

Plastic deformation mechanisms in poly(acrylonitrile-butadiene styrene) [ABS]

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Thin films of two poly (acrylonitrile-butadiene-styrene) [ABS] resins have been strained in tension, and the ensuing deformation has been characterized by transmission electron microscopy. To enhance contrast of the rubber particles, some of the specimens were stained with OsO_4 . Films containing only solid rubber particles $0.1 \mu\text{m}$ in diameter show little tendency for crazing. Instead, cavitation of the rubber particles occurs, together with localized shear deformation between the particles along a direction nearly normal to the tensile axis. For specimens containing a mixture of the same small particles plus larger ($1.5 \mu\text{m}$ diameter) particles containing glassy occlusions, some crazing does occur. Crazes tend to nucleate at the larger particles only. When crazes encounter the smaller particles these cavitate without appearing to impede or otherwise affect the craze growth. The occluded particles also show significant cavitation, with voids forming at their centres at sufficiently high levels of strain. These voids do not seem to lead to rapid craze break-down and crack propagation. In commercial ABS, which typically has both large and small rubber particles, both crazing, nucleated by the large particles, and shear deformation, encouraged by the cavitation of small rubber particles, can be expected to make important contributions to the toughness of the polymer.

1. Introduction

Glassy polymers such as polystyrene (PS) and styrene-acrylonitrile (SAN) can be substantially toughened by the incorporation of rubber particles, to give the polymers known as HIPS (high impact polystyrene) and ABS (acrylonitrile-butadiene-styrene), respectively. For these toughened polymers, significant stress-whitening occurs prior to fracture and the elongation-at-break and the notched Izod impact toughness are many times higher than those of the unmodified parent polymer (typical elongations at break are about 2% for SAN and about 30% for ABS).

Empirically it has been found that there is an optimum size for the rubber particles; in the case of HIPS, particles smaller than about $1 \mu\text{m}$ do not seem to enhance the toughness of the polymer significantly but, in the case of ABS, rubber

particles as small as $0.3 \mu\text{m}$ are efficient tougheners, and the value is even lower for toughened PVC [1]. A clear understanding has not been forthcoming of either why an optimum particle size exists or why this critical size should vary from one system to another. The situation is complicated by the internal morphology of the rubber particles themselves.

By using osmium tetroxide to stain the unsaturated rubber it has been shown for many toughened systems that, whereas the smallest particles are homogeneous, many of the larger ones contain sub-inclusions of the glassy matrix [2-6]. These sub-inclusions are surrounded by rubber and the whole particle itself is surrounded by a shell of grafted polymer; this shell leads to good adhesion between the matrix and the particle. For systems with large rubber particles (of size

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about 1 μm), which are prepared by simple mechanical blending so that the graft layer is missing, the poor adhesion at the interface leads to a much lower toughness relative to the grafted system for a given rubber content [7, 8]. This observation indicates the importance of good adhesion at the particle interface if significant toughening is to be achieved.

Attempts to understand the role of the rubber particles and why an optimum size exists have focussed primarily on their ability to initiate crazes and/or shear bands [1, 9–13]. It has been postulated [1] that in HIPS the smallest particles are able to nucleate crazes readily but are not effective at terminating them. Thus, poor termination efficiency is supposed to lead to long crazes which fail at relatively low strains. This hypothesis rests on the assumption that long crazes are weaker than short crazes which, as has recently been pointed out [14], will not be the case, at least for those polymers in which crazes thicken by surface drawing [15]. Growth studies with an optical microscope have shown little indication that crazes are terminated by rubber particles of any size [16] and an alternative explanation of the low contribution to toughness of small particles is necessary. The observation that solid rubber particles in HIPS are less able to accommodate large deformation without voids forming at the craze–rubber interface than particles containing a large number of sub-inclusions [17], suggests that the particle-size effect may be at least partially due to the different internal structure of particles (as a function of size).

However, it is clear that for the case of HIPS the major source of toughening is due to the large number of crazes than can be nucleated at the stress concentrations arising at the rubber particles, and it is this profuse crazing that leads to the observed stress-whitening. The structure of the crazes so generated are no different from that of crazes in unmodified PS [13] but, due to the complex interacting stress fields arising from the high density of rubber particles, the crazes grow along planes which may deviate locally from the nominal plane of maximum principal stress.

