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Toughening mechanisms in high impact polystyrene

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In situ scanning electron microscope crack propagation experiments have been performed on a number of polystyrene and high impact polystyrene blends so that dynamic observations can be made of the mechanisms of failure. Brittle fracture is observed in low rubber phase volume systems, whereas high rubber phase volume systems exhibit a ductile tearing mode of fracture. As the rubber phase volume is increased there is an increased density of crazes, which leads to a reduction in width of material between them. The subsequent failure of the crazes leaves bridging ligaments. Under increasing load these fail in a manner dependent on their thickness such that there is a brittle–ductile transition at a ligament thickness around 3 μm. We argue that this alteration in mechanism could be caused by either the loss of the triaxial stress state or the reduced probability of extrinsic flaws being found in the smaller ligaments, resulting in inhibition of crazing. The stress required for failure at the crack tip consequently increases from that for craze formation to the yield stress of the dense polymer. This in turn allows a larger crazed deformation zone (already increased due to the stress relief effects of crazing) to form, hence a further toughness increase.

1. Introduction

It has long been recognized that the addition of rubber particles can increase the toughness of glassy polymers. The increase has been attributed to two mechanisms: (1) crazing which initiates at the rubber particles, and (2) shear band formation (e.g. [1, 2]). In commercial high impact polystyrene (HIPS) the former dominates, since crazing of the polystyrene (PS) matrix occurs readily, as long as the rubber particle diameter is greater than 1 μm [3–5]. In contrast to this behaviour, toughened styrene–acrylonitrile (ABS) exhibits predominantly shear deformation (although a significant craze density is also present), which is promoted by the cavitation of small rubber particles to relieve the local build up of hydrostatic tension [6].

The plastic deformation associated with the large volumes of shear and cavitation in ABS, or with multiple craze formation in HIPS, leads to a large increase in fracture toughness. However, to date it has always been assumed that the mechanism of crack advance in HIPS is identical to the failure in untoughened PS; the additional increase has been attributed solely to the generation of an increased craze density.

It is difficult to test this assumption of failure mode by examining samples after fracture, or by the study of a specimen at some intermediate stage of fracture obtained by interrupting the test. However, the use of a scanning electron microscope (SEM), set up so that *in situ* crack propagation experiments can be performed, allows direct observation of failure to be made. Such *in situ* experiments have previously been carried out on a range of polymers [7]. In this paper the results of *in situ* experiments on a series of specimens of PS containing different amounts of added HIPS (0 to 100%) are presented. The study shows that the high craze density in HIPS can promote a local ductile failure of the PS matrix, because the triaxial stress state is relaxed in the ligaments separating the crazes. Furthermore, stress relaxation due to crazing ahead of the crack tip implies that, for a given level of applied stress, crack propagation is impeded, permitting a large zone of deformation to form before a crack may advance. Now the change in failure mode means that the stress required to propagate the crack is increased from that for crazing to that for yielding. This means that the deformation zone can grow even further and the toughness is increased.

2. Experimental techniques

PS and HIPS granules, supplied by Shell Chemicals UK Ltd (grades DG310 and 581x, respectively), were mixed in proportions of 0, 10, 20, 50 and 100% HIPS in PS and injection moulded into 6 mm thick plates. These were annealed for 24 h at 373 K, allowed to oven cool and each plate was then cut into a compact tension (CT) specimen, as shown in Fig. 1. To produce sharp starter cracks, a razor blade was gently tapped into the machined notch. A rig, constructed so that crack propagation could be observed inside the

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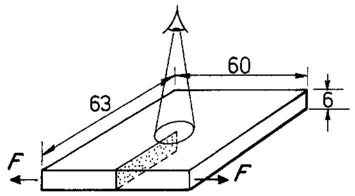


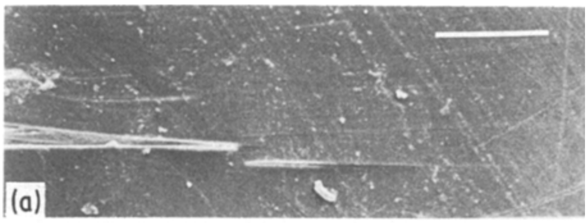
Figure 1 Compact tension specimen showing orientation to observer. Dimensions in mm.

