

Internal structure of rubber particles and craze break-down in high-impact polystyrene (HIPS)

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Polystyrene can be substantially toughened by the addition of rubber particles, their role being to act as craze initiators permitting substantial plastic deformation to occur prior to fracture. The internal structure of these particles is variable: typically the smaller ($\sim 1 \mu\text{m}$) particles are solid rubber and the larger particles contain sub-inclusions of polystyrene. Thin films of a toughened high-impact polystyrene (HIPS) suitable for optical and transmission electron microscopy (TEM) have been prepared, and the interplay between the internal structure of the particles and the crazes they generate has been examined by TEM. It is found that as crazes form around the solid rubber particles, significant lateral contraction occurs accompanying their elongation in the tensile direction. As this contraction proceeds, decohesion occurs just beneath the particle-craze interface, resulting in the formation of a void. This void will grow under increasing stress, leading to premature failure of the craze. In contrast to this behaviour, occluded particles can accommodate the displacements due to crazing by local fibrillation of the rubber shell which surrounds each sub-inclusion, without the formation of large voids. Consequently, the occluded particles do not act as sites for early craze break-down. These results suggest that the optimum morphology for rubber particles in HIPS will consist of a large number of small PS occlusions, each surrounded by a thin layer of rubber, in which case the size of the inherent flaws introduced during crazing will be minimized.

1. Introduction

A "brittle" polymer such as polystyrene (PS) can be substantially toughened by the introduction of dispersed rubber particles. It is now well established [1-3] that the role of these particles is to act as craze initiators, permitting a large volume of plastic deformation to be formed before individual crazes break down to form cracks leading to fracture.

Experimentally, it has been determined [4, 5] that there is an optimum particle size of about 1 to $4 \mu\text{m}$, leading to a maximum toughness. However, the underlying reason for this size dependence has not been well established. One suggestion has been that the rubber particles are not only effective as craze initiators but also as

craze terminators, thus limiting the size of the crazes. However, if the particles are too small, it was suggested that this craze termination mechanism would become inoperative. It has been pointed out recently [6] that this explanation is based on two assumptions whose validity must be questioned. Firstly, if a rubber particle acts as a stress concentrator to initiate crazes it cannot also be a craze terminator; and, secondly, the model assumes that a large craze is a weak craze. It has been demonstrated [7] that the mechanism for craze thickening in polystyrene involves the drawing of fresh material into the craze at constant extension ratio, λ , rather than creep of the material already in the fibrils; this mechanism implies that a large craze is not neces-

arily more likely to break down than a small craze.

A complication in trying to understand the role of the rubber particles in the toughening of high-impact polystyrene (HIPS) arises because the particles are not homogeneous. Under suitable polymerization conditions, addition of about 6 wt% rubber may lead to a rubber-phase volume-fraction of 20 to 30%. Examination of the particles by electron microscopy has shown that many of the particles have a cellular structure, consisting of occluded polystyrene particles each surrounded by rubber and with an outer shell of rubber surrounding the whole. In general, the smaller particles tend to be solid rubber whereas the larger ones contain occlusions; however, there is apparently no simple relationship between particle size and the internal structure of the particles, and the structure itself is likely to be a sensitive function of the precise conditions of polymerization.

It has been established [8,9] that one prerequisite for obtaining a toughened polymer is that good adhesion be achieved between the rubber particles and the matrix. If this were not the case, voids or glass beads would act equally well as tougheners and this is not so [10,11]. It is because the rubber may be directly grafted to the matrix that voids do not form at the interface as soon as crazes are initiated, leading to sub-critical crack growth and subsequent fracture before a large volume of plastic deformation has occurred. However, the detailed response of the rubber particles themselves to the deformation caused by the crazes has not been explored.