Whereas in HIPS crazing is essentially the only form of plastic deformation to occur, ABS may show significant macroscopic necking prior to fracture [1]. The techniques developed by Bucknall and co-worker [1, 18] to distinguish between crazing and shear deformation by separating the

volume changes, ΔV , (due to crazing) and the lateral contractions, $-e_1$, (due to shear deformation) suggest that in ABS significant shear occurs as well as crazing. According to Bucknall and co-worker, crazing becomes important only at relatively high stresses or at high strain rates.

Direct observation of crazing in ABS has been accomplished both by the OsO_4 staining of specimens strained in the bulk and subsequently microtomed prior to observation in the transmission electron microscope (TEM) [10, 19] and by the straining of thin solvent-cast films followed by OsO_4 staining. These studies showed that the rubber particles surrounded by crazes undergo large elongations. A second response of the rubber particles to stress was briefly noted by Ramsteiner [20] where small voids were seen to form inside the rubber particles. Ramsteiner discounted this rubber-particle cavitation as a significant contribution to impact toughness. However, cavitation of small rubber particles in a polymer which more readily deforms by shear offers a mechanism to relieve the hydrostatic tension that tends to build up as inhomogeneous deformation by shear continues, for example, beneath a blunt notch. Removing the plastic constraint by cavitation leads to a larger volume of plastically deformed material and, thus, to a higher impact toughness.

Cavitation of rubber particles in toughened PVC has been more extensively studied [5, 21]. It was shown by TEM that these cavities were the major contributors to stress-whitening, with crazing playing virtually no part. It was further found that the highest toughness was achieved where the grafting level was low to give a “network” structure of rubber particles in the PVC matrix; the uniform suspension of particles obtained by increasing the degree of graft led to less stress-whitening and a lower impact strength. Combining these TEM observations with light-scattering and optical microscopy observations, Haaf *et al.* [21] concluded that the stress-whitening observed in PVC arose from cavities aligned at 55 to 64° to the stress direction, i.e., along the shear bands. They further suggested that this type of shear deformation might not be limited to toughened PVC, and verified [5] that ABS could show a similar cavitation without crazing, casting doubts on the method of volume dilation measurements developed by Bucknall and co-worker [1, 18] as a means of identifying the occurrence of crazing.

The role of the rubber particles in ABS is thus seen to be unclear from the literature. From the work of Bucknall and co-workers [1, 18] and others [11, 19] it would seem that, as in HIPS, the particles act primarily as craze initiators, whereas Ramsteiner [20] and Haaf and co-workers [21, 22] suggest that craze initiation is not important. In the TEM study of thin films of ABS presented here (both stained and unstained), the role of small unoccluded rubber particles and larger particles with glassy sub-inclusion will be assessed. Finally, the behaviour of rubber particles in ABS of different sizes and structures will be compared with that of similar rubber particles in HIPS.

2. Experimental procedure

Two types of non-commercial ABS samples were examined*. The first of these, S ABS, had a rubber (butadiene–diene 55) content of 10.7% in the form of small solid rubber particles of diameter about 0.1 μm . The SAN matrix contained 26 wt% acrylonitrile and had a weight-average molecular weight, \bar{M}_w , of 130000 and a number-average molecular weight, \bar{M}_n , of 52000. The second resin, L/S ABS, was a melt blend of S ABS with a second ABS. It had the same overall rubber content but a bimodal particle distribution with an equal volume of particles with diameters of 0.1 μm (solid rubber) and 1.5 μm (containing sub-inclusions). \bar{M}_w and \bar{M}_n for L/S ABS were 180000 and 69000, respectively, with an acrylonitrile content of 23 wt%.

Specimens were produced by dissolving the resin in methyl ethyl ketone or tetrahydrofuran. To obtain specimens with a lower particle density, solutions were also prepared by mixing the ABS with 90% unmodified SAN ($\bar{M}_w = 216000$, $\bar{M}_n = 102000$ and containing 24 wt% AN) and dissolving the mixture in tetrahydrofuran. Glass slides were drawn from all these solutions to give thin films (about 1.7 μm in thickness) which could be floated off the slide, after drying, on a water bath. The films were then picked up on annealed copper grids which had been precoated with the same solution. Bonding of the films to the grids was achieved by a short exposure to the solvent vapour followed by drying overnight to remove excess vapour.