SEM, permitted step loading of the CT specimen, via a flexible drive shaft from a remote stepper motor. Loads were monitored by a single cantilever load cell inside the SEM. Using ASTM99 [8] the stress intensity at the crack tip can be calculated at any point during the loading. (It should be noted that toughened grades do not conform with the ASTM thickness requirements, so results quoted should only be used as a guide as to the stress state of the material when it was photographed.) A small beam current and low acceleration voltage (10 kV) were used to prevent beam damage to the polymer. Charging effects were reduced by coating each specimen with a thin Au/Pd film; but as the crack propagated, new surfaces of non-conducting material were exposed and charging took place. These conditions normally lead to poor resolution, but we found that if only a small area of the crack is in view, careful control of contrast and gamma levels can actually enhance the detail available from the inside of the crack. A continuous video recording was made of each experiment and photomicrographs were taken at each load step.

3. Results

Typical regions ahead of the crack tip in five members of the PS-HIPS series are shown, taken at the same magnification, in Figs 2a to e. Fig. 2a shows that in pure PS, a few, long crazes are initiated ahead of the crack tip; this is also found by Marshall *et al.* [9]. By comparison in HIPS (Fig. 2e) a large region of deformation is formed ahead of the crack tip, within which there are many short crazes. There is a steady change from one type of behaviour to the other as increasing amounts of HIPS are added to PS. The increase in craze density and craze interaction as the HIPS content increases leads to a reduction in the width of the ligaments that are formed between crazes. Thus in blends of low HIPS content large ligaments of essentially pure PS are formed by the breakdown of crazes (Fig. 2b). In these ligaments, secondary crazes may be nucleated as the load is increased (Fig. 3; crazes are arrowed), and these grow across the ligament which then fails in a brittle manner; alternatively, crazes may only grow partially across with a plastic hinge forming in the remaining material, which eventually pulls apart.

Ligaments formed in specimens with high rubber content are much narrower on average and behave rather differently. Secondary craze deformation is suppressed, the ligament elongates markedly and may even bend (Fig. 4; arrow shows bent, elongated ligament). Eventually these ligaments neck down and fail, at which point the crack/craze may advance. Analysis



