to the profiles obtained for the polydisperse samples. It is clear that there is a significant difference between the profiles obtained for the polydisperse and monodisperse systems, with Blend I being intermediate in behaviour.

The displacement profiles of *Figure 1* show that the crazes in monodisperse PS are 'blunt' with a sudden decrease in the displacement just behind the craze tip. Similar displacement and stress profiles are observed for monodisperse polystyrene with M_w of 390 000, 680 000, 1 $\times 10^6$ and 2×10^7.[15] In contrast to this behaviour the polydisperse PS sample shows crazes that taper gradually towards their tip. The sharp drop in the $w(x)$ profile of the monodisperse PS leads to a large and localized stress concentration at the craze tip whereas the polydisperse system shows a much less confined region within which the stress lies above σ_∞, the applied stress level. This latter observation is in agreement with the findings of Lauterwasser and Kramer[5]. The magnitude of the stress concentration at the craze tip is significantly lower for the polydisperse system than for the monodisperse.

From these observations it is clear that the low molecular weight chains in the polydisperse PS are responsible for the changes in $w(x)$ and $S(x)$ profiles. This conclusion is corroborated by the results on Blends I and
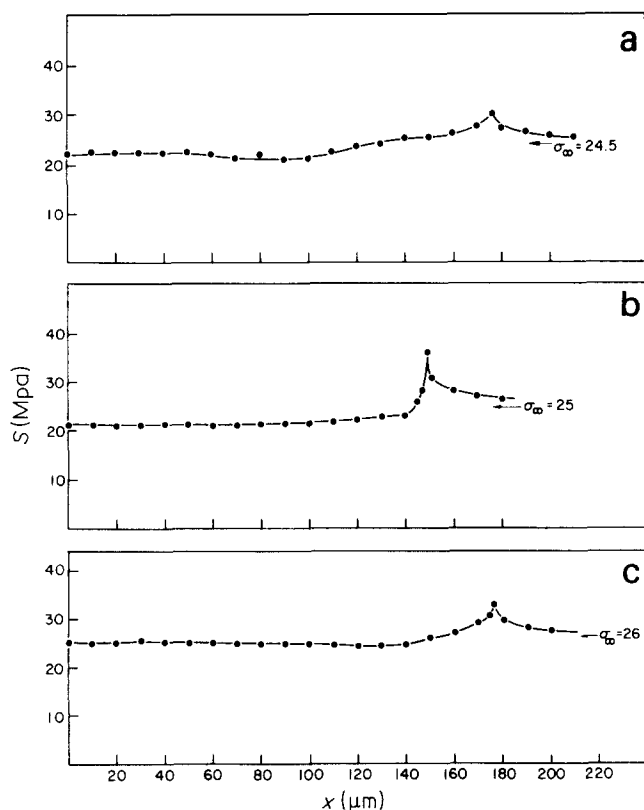
solution. The film was bonded to the grid by a short exposure to toluene vapour, and excess vapour was subsequently removed by placing in a vacuum dessicator overnight. This method is further discussed by Lauterwasser and Kramer[5].

Isolated crazes were grown in the films by straining the copper grid while observing the specimen with an optical microscope. Suitable grid squares for electron microscopy were then cut out. Because the copper grid deforms plastically during straining, the level of strain is maintained even after individual squares have been removed.

Stress analysis

The method of stress analysis is identical to that described by Lauterwasser and Kramer[5]. A series of electron micrographs are taken along the entire craze length. From these, the craze thickness $T(x)$ can be measured at all points. The local value of the volume fraction $v_f(x)$ of the craze can be obtained by microdensitometry of the electron image plate. This analysis relates the optical density of the craze, ϕ_{craze}, the undeformed polymer ϕ_{film}, and a hole through the film ϕ_{hole} to give:

Figure 2 Surface stress profiles $S(x)$ computed from measured $w(x)$ profiles for (a) polydisperse PS M_w=300 000; M_n= 113 000 (b) monodisperse PS M_w = 200 000; $M_w/M_n \leqslant$ 1.06 and (c) blend I

II. The addition of 5% of very low molecular weight PS (M_w = 4000) to the high molecular weight monodisperse PS causes the magnitude of the stress concentration at the craze tip to drop, and it extends further back along the craze. The addition of 15% of PS with M_w = 20 400 to monodisperse 200 000 M_w PS causes crazes in this blend to have similar micromechanics to those in polydisperse PS.

DISCUSSION

Recent experiments[8,16,17] have indicated that the entanglement network plays a fundamental role in the crazing of glassy polymers. Both the stress levels necessary for craze growth and craze fibril volume fraction increase as the entanglement density increases for a wide variety of homopolymers, copolymers and polymer blends. In particular if chains of molecular weight M_w less than twice the entanglement molecular weight M_e are added to a high molecular weight component, these short chains cannot form part of the entanglement network, and in effect simply dilute the entanglement network for the longer chains[17]. While the original experimental results were for addition of low M_w PS to polydisperse poly(phenylene oxide) (PPO), recent experiments[18] show that similar behaviour is observed if low M_w monodisperse PS (M_w < $2M_e$ = 19 000) is added to monodisperse PS of high M_w.