In this study, transmission electron microscopy (TEM) has been used to examine the way in which both solid rubber and occluded rubber particles accommodate the displacement produced at the particle-matrix interface during crazing of thin solvent-cast films. Only one previous study by Beahan *et al.* [12] has examined crazing in thin solvent-cast films, as opposed to microtomed sections from bulk specimens. These workers [12] found a basic similarity in the deformation in the thin films and microtomed sections. However, despite staining by OsO_4 which tends to reinforce the crazes, microtomed samples always exhibit craze collapse, both because the stress is removed prior to staining and observation, permitting the rubber particles to relax and the fibril structure within the crazes to buckle, and because of the

cutting stresses. Thus, microtomed samples cannot be used to study the detailed interaction of the craze with the rubber-glassy polymer interface. It has been demonstrated [13] that for PS thin films, the craze morphology is unchanged from that of crazes grown in bulk specimens when the film thickness is greater than about $0.15\ \mu\text{m}$, and Beahan *et al.* [12] also noted that the morphology of crazes in HIPS is identical to that of unmodified PS. The limitation of the thin-film technique for the study of HIPS is therefore not in the final craze microstructure, but in the altered conditions for craze initiation when the mean rubber-particle size is comparable to or greater than the film thickness. Even working with films of about $2\ \mu\text{m}$ thickness, as in this study, crazes tend to nucleate only at particles of approximately this diameter of $2\ \mu\text{m}$ or smaller because of the reduced stress concentration factor when the particle-size is greater than the film thickness. For the purposes of studying the craze-particle interface, thin-film techniques are nevertheless both useful and appropriate.

Using an OsO_4 stain, as has previously been employed in TEM studies [12,14], permits ready identification of the rubber phase and this technique has enabled the nature of the occluded particles to be examined. However, it will not necessarily be helpful in locating the rubber in crazed samples. When mass thickness contrast is used to obtain information, as in a TEM micrograph, a region of Os-stained rubber will undoubtedly appear darker than the PS matrix; however, once deformation has occurred, local extension of the rubber can compensate for this staining contrast. This point was discussed by Beahan *et al.* [12] who concluded that the rubber between the PS occlusions "fibrillated" although the stained rubber "fibrils" were difficult to distinguish from PS fibrils within a craze. Since in this study the interest lay in examining the craze-particle interaction it was felt that there was no advantage to be gained by using staining.

2. Experimental procedure

The HIPS used in this study was a non-commercial resin containing 10 vol% butadiene rubber (diene-55) with an average particle size of $2.9\ \mu\text{m}$ in polystyrene with a weight-average molecular weight, \bar{M}_w , of 250 000 and a number-average molecular weight, \bar{M}_n , of 115 800. This HIPS was supplied by Dr R. A. Bubeck of the Dow Chemical Company

and contained no mineral oil as a plasticizer, in contrast to commercial HIPS. It was produced by the free radical polymerization of styrene containing dissolved butadiene rubber molecules [15]. Some of the rubber particles are solid rubber due to their formation under somewhat different phase inversion conditions than occur during production of commercial HIPS. To permit craze growth and breakdown from individual rubber particles to be investigated without significant stress-field overlap from neighbouring particles, this HIPS was diluted in the ratio 1:9 with polystyrene of $\bar{M}_w = 300\,000$ and $\bar{M}_n = 124\,000$, also containing no mineral oil and supplied by Dr Bubeck.

This mixture was dissolved in toluene from which glass slides were drawn to produce thin films 1.5 to 2 μm thick. The films were floated off the slides onto a water bath from which they could be picked up on annealed copper grids which had been precoated with the same solution of HIPS. The film was bonded to the grid by a short exposure to toluene vapour and then dried to remove excess toluene by placing in a vacuum overnight. If not removed, the presence of excess toluene in the film could lead to the rubber particles remaining in a swollen state, thus changing their properties. Further details of this method of specimen preparation are given by Lauterwasser and Kramer [7].

The specimens were then strained in tension in air, whilst being observed with an optical microscope. This procedure permitted both the strain at which the crazes first nucleated and the strain at which the first signs of craze break-down occurred to be monitored. Suitable grid squares for observation in the TEM (a Siemens 102 electron microscope operating at 125 keV) were then cut from the specimen. The copper grid deforms plastically, maintaining the level of applied strain and thus preventing craze collapse.