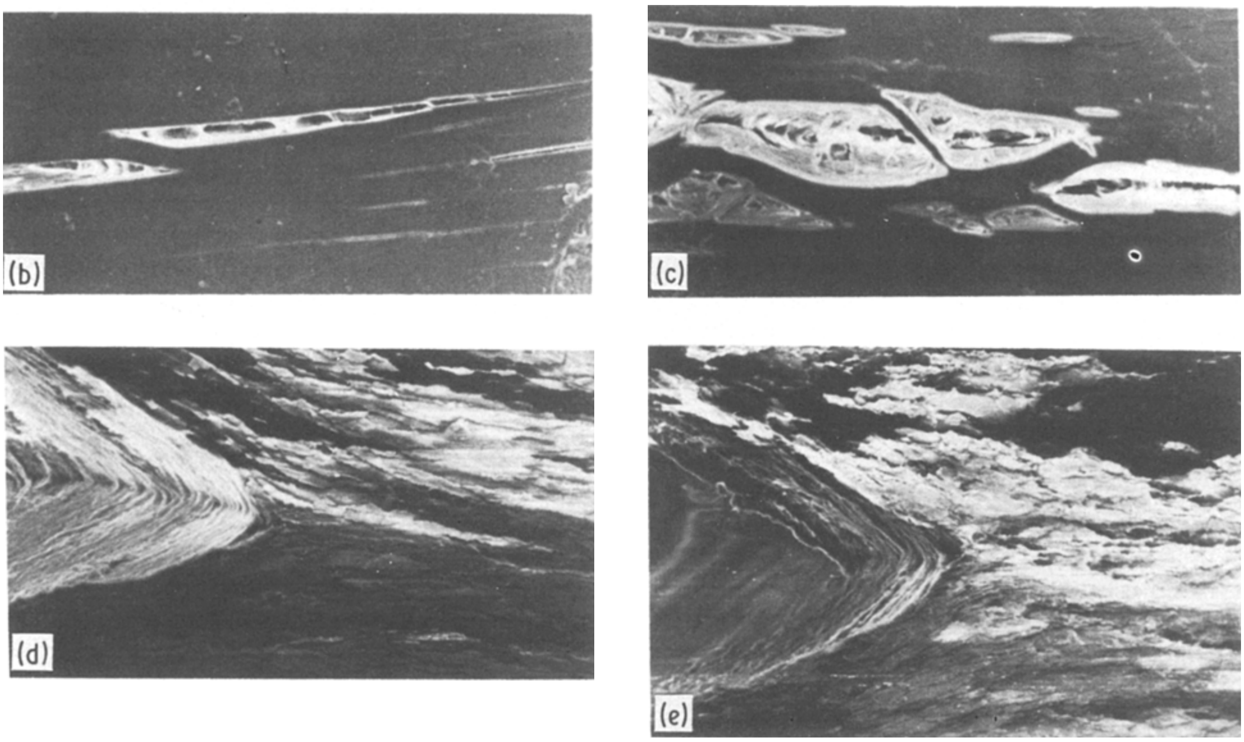


Figure 2 Crack tip deformation zones in (a) pure PS with $K_I = 0.33\,\mathrm{MN\,m^{-3/2}}$, (b) 10% HIPS in PS with $K_I = 0.60\,\mathrm{MN\,m^{-3/2}}$, (c) 20% HIPS in PS with $K_I = 1.22\,\mathrm{MN\,m^{-3/2}}$, (d) 50% HIPS in PS with $K_I = 1.42\,\mathrm{MN\,m^{-3/2}}$, (e) Pure HIPS with $K_I = 1.47\,\mathrm{MN\,m^{-3/2}}$.

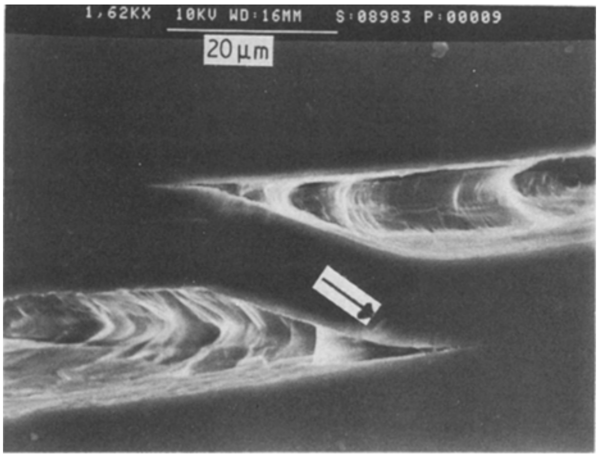


Figure 3 Close up of bridging ligament shown in Fig. 2b at a later stage of loading.

of a number of micrographs shows that the transition from ductile extension to secondary craze formation occurs for ligament widths of $\sim 3\,\mu$m. The rippled surface within the crack in Fig. 4 can be seen to derive from the extension of these ligaments. The mechanism producing this ripple formation can be clearly seen in the dynamic experiments, but single photographs such as Fig. 4 are unable to demonstrate the origin of the ripples.

4. Discussion

The increase in toughness associated with the addition of rubber particles to a PS matrix is well known, as is the importance of multiple craze formation in contributing to this toughness enhancement [1]. The observations presented here show additionally that further ductility is associated with the matrix when the rubber content is sufficiently high.

PS is generally classed as a brittle polymer, and extensive ductility at room temperature is not observed so that, for instance, macroscopic necks do not form under uniaxial tension. At room temperatures other polymers, notably polycarbonate, show behaviour that is markedly thickness dependent; the ductility, and toughness, of thin (1 mm) specimens being significantly larger than for thick (6 mm) specimens [10–12]. Such behaviour has been rationalized in terms of the lack of constraint in thin specimens, which implies a state of plane stress is achieved throughout the specimens, as distinct from the plane strain conditions which predominate in thick specimens. A model of the transition from ductile to brittle behaviour as thickness is increased has recently been proposed, in which the size of shear lips associated with stable crack growth is shown to be the determining factor [13]. Such a ductile–brittle transition has not been reported in PS. Logically, however, it seems likely that a similar ductile–brittle transition should occur, if the specimen was sufficiently thin.

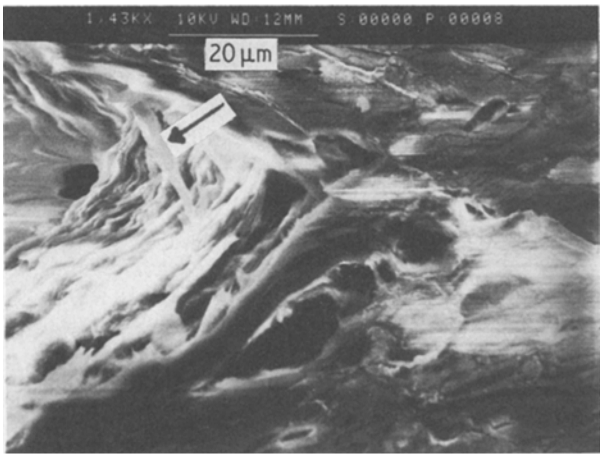


Figure 4 Close up of crack tip in pure HIPS.