The grids were then mounted in a strain-frame

and strained in tension in air whilst being observed with an optical microscope, permitting the onset of deformation to be detected. Following straining, grid squares of interest were cut out from the copper grid for observation in a Siemens 102 transmission electron microscope operating at 125 keV. Because the copper grid deforms plastically during deformation, the level of applied strain is maintained even after removal from the strain-frame. Further details of this method of specimen preparation are described by Lauterwasser and Kramer [15].

It has been noted previously that thin films of ductile polymers such as polycarbonate [22], polyphenylene oxide and SAN [23, 24], tend to form plane stress deformation zones, either as a completing process with crazing, as in SAN, or to the exclusion of crazing, as in polycarbonate. The propensity for crazing can be enhanced by physical ageing of the films, by annealing just below the glass transition temperature, T_g . For some of these specimens, such an annealing treatment (1 h at 100° C) was carried out to promote craze formation.

Some specimens were stained by exposing them for 10 min to a 2% solution of OsO_4 , followed by thorough washing. This staining could be performed either before or after straining.

3. Results

3.1. S ABS

When thin films of S ABS are strained, true crazes do not form readily. Fig. 1a shows the typical appearance of the deformation in these specimens. Although a “void–fibril” network is formed, the structure is much coarser than that of typical crazes in SAN, and in some regions the voiding does not occur throughout the entire film thickness. It appears that the high density of small rubber particles forms a continuous path of easy deformation, with fibrillation of the rubber occurring, rather than fibril formation in the SAN and true craze formation.

This interpretation is substantiated by an examination of Fig. 1b, which is of the same type of specimen but OsO_4 -stained following straining. This micrograph shows both that the rubber particles are densely packed (a close-packed regular array of 0.1 μm size particles with a volume-fraction of 10.7% would have 0.09 μm of SAN between nearest-neighbour particles), and that the localized plastic deformation does pass through many of the particles. (Since the particle diameter

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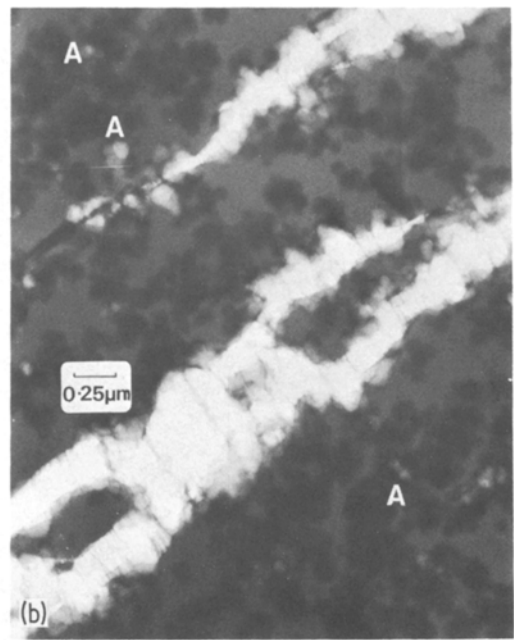
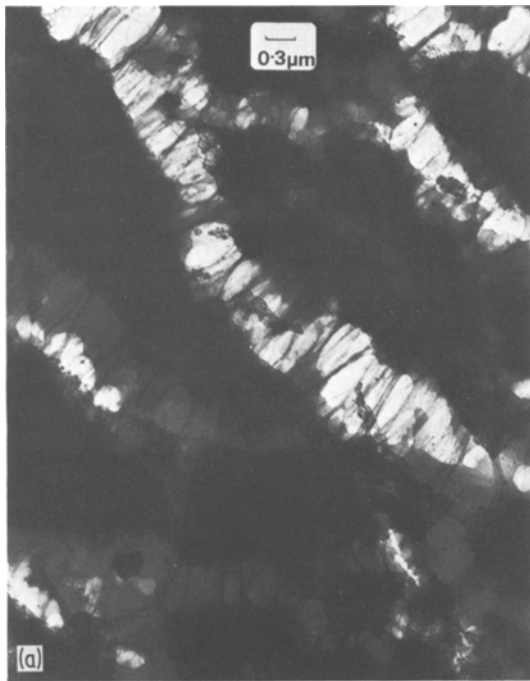