3. Results

As the strain level in the film was increased, a profuse array of crazes was generated, initiating at the rubber particles. A typical optical micrograph of crazes in a thin film of HIPS is shown in Fig. 1.

Optical microscopy alone cannot distinguish between the homogeneous solid rubber particles, and those particles containing polystyrene occlusions, although at very high levels of deformation it is occasionally possible to detect the

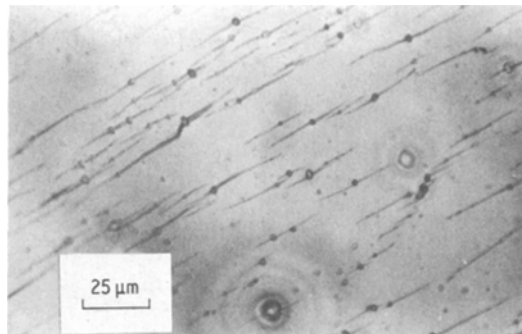


Figure 1 Optical micrograph of crazes generated at rubber particles in HIPS.

presence of occlusions within a few of the largest particles. However, in the TEM the two types of particles can be readily distinguished after crazing without the use of OsO_4 staining to enhance the contrast of the unsaturated rubber. Crazes grown from the two kinds of particles are shown in Fig. 2. Because the strain in the films was increased in steps, to permit (optical) identification of the particles which nucleated crazes first, stress relaxation occurs at each stage at the edge of the craze before further craze thickening takes place. This effect, discussed further in [16], gives rise to “ridges” of less highly-drawn material, marking the position of the craze–matrix interface at the time of the increase in strain. These ridges can be seen in Fig. 2b and some of the later micrographs (see, for example, Figs 4b and 6). It should be noted that, although the rubber particles can be conveniently divided into two types, i.e., solid rubber and occluded rubber particles, the latter category encompasses a wide range of particles with differing internal morphologies, as can be seen in Fig. 3, which shows crazing in an undiluted HIPS sample.

As an occluded particle responds to the externally applied strain, the rubber elongates, whereas the PS occlusions remain essentially undeformed because of the much higher value of Young’s modulus of the PS. Locally the rubber will break up into “fibrils” but, because of the occlusions separating the various domains of fibrillation, no large voids are formed. Thus, as crazing and deformation proceeds, the dimension changes imposed upon the particle can be accommodated without harmful subcritical cracks being formed. This effect can be seen in Fig. 2a.

The response of a solid rubber particle is very different, as is clear in Fig. 2b. As deformation proceeds the rubber particle deforms as a whole,

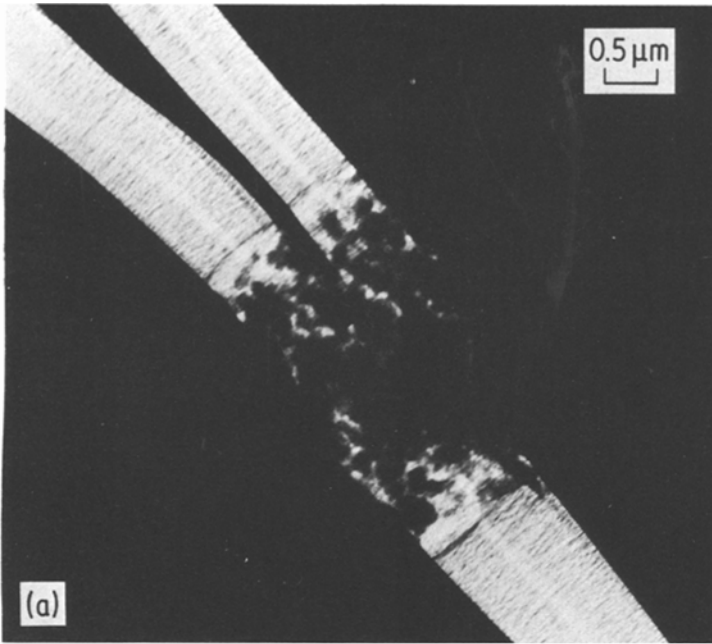


Figure 2 (a) Crazes nucleated at a highly occluded particle. (b) Crazes at a solid rubber particle.