The behaviour of pure HIPS and HIPS diluted with relatively small amounts of PS, typified by Figs 2d, 2e and 4, demonstrates that for ligaments less than $3\,\mu$m in thickness significant ductility of the PS matrix does indeed occur. Therefore, it seems plausible that the critical thickness for the ductile–brittle transition can be identified with the critical ligament thickness of $3\,\mu$m, i.e. three orders of magnitude lower than for polycarbonate. Since this value lies well below typical thicknesses used in macroscopic mechanical tests, it is not surprising that the existence of the transition has not previously been documented. A much lower value of $0.15\,\mu$m has previously been found for the transition from a normal craze microstructure to a "perforated sheet" structure, this transition also being associated with a change from plane strain to plane stress conditions [14]. However, test conditions for the earlier study were very different to those here, both strain rate and geometry being changed. Since the ductile–brittle transition is known to be strain rate and geometry sensitive this may account for the difference. An alternative explanation could lie in the model of Argon and Hannoosh [15]. As the ligament width is reduced the probability of finding a craze initiation site (an extrinsic flaw) is reduced so that yielding is favoured.

The demonstration of significant deformation of the PS matrix is of interest in itself, but also of importance is its role in permitting a larger volume of craze deformation to form in HIPS, before a single craze fails, thereby permitting crack advance. These observations enable the arguments originally due to Bucknall [1], based on an increase in toughness due to multiple craze formation, to be expanded. First we consider the case of PS/HIPS blends with a low rubber particle density, where little ductility is present. Ahead of a crack in such a diluted HIPS blend, the stress causes many crazes to be initiated at rubber particles, at inhomogeneities in the material and at surface defects. These grow in length and overlap until the stress fields ahead of the craze tips interact; at this point craze growth is retarded. The rise in stress ultimately becomes sufficient to cause the breakdown of the crazes themselves. A "bridge" or ligament is left, formed from the overlapping material. This bridge then deforms under the increasing load causing secondary crazes to be nucleated. These (as can be seen in Fig. 3) grow at an angle to the original craze direction.

To understand the growth of these secondary crazes, the bridging material can be treated as a fixed beam under load. Fig. 3 shows a close up of such a

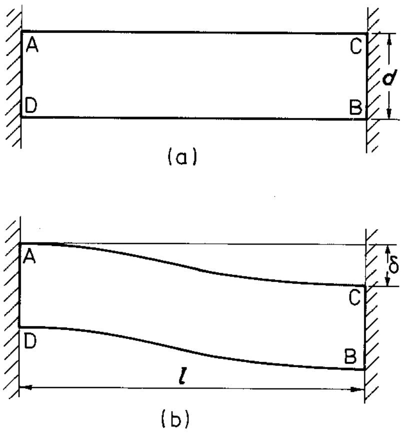


Figure 5 Schematic diagram showing the geometry of a fixed beam (a), undergoing displacement (b).

bridge containing crazes. Fig. 5a is a schematic drawing of the situation (with the parameters used in the treatment defined). If the bridge is considered as a fixed beam, of width d and length l, when a relative end displacement δ is applied it bends, producing a maximum bending moment at the points A and B (Fig. 5b). This produces a maximum tensile strain at these points, giving by $e = 3\delta d/l^2$ [16]. Points C and D are subjected to a compressive strain of equal magnitude. From Fig. 2 the appropriate values for the parameters can be measured to be $\delta = 10\,\mu\text{m}$, $d = 10\,\mu\text{m}$ and $l = 30\,\mu\text{m}$ giving $e_{\max} = 0.33$. This is clearly well beyond the limit for beam theory to hold; it emphasizes the point that the points A and B experience a large strain well above the critical strain for craze nucleation in PS (typically a macroscopically applied strain of 0.1%) [17]. Crazes in general grow along the direction of minor principal stress [18, 19], which is approximately along AD in this case. This is consistent with Fig. 3. These secondary crazes now grow right across the bridge causing brittle fracture of the bridge.

The bridge, in these low rubber content samples, is likely to be essentially devoid of rubber particles (rubber particles capable of initiating crazes will already have done so, and therefore cannot by definition lie within the bridge), and hence its final brittle fracture will be similar to the behaviour of a block of pure PS. Therefore in materials of low rubber content, the final fracture event, permitting the crack to advance, is brittle: the toughness of these materials can be adequately described in terms of multiple crazing alone, without additional ductility of the PS matrix. However, the failure of bridges formed between primary crazes will be affected by the interaction of neighbouring craze stress fields.

