Plastic zone in front of a mode I crack in acrylonitrile–butadiene–styrene polymers

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The shape of the mode I plastic zone observed in the acrylonitrile–butadiene–styrene (ABS) polymeric material is different from that described by the Von Mises or Tresca criterion for yielding in metals. Two distinct, overlapping plastic zones are observed. One has cardioid shape whose through-thickness zone shape is completely different from the dog-bone shape in metals. The other consists of fingers radiating from the crack tip. The cardioid zone is associated with cavitation in the larger rubber particles. The fingers are branching crazes associated with the cavitation inside the small rubber particles. The stress criteria for the formation of these plastic zones are suggested. Also, the way the small rubber particles interact with the crazes to increase the fracture toughness is discussed.

(Keywords: mode I crack; plastic zone; ABS; cavitation; TEM; microstructure; crazing)

INTRODUCTION

The acrylonitrile–butadiene–styrene (ABS) polymer is a composite material in which the rubber particles (polybutadiene) are grafted onto the brittle styrene–acrylonitrile (SAN) matrix to toughen the material. The plastic deformation mechanisms, which are also the toughening mechanisms in ABS, are basically crazing, cavitation and shearing[1]. The study of the plastic zone size and shape as well as its microstructure in ABS not only may help explain how the rubber particles contribute to plastic deformation and fracture toughness, but also may provide important information relating the microscopic mechanism to the macroscopic mechanical properties.

The plastic zone in front of a mode I crack

It is believed that, for metals, yielding takes place by shear. Both the Von Mises and Tresca yield criteria give similar plastic zone shapes in mode I fracture. This dog-bone type of plastic zone shape through the thickness of the specimen has a size at the centre (plane strain) only about 33% of that at the surface (plane stress)[2]. The deformation mechanism in polymeric materials is no longer dominated by the shear mechanism as in metals, though the Von Mises criterion[3] is still used in some cases. Basically, the stress states for crazing and cavitation are different from those of the Von Mises and Tresca criteria. Since a lot of factors[4,5] can affect the plastic deformation mechanism in polymers, such as molecular weight, molecular-weight distribution, entanglement density, degree of crystallization, etc., the criteria of the plastic zone ahead of a crack may vary from case to case. It was reported[6] that in polystyrene the craze distribution around the crack tip seemed to be determined by major and minor principal stresses. The crazes followed the paths defined by minor principal stress trajectories, and the extent of the craze pattern was defined by a maximum principal stress contour. It was also reported[4] that in the thick single edge-notched specimen of semicrystalline high-density polyethylene (HDPE), the plastic zone could be explained by the dog-bone model. In this paper an attempt will be made to develop a suitable stress criterion to describe the plastic zone of mode I fracture in the ABS material.

Crazing mechanism

Crazing is a common mode of plastic deformation in glassy polymers. Crazes are crack-like defects with the two craze surfaces connected by fibrils. Two reviews on various models of crazing mechanisms appeared recently[4,7]. Although the stress states needed for craze formation are still not quite clear, in general the craze nucleation is believed to be closely related to hydrostatic tension σ_h and deviatoric stress (ref. 8). The craze propagation is believed to undergo a Taylor type of instability, which requires an increase of hydrostatic tension in front of the craze tip[9,10]. Argon[11] also suggested that the mechanism of craze growth in polystyrene/polybutadiene copolymers is by stable, interfacial cavitation degradation in a process zone ahead of the craze tip. So far, the mechanism of craze breakdown is less well understood than craze initiation or propagation. In some cases, the slow crack growth occurs along the centre of a craze, but the initiation of failure in crazes tends to occur at the craze–matrix interface in polystyrene. This interface initiation is considered to be a heterogeneous process that occurs at flaws such as dust particles. Overall, the problem of stress state of the failure