Figure 1 (a) The “void–fibril” structure formed in strained S ABS (unstained) passing along the densely populated lines of rubber particles. (b) A strained and OsO_4 -stained specimen of S ABS. Cavitation of an isolated rubber particle can be seen at A.

of $0.1 \mu\text{m}$ is much smaller than the film thickness, particles may appear to overlap one another in the TEM image, simply due to projection effects.) Clearly, the rubber particles themselves are playing an important role in the deformation. Away from the continuous path of cavitated rubber particles, isolated particles also can be seen to have cavitated (as at Points A in Fig. 1b).

When the S ABS is diluted to 10% with unmodified SAN, such easy paths for continuous deformation are no longer present. In this case the response of the SAN itself assumes more importance, and the role of the rubber particles becomes secondary. In unannealed films, plane-stress deformation zones readily form, engulfing the small rubber particles which become highly elongated with voids forming at their centres (see Fig. 2). These particles clearly do not act as terminators for the zones, and also do not seem very effective at initiating them. The deformation zones grow as readily from imperfections in the film, such as dust particles, as from the rubber particles. Some crazes are also generated and one is visible in Fig. 2. As with the deformation zones, the rubber particles are elongated within the craze, with voids forming at the centre of each, and the

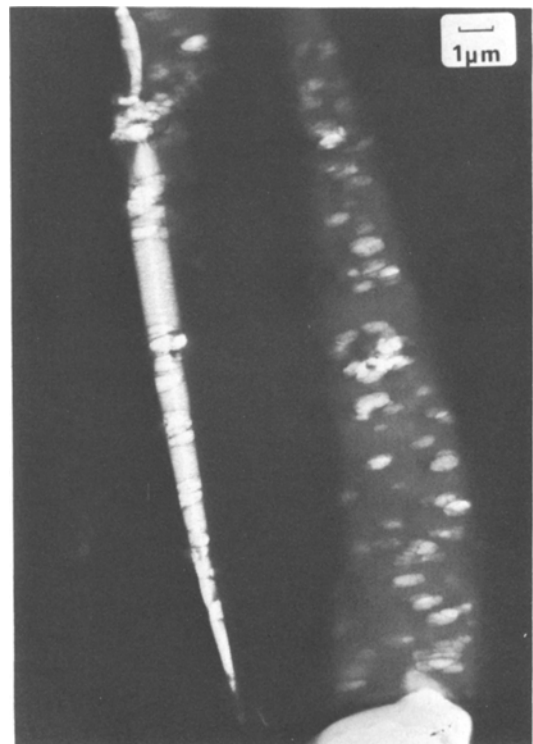


Figure 2 A craze and deformation zone in S ABS diluted with 90% SAN (unstained).

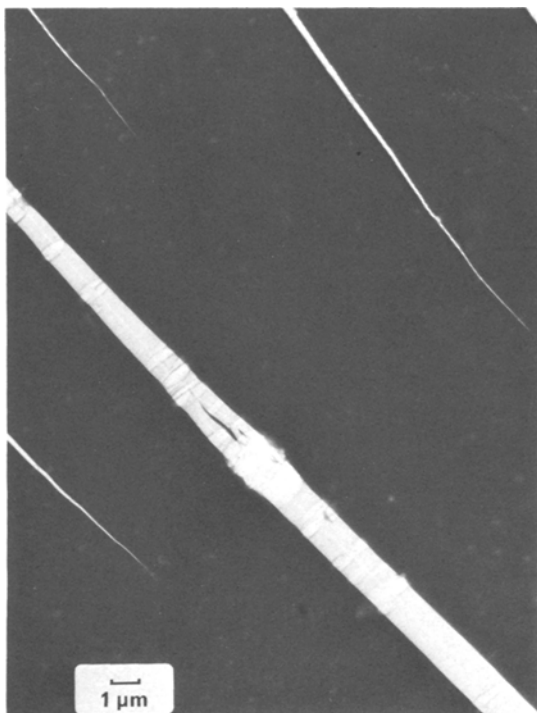


Figure 3 Crazes passing through cavitated rubber particles in diluted S ABS which had been annealed prior to straining for 1 h at 100° C (unstained).

passage of the craze is essentially unimpeded by the particles.