The dilution of long chains with shorter ones should have several effects on the entanglement network. One effect, which is minor as long as the volume fraction χ of the longer chains is close to 1, is to increase the maximum

extension ratio, λ_{max} of the entanglement network, according to the equation:

$$\lambda_{max}(\chi) = \lambda_{max}(PS)/\chi^{\frac{1}{2}} \qquad (1)$$

where $\lambda_{max}(PS)$ is the maximum extension ratio of the monodisperse high molecular weight PS. (The derivation of this equation assumes that the low molecular weight chains are long enough to qualify as a 'θ solvent' for the high molecular weight chains, which requires that the number of rotatable bonds in the short chains be greater than the square root of the number of rotatable bonds in the long chains[19]. This condition is satisfied for the blends above.)

The second effect, which is potentially more important, is an increase in the stress that the load bearing chains in the network must carry for a given applied stress. This quantity, which we have called the molecular stress, is given approximately by[17]:

$$\sigma_m = S\lambda_{max}(PS)/\chi^{3/2} \qquad (2)$$

The rapid increase in σ_m as χ decreases, is responsible for the fact that crazes in low M_w PS:high M_w PPO blends become unstable and break down rapidly to form cracks below χ = 0.3, even though crazes with higher predicted extension ratios are stable in other undiluted homopolymers (e.g. poly(tertbutylstyrene))[8,16].

Finally, the addition of short chains may decrease the time for disentanglement (by reptation or by tube relaxation[20] for example) of the longer chains under stress. Such effects of shorter chains in the melt are well known and are to be distinguished from a general increase in polymer chain mobility caused by a depression in T_g, which should be very small for the blends and polydisperse polymer considered here.

Two main experimental observations need to be explained. (1) The lower value of stress necessary to propagate the craze tip in the polydisperse systems *vis à vis* monodisperse PS and (2) the fact that the $w(x)$ profile just behind the craze tip changes from concave downwards to straight or even slightly concave upwards as the shorter chains are added.

The lower craze tip stress can be rationalized in a quite straightforward manner. Propagation of the craze tip by the meniscus instability mechanism[21] requires the generation of a large surface area in a small volume. In a highly entangled polymer, chains must either break or disentangle to form these surfaces. The rates of both chain scission and molecular reptation should increase with the molecular stress σ_m, hence as χ is decreased by increasing the volume fraction of molecules below the entanglement molecular weight, the craze stress S can decrease and still produce the required local modification of the entanglement network. Any increase in the rate of disentanglement, at constant σ_m, due to the addition of short chains will amplify this effect. The change in stress alone however appears to be large enough to account for the results. In the 5% blend the molecular stress is enhanced by 8% whereas in the 15% blend it is enhanced by 50%. The polydisperse PS which has approximately 5 volume per cent of molecules below the entanglement molecular weight should have an enhancement of molecular stress of 8% above that of the monodisperse PS.

The second observation is much more difficult to

understand and only a very speculative idea can be put forward at this time. The significance of the change in shape of the craze tip displacement profile observed is that, if such tips are also characteristic of crazes propagating at constant velocity (this point cannot be proved since the crazes observed in *TEM* have stopped growing), the relation between the local fibril drawing stress and local fibril drawing rate $\dot{w}$ must be severely altered by adding the short chains. For a craze propagating at a constant velocity v the displacement rate is given by:

$$\dot{w} = -\frac{dw}{dx}v \qquad (3)$$

so that regions of high slope $\dfrac{dw}{dx}$ correspond to high fibril drawing rates. One also expects that $\dot{w}$ is a monotonically increasing function of the local stress at the craze boundary $\sim \lambda S$; e.g.

$$\dot{w} \sim (\lambda S)^m \qquad (4)$$

where m is an unknown constant.

Analysed in this way, the $w(x)$ profile in monodisperse PS appears perfectly reasonable. As the stress $S(x)$ falls with distance behind the tip, (dw/dx) also decreases producing a displacement profile concave towards the x-axis, as observed. However, the $w(x)$ profile in the polydisperse systems is seen to behave quite differently. As $S(x)$ decreases behind the craze tip, $\left|\dfrac{dw}{dx}\right|$ is approximately constant. The local fibril drawing rate appears to be independent of stress. A very speculative suggestion is that in this case the rate of fibril drawing is diffusion controlled, where the diffusion involved is diffusion of the short chains in the blend/polydisperse system. In the plastically deforming glass such diffusion might occur to those regions of triaxial tension which will subsequently cavitate to form the new fibril surfaces. The accumulation of the low molecular weight species here will aid the cavitation process. There are many objections which can be raised to this idea: for example, is the diffusion coefficient of the shorter chains in the plastically deforming glass large enough to allow even short range lateral transport? However, it seems to be the only one at present capable of explaining the change from a stress dependent $\dot{w}$ to a stress independent $\dot{w}$ on adding short chains.

ACKNOWLEDGEMENTS

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