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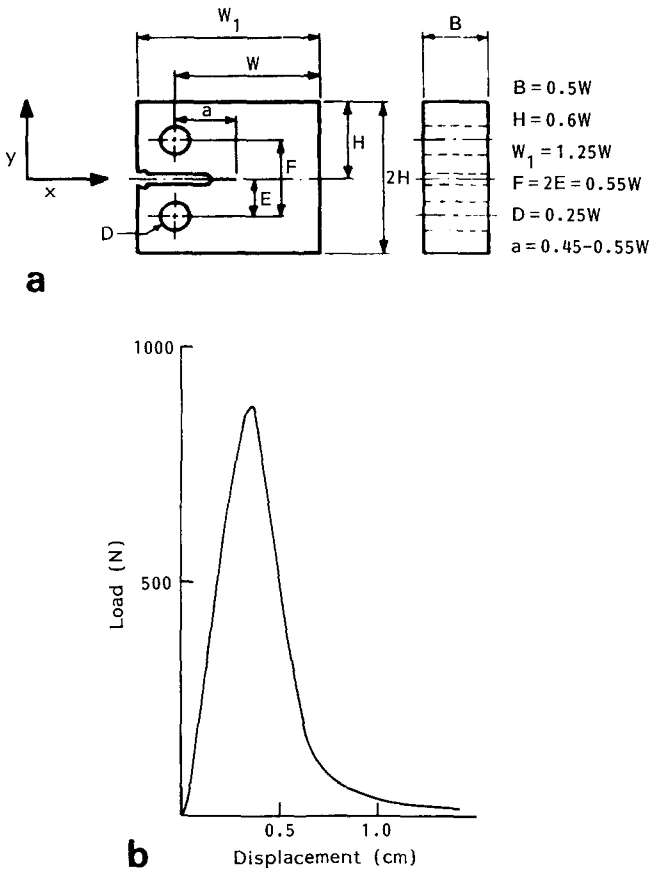

Figure 1 (a) The dimensions of the ASTM Compact Tension (CT) specimen with thickness $B = 1.20$ cm. (b) A typical load–displacement curve of the 17.5% rubber CT sample. The Instron crosshead speed = 1.0 cm min^{-1}

of the craze fibril is not answered yet. Here we present an attempt to study the stress state for the crazing mechanism by examining the microstructure of the plastic zone and to relate that to the stress fields that are responsible for the macroscopic plastic zone shape in ABS.

EXPERIMENT

ABS polymers ($MW = 100\,000$ in SAN copolymers) with 17.5% volume fraction (in which 0.6% is in the form of large particles and 16.9% is in the form of small particles) and 25% volume fraction (0.2% large and 24.8% small) rubber content were supplied by Dow Chemical Company. The sizes of small and large particles are 0.1 and 0.4 μm respectively. The samples were shaped into ASTM Compact Tension specimens with thickness 1.2 cm (B in *Figure 1a*)[12] and the precracks were cut either by a diamond saw (0.5 mm thick) alone or sharpened further by a razor blade. The loading process of the Instron crosshead at 1.0 cm min^{-1} was stopped at a maximum load (see *Figure 1b*) so that the plastic zone ahead of the crack tip could be fully developed. Some plastic zone sections were made by cutting with a diamond saw parallel to the xy plane containing the loading axis to reveal the microscopic features under a light microscope. The 0.3 mm thick sections could be ground to 50 μm when necessary. In order to observe the microstructure under TEM, the whole plastic zone was cut out and stained in 2% osmium tetroxide solution for 48 h before it was microtomed into thin sections about 100 nm parallel to the xy plane. The TEM thin sections were taken from different areas inside the plastic zone.

RESULTS

A typical load–displacement curve of ABS Compact Tension specimen is shown in *Figure 1b*.

Macroscopic plastic zone in ABS

The plastic zone developed before fracture has two distinct parts (*Figure 2*). One is a homogeneous zone that has a cardioid shape and its size is larger inside than at the surface of the specimen (*Figure 3*). The size of the centre zone is about 1.3 times the size of the surface zone. Superimposed on this zone and radiating from the crack