Upon annealing the diluted S ABS specimens for 1 h at 100° C, the formation of deformation zones is suppressed. The appearance of the crazes that form is similar to those observed in unannealed films. In both cases the crazes are essentially identical to those formed in unmodified SAN [23] (see Fig. 3).

3.2. L/S ABS

The second type of ABS, L/S ABS, contained large (1.5 μm size) particles with glassy occlusions as well as the 0.1 μm size solid rubber particles. The two different types of particles are clearly visible in Fig. 4a (a specimen of L/S ABS diluted with SAN and annealed prior to straining) which was strained following crazing. The particle labelled A is an occluded and undeformed rubber particle. The occlusions are relatively large and the volume-fraction of rubber is high compared with the internal morphology of occluded particles in most commercial HIPS (see, for example, [10, 19]). The particles labelled B and B1 are also the large occluded particles, but these have initiated

crazes and have themselves undergone large deformations with the generation of internal voids. Within the apparently undeformed matrix, i.e. well away from the crazes, there is evidence that some of the 0.1 μm particles have cavitated (for example, at C) and where a craze has passed through one of the small particles cavitation has also occurred (for example, the points labelled D). In both these cases the heavy staining around the outer rim of the particle indicates how the rubber has sprung back following cavitation.

Close examination of one of the craze-initiating particles (B1), shows how the particle has deformed as the craze grew (Fig. 4b). Internal voiding and fibrillation of the rubber has occurred, in a fashion somewhat similar to that observed in the undiluted S ABS (see Fig. 1a and b). The occlusion structure of the particle around its pole, where crazing has not occurred, is essentially undisturbed.

4. Discussion

This TEM study shows clearly that for both solid and occluded rubber particles in ABS, internal voiding and cavitation are of prime importance. When only small solid rubber particles are present, crazing is not readily initiated and, thus, shear deformation promoted by rubber particle cavitation is the major toughening mechanism. Since the particles are small, so are the voids generated during the cavitation process.

The larger occluded particles act as more favourable sites for craze initiation, as is clear from the fact that even without prior annealing they readily nucleate crazes in L/S ABS, and deformation zones (comparable to those observed in S ABS) are not seen. The reason why small solid rubber particles fail to nucleate crazes will be discussed in a separate paper [16].

When the small particles cavitate, a spherical void of diameter 0.1 μm is formed. However, when cavitation occurs within the 1.5 μm size particles, as crazing proceeds the size of the voids formed may be much larger. Such a large void, which has formed at the centre of the particle with a major diameter of about 0.7 μm, may be clearly seen in Fig. 4b.

For HIPS [17], the formation of large voids at solid rubber particles leads to crack propagation through the craze. However, in the ABS samples studied here the crazes were rarely seen to fail despite the growth of voids of about 0.7 μm in diameter, as typified by Fig. 4b. The greater