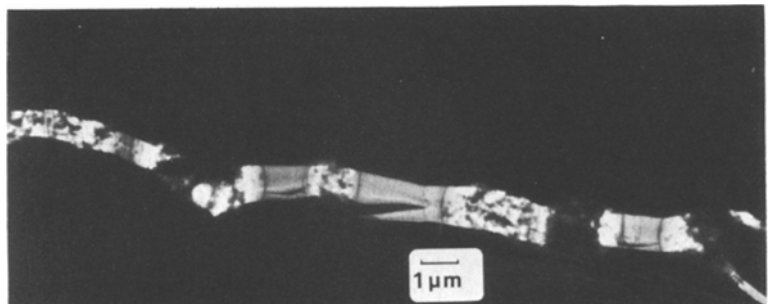
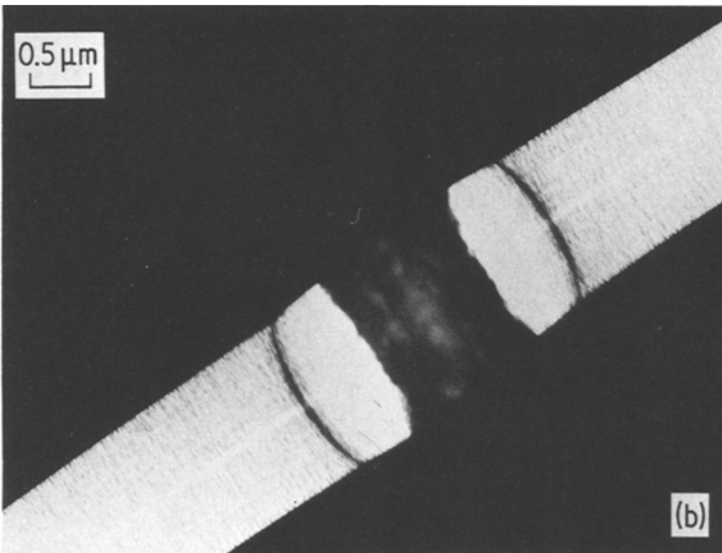


Figure 3 Crazing in undiluted HIPS, showing the range of internal morphologies of the rubber particles.

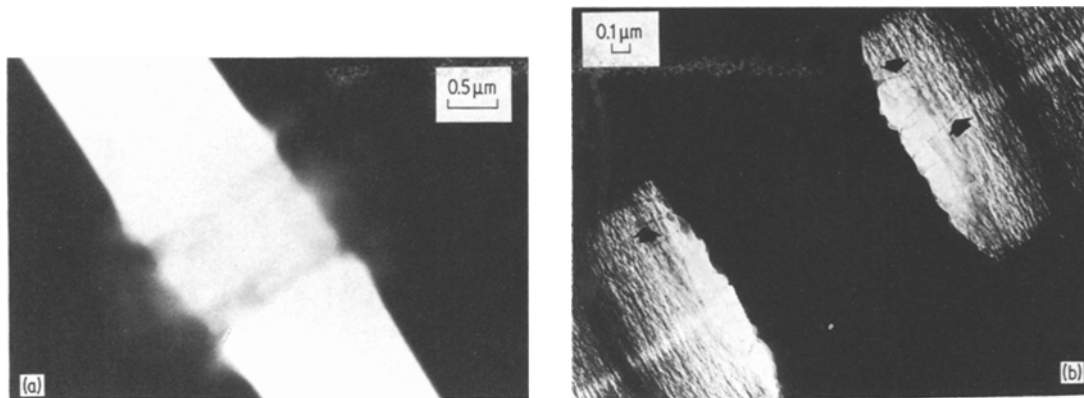


Figure 4 (a) View of the same particle as in Fig. 2b, showing the nature of the rubber particle deformation. (b) Ligaments (see the examples indicated by arrows) of rubber are drawn out as decohesion of the rubber particle from the craze occurs.

with an elongation, λ , in the direction of the tensile axis being accompanied by significant contraction, approximately $\lambda^{-1/2}$, along directions normal to this axis. The exact nature of the deformation of the particle can be seen most clearly in Fig. 4a, which has been over-exposed to enhance the contrast of the rubber particle itself. Little internal voiding of the particle occurs.