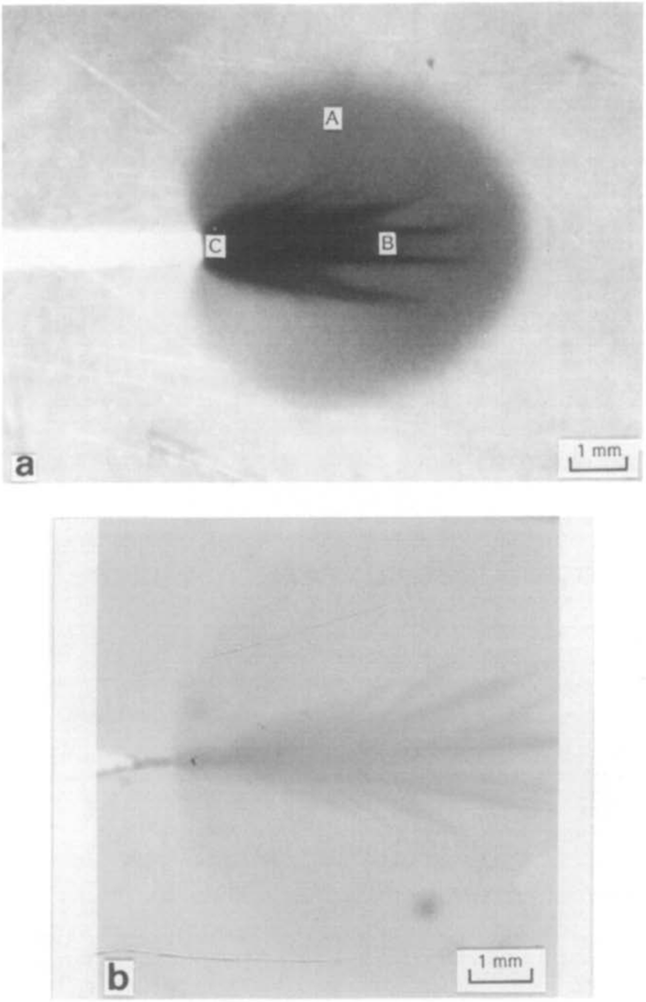

Figure 2 Two distinct plastic zones developed before fracture in ABS: (a) blunt crack; (b) sharp crack

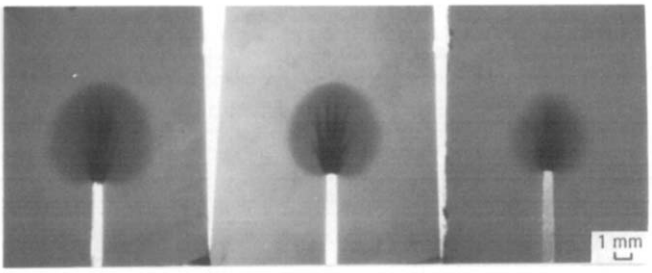

Figure 3 Through-thickness plastic zone. From surface zone (right) to centre zone (left)