In some cases completely brittle failure may not occur. If when secondary crazes have grown across the ligaments, their breakdown does not produce brittle failure, the remaining ligament may then bend around the base of the ruptured crazes. This bending can take place because of the brittle–ductile transition, described earlier, occurring in the remaining material. Further crack propagation then takes place by the rupture of these yielded zones. This process produces a high toughness but is the exception not the rule, as in most cases catastrophic brittle failure occurs.

We now consider pure HIPS, or PS with a high rubber content. As the load is increased, the initial response is identical to the above: crazes are initiated at the stress concentrations around the rubber particles, surface defects and material heterogeneities. These crazes grow towards each other and overlap until the stress fields interact, retarding further growth. However, because the density of nucleating sites is high, the average ligament width between neighbouring crazes is substantially reduced. The critical thickness for the brittle–ductile transition within a ligament may now be reached. The stress relief, caused by the intense deformation zone, means that the actual stress intensity factor at the crack tip is lower than would be calculated from previous knowledge of crack geometry and the level of applied stress, σ, alone. Such a drop in the stress intensity factor is associated with any local deformation at a crack tip [20, 21], and can be considered as an effectively "screened" stress intensity factor.

As a consequence of the substantial screening in the vicinity of the crack tip, the external load can be significantly increased without the stress at the crack tip reaching that needed for crack propagation. Owing to the stress concentration at the crack tip an increase in σ will lead to more and more rubber particles, both those at ever greater distances as well as those near the crack tip which were initially insufficiently effective concentrators, nucleating crazes. Thus the deformed volume will grow in extent, and lead to further screening of the applied stress intensity factor and further craze initiation. Thus a co-operative process is in operation which must produce a very pronounced effect on toughness. This may explain the more rapid increase in impact resistance with temperature seen by Bucknall [1]. Bucknall's association of this increased rise in impact resistance with a fully whitened fracture surface may, in fact, imply the co-operative process in operation. Eventually the stress concentration effect of the crack tip becomes small at larger distances from the crack tip and further crazing does not take place with an increase in the external load. Now the increasing load will increase the stress at the crack tip and crazes adjacent to the crack tip fail. These form microcracks, as with the diluted systems, and ligaments of material. These ligaments because they are narrower, fail in a ductile manner which again adds to the energy absorbed during the fracture process. The description of the toughening mechanism described here provides a rationale for why such a large volume of crazed material is seen ahead of a crack tip in HIPS. It should be noted that since a triaxial state of stress is necessary for craze propagation via the meniscus instability [18, 19, 22], the absence of secondary crazes within the narrow ligaments is not surprising. Also, although elasticity theory predicts that as the ligaments become thinner the strain will decrease for a given radius of curvature, even for a ligament 3 μm thick (for the same parameters as used earlier) the strains would still be sufficient to nucleate crazes. Thus this argument alone cannot predict a change to a ductile response, and hence cannot be a major factor here.

This analysis can be compared with recent studies on two somewhat different systems. In ABS, it has been shown that cavitation of small rubber particles leads to a reduction in constraint, preventing the build up of hydrostatic tension which accompanies shear of the styrene–acrylonitrile matrix, allowing further shear to occur [6]. In toughened epoxy systems, a similar model has been proposed; cavitation of rubber particles leads to a reduction in the constraint, and hence yield stress, producing more extensive local ductility [23]. In HIPS, small (less than 1 μm) rubber particles do not lead to such substantial toughening as an equal volume of rubber dispersed in particles of diameter 3 to 5 μm. The reason for the inefficiency of small particles is due to their inability to initiate crazes [5]. However, the arguments put forward here show that, even if no crazes whatsoever are nucleated, some toughness will be associated with local ductility if the rubber particles are able to cavitate or if they are sufficiently close together to relax constraint. Such a slight increase has been observed [4]. However, the toughness contributed by multiple crazing followed by ductility of ligaments, will be much greater in magnitude than that simply due to relaxation of constraint around small, cavitated particles.

5. Conclusions

In situ SEM crack propagation experiments can be performed on polymer systems, even though charging of the newly formed surfaces takes place. The results obtained from such observations can substantiate the previous models of mechanisms of failure and furthermore elucidate dynamic mechanisms previously unobserved.

Brittle fracture takes place in PS systems of low rubber content, whereas a tougher ductile tearing failure mechanism is exhibited by systems with a high rubber particle density. The matrix ductility is possible because the ligaments formed with the dense array of crazes are sufficiently narrow to lie below the critical thickness for the brittle–ductile transition of PS, experimentally found to be 3 μm. The formation of many crazes at the crack tip also leads to a screening of the local stress intensity factor, which in turn permits further craze formation at greater distances from the crack tip before crack advance occurs. This co-operative effect leads to large toughness enhancement in HIPS compared with unmodified PS.

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