However, due to the nature of the chemical graft that is formed at the rubber–matrix interface during polymerization, two effects arise. Firstly, the outer layer of graft cannot deform in this way and is left as a “halo” of relatively dense material, marking the original position of the craze–particle interface (a similar halo may also be seen faintly around the occluded particles). Secondly, ligaments of rubber are drawn laterally from the particle

linking the remnant of the outer shell to the waisted particle. These ligaments, which can be up to $3\ \mu\text{m}$ long, can be seen in Fig. 4b. Clearly, these ligaments will need to support a large stress and will tend to break down at an early stage.

For particles deforming in this way, relatively large voids are formed locally which may act as preferential sites for craze break-down. That this is indeed so can be seen by applying yet higher levels of strain. Fig. 5 shows a rubber particle at which the craze has completely broken down on one side and is almost torn on the other with a few ligaments still remaining intact. In this case the applied strain was 12%, and some internal voiding of the rubber particle has also occurred. Occasionally break-down within a solid rubber particle may also occur if this internal voiding

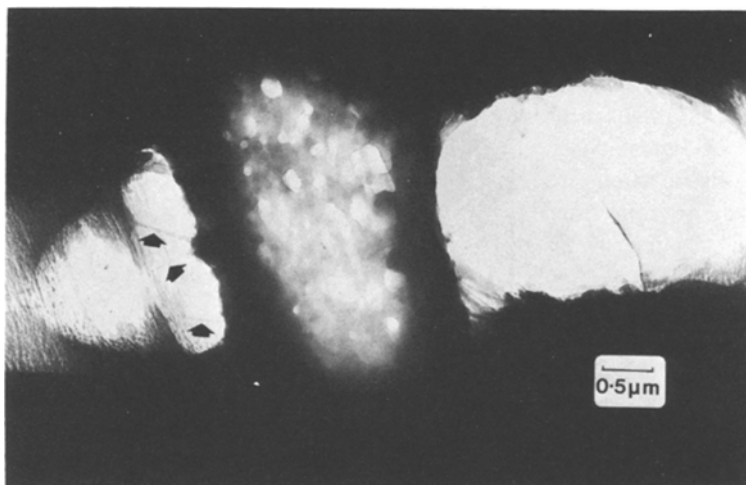


Figure 5 Craze break-down at the edge of a rubber particle. Some ligaments (arrowed) still remain intact.

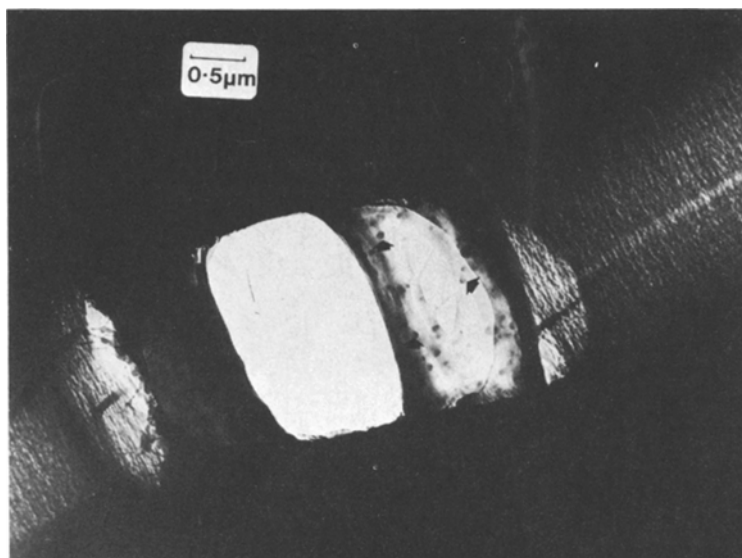


Figure 6 Internal voiding of a rubber particle. Arrows indicate stumps of the retracted rubber ligaments.

becomes too severe, since these particles lack the reinforcement due to the occlusions of the inhomogeneous particles. An example of this behaviour is shown in Fig. 6. Stumps of retracted rubber ligaments are also visible.