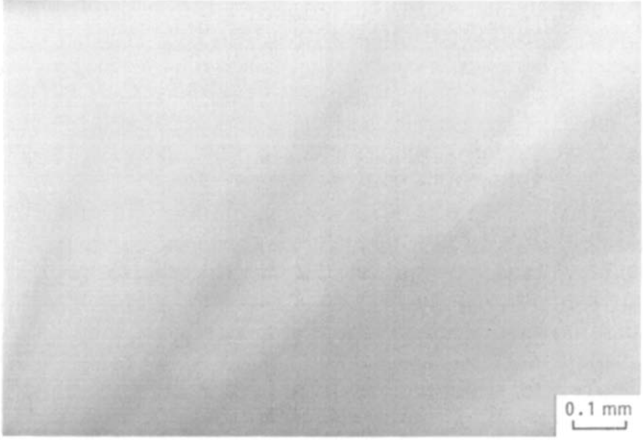

Figure 4 Optical micrograph of internal finger structure

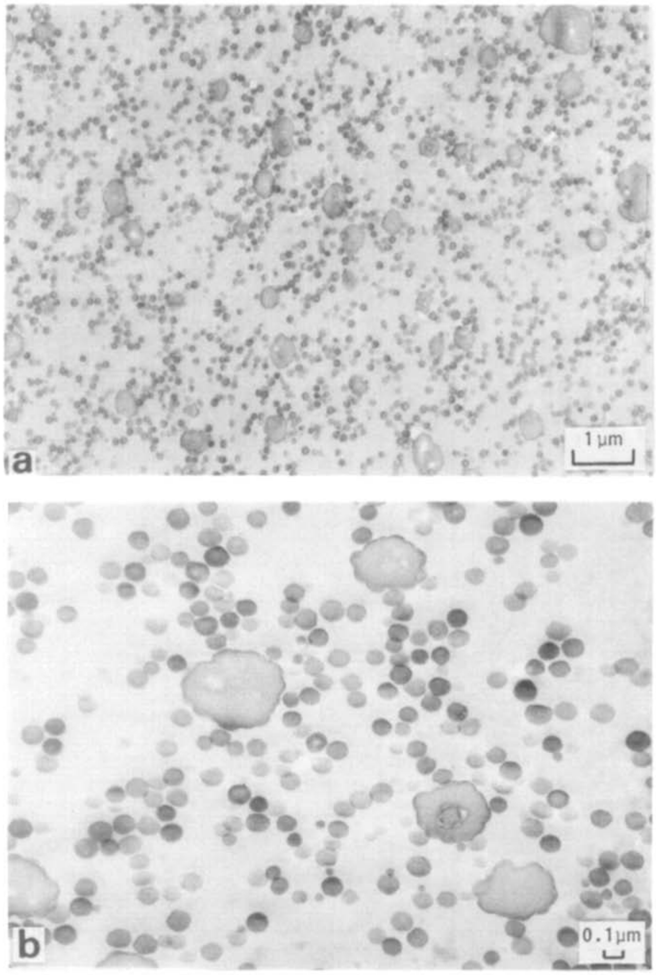

Figure 5 TEM micrographs of cardioid zone (area A in *Figure 2a*); 17.5% rubber

tip are a set of fingers, which are irregular (*Figure 2*). A close look at these fingers under an optical microscope reveals that the fingers consist of numerous fine lines in the general direction of the fingers (*Figure 4*).

Microstructure of the plastic zone in ABS

The TEM micrographs taken from the cardioid zone (area A in *Figure 2a*) show that the deformation in this area is basically cavitation inside the big rubber particles (*Figure 5a*). There are no crazes and no cavitation inside the small rubber particles (*Figure 5b*). The TEM micrographs from the finger zone at some distance away from the crack tip (area B in *Figure 2a*) show that there are crazes between fingers (*Figure 6a*) and that inside the fingers some of the small rubber particles on the crazing path are cavitated (*Figure 6b*). *Figure 6* also shows that the crazing path changes its direction or branches in the matrix and at small rubber particles. The TEM micrograph from the area close to the crack tip inside the finger zone (area C in *Figure 2a*) shows that there are a lot of crazes and severely cavitated small rubber particles (*Figure 7*), but some of the undeformed particles can also be seen.

DISCUSSION

The stress field of macroscopic plastic zone

Figure 8a[13] shows theoretical loci of the hydrostatic tension and its gradient field in front of a mode I crack. By comparing *Figure 2a* with *Figure 8a*, it suggests that the cardioid zone basically follows the contour of a critical hydrostatic tension. The TEM studies support this argument since the deformation within the cardioid zone is merely the cavitation in the larger rubber particles. Also the hydrostatic tension criterion is consistent with the experimental observation in *Figure 3* because the hydrostatic tension is larger at the centre (plane strain) than at the surface of the specimen (plane stress) by a