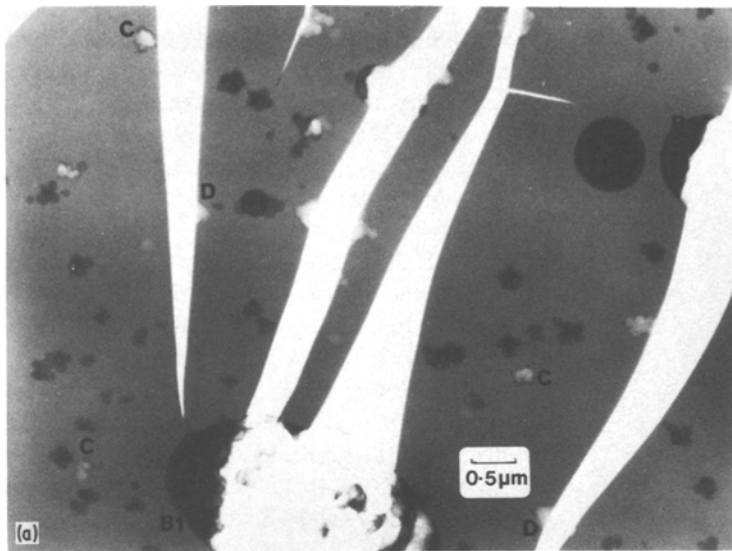
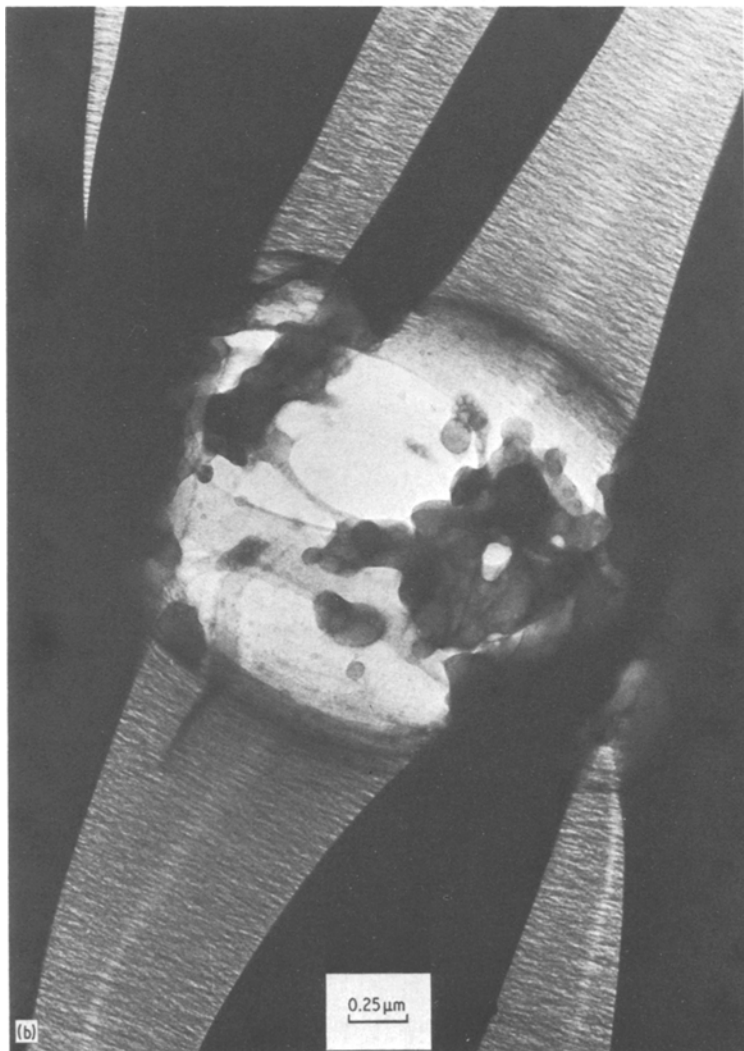


Figure 4 (a) An OsO_4 -stained specimen of L/S ABS, diluted with SAN, which has been annealed for 1 h at 100°C prior to straining. Undeformed occluded particles (A), occluded particles which have initiated crazes (B and B1) and cavitated solid rubber particles within (D), and away from crazes (C) are all visible. (b) Internal voiding occurring within one of the occluded particles (B1 in Fig. 4a).



strength of the craze fibrils in the SAN matrix, relative to that of the PS matrix in HIPS, can be rationalized in terms of the volume-fraction, v_f , of the craze fibrils, or equivalently the extension ratio, λ , of the craze fibrils. (Since crazing occurs at constant polymer volume, $\lambda = v_f^{-1}$.)

Typical values of λ_{craze} have been experimentally determined [23] for P(SAN) and PS. For P(SAN) of the composition used here, the average value of λ_{craze} is 2.7; for PS the average value of λ_{craze} is 3.8. The higher value of λ for PS leads to higher fibril true stresses, σ_t , for a given level of stress at the craze surface, S_c , since

$$\sigma_t = \lambda S_c; \quad (1)$$

consequently, the stress concentration arising ahead of a void of a given diameter will be more damaging for a craze in HIPS than for a craze in ABS.

A second consequence of this difference in λ_{craze} is that the internal morphologies of the occluded particles in ABS systems are less crucial than in HIPS. It has been suggested [17] that the optimum morphology for HIPS of a large number of small occlusions, each surrounded by a thin layer of rubber. The coarser microstructure in the L/S ABS resin is acceptable since larger voids can be tolerated without craze break-down.