4. Discussion

It has previously been shown that good adhesion between the added rubber particles and the glassy matrix is a necessary requirement for rubber toughening of "brittle" polymers. For instance, glass beads added to styrene acrylonitrile (SAN) will act as effective craze nucleators but, because they rapidly debond from the matrix, the strain-to-failure of SAN modified by their introduction is little improved [10, 11]. Thus, to achieve significant toughening of a glassy polymer that deforms principally by crazing requires not only the introduction of suitable craze nucleating centres, but also that these centres should not subsequently become preferential sites for craze break-down before a high overall level of plastic strain by crazing has been achieved. Clearly anything that promotes void formation in the vicinity of the particle will be detrimental to the toughness.

The results presented here show that solid rubber particles act as sites for premature craze failure and, thus, that their presence in rubber-modified plastics is likely to produce less favourable results (a lower toughness) than if only occluded particles were present. Clearly, it is not simply a case of the rubber being unable to accom-

modate the high elongations imposed. Fig. 7 shows a highly occluded particle almost totally engulfed by the surrounding craze. The outer rubber shell at the poles is highly extended and fibrillated and

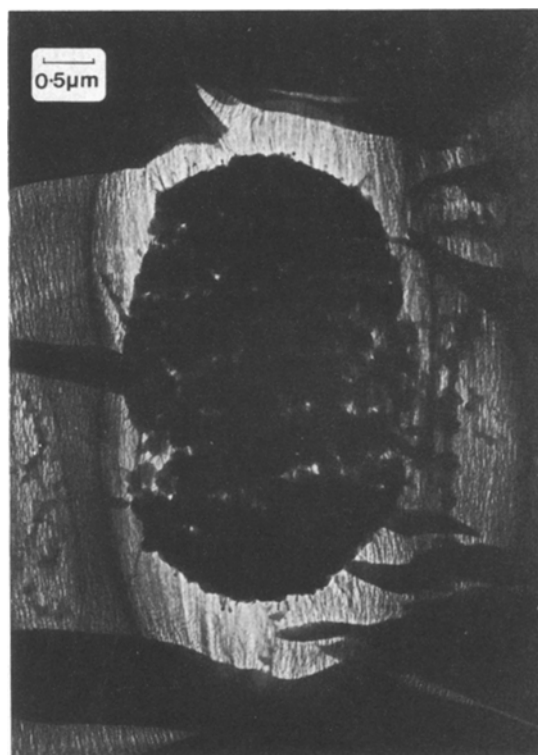


Figure 7 A highly occluded particle which has been surrounded by crazes. Fibrillation of the rubber shell occurs at the poles.

there are a few broken and retracted fibrils visible, but no gross voiding has occurred. Because the particle is highly occluded, significant lateral contraction at the equator has not occurred and good adhesion at the equatorial craze-particle interface can be maintained.

However, at comparable strains for a solid rubber particle, a pronounced "waist" develops in the particle. As this process occurs, rubber ligaments are drawn out normal to the applied stress, as the rubber tries to maintain continuity between the particle and the craze. As the ligaments fail a void will form at the equator. To establish that this observed voiding contributes significantly to failure, it is necessary to examine what proportion of craze break-downs actually initiate at rubber particles. A heavily crazed specimen, with voiding just visible optically but with no gross cracks present, was examined in the TEM and a map obtained of a large area of the specimen. The analysis showed that, of the particles that had initiated crazes within the area, only 28% were solid rubber. However, of these rubber particles 25% had failed (i.e., 7% of the total number of particles involved in crazing), whereas none of the occluded particles which nucleated crazes (72% of the total) had initiated cracks. Clearly, the weakness at the solid rubber-particle interface is of prime importance.

The analysis can be taken further by considering the effect the size of the generated void at the edge of the rubber particle has upon the ultimate time-to-failure. This problem has been considered [6] specifically for the case of debonded rubber particles. Using an analysis based on the subcritical crack growth rate, V , for an initial crack of radius, a_i , with stress intensity factor, K_i ($\ll K_c$, the critical stress intensity factor for unstable crack propagation) it was found that the time to failure, t_f , is given by

$$t_f = \frac{2}{(n-2)A} \left(\frac{2\sqrt{\pi}}{\sigma_\infty} \right)^n \left(\frac{1}{a_i} \right)^{\frac{n-2}{2}}, \quad (1)$$

where A and n are defined by

$$V = AK^n, \quad (2)$$

and σ_∞ is the applied stress. The value of n may be as high as 25 or more [14]. Clearly, to achieve a high value of t_f , permitting a large number of crazes to form prior to the break-down of one of them, it is necessary to ensure that only small flaws are initially present. However, if break-down

around the solid rubber particles does occur, flaws of radius about $1 \mu\text{m}$ are generated, much larger than flaws generated either by isolated fibril break-down within a craze (of radius about 50 nm), or by the voids developing within and around the occluded particles. These large voids can lead to a decrease in t_f of many orders of magnitude, for example, a decrease of 10^{-8} in the case of a comparison of initial flaws of radius $1 \mu\text{m}$ and 50 nm.

It is also clear that the scale of the rubber fibrillation around the occlusions will determine the size of possible flaws generated within the occluded particles. One can imagine that this rubber fibrillation occurs by the Taylor meniscus instability, the same mechanism which governs the advance of the craze tip in the glassy matrix [17]. It can be shown [18] that the fastest growing wave-length of the instability, and thus approximately the interfibrillar spacing, Λ_c , which corresponds to the initial void size, is given by

$$\Lambda_c = 2\pi\sqrt{3} \left(\frac{\Gamma h^2}{12\eta v_0} \right)^{\frac{1}{2}}, \quad (3)$$

for a meniscus propagating at a velocity, v_0 , in a rubber layer which has a surface tension, Γ , a Newtonian viscosity, η , and a thickness, h . The initial void size between rubber fibrils in this model will decrease linearly with the thickness of the rubber layer between glassy occlusions, h .

These arguments show that, to obtain a toughened polymer with a large t_f one requires:

(a) the presence of few or no solid rubber particles; and

(b) highly occluded particles, with each sub-inclusion being surrounded by as thin a rubber layer as possible.

The evidence in the published literature suggests that the toughest rubber toughened polymers that deform by crazing do indeed have such microstructures. Contrary to this view, it has previously been suggested [3] that solid rubber particles are actually more effective than occluded particles in toughening PS, on the basis of work carried out on block co-polymers [19]. In that study it was demonstrated that a 50:50 (vol/vol) styrene-butadiene block co-polymer blended with styrene to give a HIPS of total butadiene content of 20 vol%, gave a five-fold increase in impact strength over commercial HIPS. The reason for this increase does not lie, as assumed by Bucknall [3], in the absence of occluded particles; rather, the rubber particles contain a very large number of small occlusions,

as is clear from the micrographs in [19]. The structure of the occluded particles can be compared directly with the typical HIPS particles: the latter contain relatively few, coarse occlusions surrounded by a rubber layer of 100 to 200 nm in thickness whereas the block co-polymer occlusions are on a fine scale with interspersed rubber layers of about 30 nm in thickness.

Thus, the work of Durst *et al.* [19] corroborates the evidence presented here; highest impact toughness will be achieved when the lowest proportion of unoccluded particles is present. Furthermore, the most favourable distribution of occlusions within the particle will correspond to a large number of small occlusions (and not to a few large ones), since, as a fibrillation of the rubber inside the particle occurs, the smallest initial flaw size will be generated in this case. It is for this reason that the particle in Fig. 7, which has this most favourable occlusion distribution, is able to accommodate the large displacements of the thick craze it has initiated, with no sign of voiding or incipient break-down,

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