The evidence presented here indicates that crazes do not readily grow in ABS containing only small particles. This result is in excellent agreement with the work of Haaf and co-workers [5, 25]. Examining microtomed samples of deformed and stained ABS by TEM, and examining bulk specimens of deformed ABS by light scattering, they demonstrated that when only small (about 70 nm) particles are present most deformation occurs via rubber-particle cavitation and shear. The sheared zones lie along directions close to the normal to the tensile axis and the macroscopic stress-whitening observed is due to rubber-particle cavitation. When larger particles are also present, these may initiate crazes but also show internal voiding. It should be noted that because of simultaneous occurrence of cavitation and crazing, both of which will contribute to a volume change, ΔV , techniques that rely on dilatometry alone cannot yield a true value for the percentage of deformation that occurs by crazing.

Breuer *et al.* [25] also noticed that the contribution due to crazing was reduced as the strain rate of testing was increased. Recent studies [23, 24] have indicated that shear processes in

SAN can occur rapidly, whereas the development of crazing (which will require chain scission and/or slippage via chain disentanglement for fibrillation to occur) takes place over a longer time scale. Consequently, crazing will be suppressed as the strain rate is increased, in accord with the experimental observations.

Under impact conditions, chain scission is likely to become important; in this case one can speculate that crazing will once again be favoured, voiding and fibrillation being aided by the scission processes rather than by viscous disentanglement via reptation of slow strain-rate tests. Thus, the presence of large particles will once again assume importance.

The next question to address is the absence of crazing in S ABS. Recent experiments have shown that small ($\leq 1 \mu\text{m}$) rubber particles in HIPS are unable to nucleate crazes. This inability arises because the size of the region within which a significant stress enhancement occurs around the particle scales with the rubber particle radius and, thus, is highly localized for the smallest particles. To develop the void-fibril network of a craze, the region of high stress around the particle must extend over a distance of several (~ 3) interfibrillar spacings; in HIPS this condition is not met for particles of size less than $1 \mu\text{m}$. Since the craze microstructure in SAN is similar to PS, one may expect a comparable critical size-effect to exist here.

However, even if crazes can be nucleated from other adventitious flaws, the dense packing of the small particles in S ABS prevents craze propagation from occurring. Consideration of the packing of the rubber particles indicates an average rubber particle centre-to-centre spacing of only about $0.19 \mu\text{m}$, which leaves an average of approximately 90 nm of polymer glass between rubber particle surfaces. Recent experiments have demonstrated that the craze-tip advances via the Taylor meniscus instability [26], the tip breaking up into a series of "fingers", with the fibrils forming at the webs between. This mechanism requires a tri-axial stress state and a negative pressure gradient, $d\sigma_h/dx$ ahead of the tip. If the film thickness becomes too small (about 150 nm in the case of PS), the lack of constraint through the film thickness leads to a reduced value of $d\sigma_h/dx$, in turn causing an increase in the wavelength of the instability until it becomes comparable with the film thickness, and the mechanism becomes inoperative [27].

Thus, the absence of crazing in S ABS may also be attributed to the fact that the meniscus instability in the thin glassy membranes between cavitating rubber particles cannot occur, as well as the poorer craze nucleating power of these particles. For the diluted S ABS specimens, where greater distances between particles exist, some crazing does occur, although not as readily as in the L/S ABS and diluted L/S ABS specimens. For a given rubber content, concentrating the rubber in a lower number density of larger rubber particles will increase the average interparticle spacing which will then be sufficiently large to permit crazes to grow; this situation occurs in L/S ABS.

From this study it is clear that the possibility of cavitation of rubber particles in a system where shear deformation may occur, is likely to contribute significantly to toughness. Without cavitation, the local build-up of hydrostatic tension produced by local shear processes cannot be relieved, further shear will be suppressed and fracture encouraged by the hydrostatic tension. The presence of many, closely-packed particles which can cavitate permits even bulk specimens to behave as if the matrix were everywhere under plane stress conditions. For PS, which does not readily shear, this mechanism is not available and voiding of rubber particles can only be damaging.

To optimize toughness of ABS it is clearly desirable to utilize the possibilities of both cavitation and concomitant shear, and crazing. Commercial ABS resins achieve this by incorporating both large and small rubber particles. The small particles are likely to encourage cavitation and shear, but crazing will only be initiated at the larger particles. Both these processes will contribute to toughness.

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