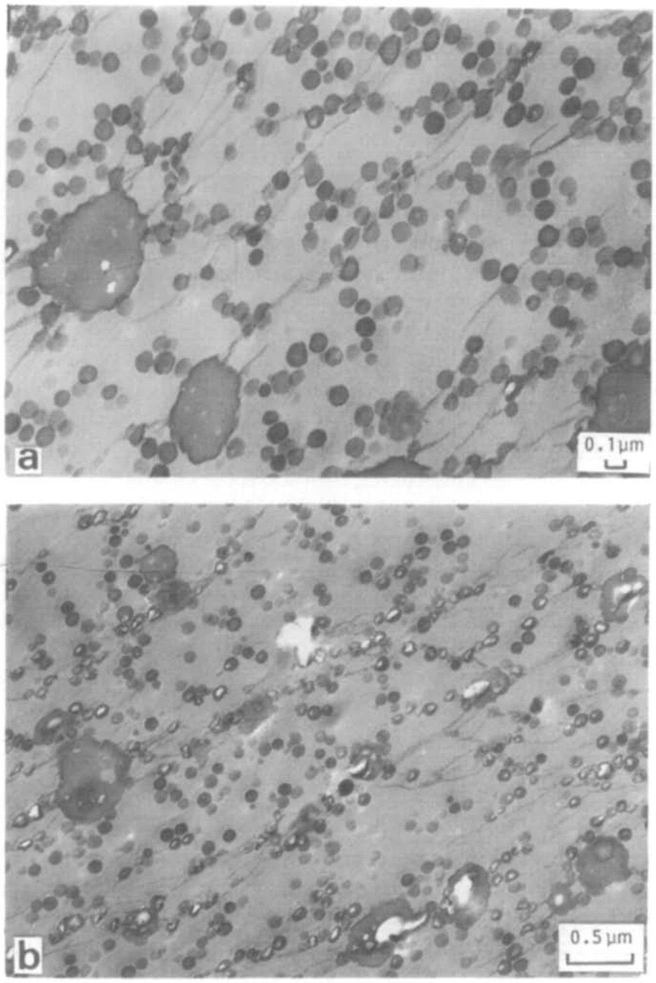

Figure 6 TEM micrographs of finger zone away from crack tip (area B in *Figure 2a*); 17.5% rubber

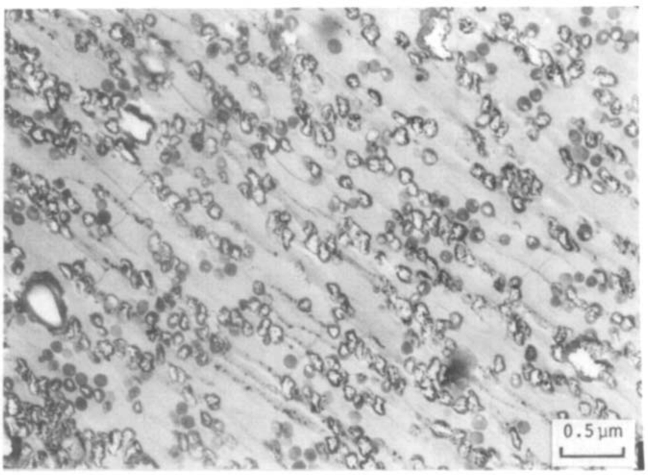

Figure 7 TEM micrograph of finger zone in the crack tip area (area C in *Figure 2a*); 17.5% rubber

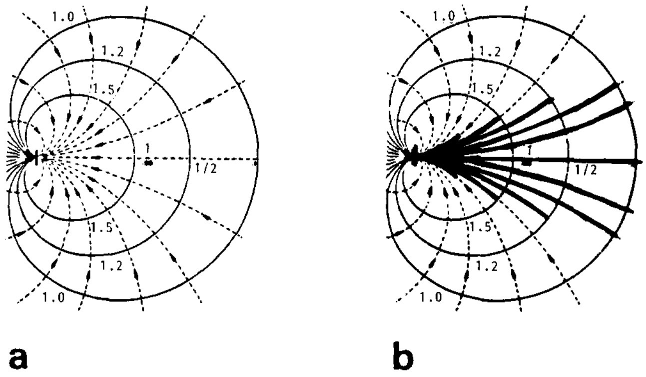

Figure 8 (a) The theoretical hydrostatic tension and its gradient field. (b) The predicted finger zone shape

factor of $(1+\nu)^2$. The Poisson ratio ν of the tested ABS polymers is 0.36, so the calculated factor $(1+\nu)^2$ is 1.85 rather than our experimental value 1.3. The discrepancy may come from the fact that our specimen is not thick enough to endure the plane strain state in the middle of the specimen. According to ASTM size requirement, in order to guarantee the plane strain condition, the specimen thickness should be about 3.0 cm instead of 1.2 cm in our experiment. However, this football-type through-thickness zone shape will result in a higher fracture toughness for a thicker specimen than for a thinner one. This is borne out of experiment because it was reported[14] that the fracture toughness of a rubber-modified poly(methyl methacrylate) (PMMA) measured by using double torsion specimens increases linearly with specimen thickness. On the other hand, the samples of brittle PMMA yield consistent fracture toughness values under the same testing conditions, irrespective of specimen thickness.

However, we noticed that the cardioid zone is slightly different from the pure hydrostatic tension contour. A preliminary analysis shows that, besides hydrostatic tension, a small amount of shear stress is needed to determine the exact cardioid zone shape. The details of how much each stress component contributes to the cavitation process will be discussed elsewhere.

The finger zone seems to follow the gradient of the hydrostatic tension field. The TEM pictures give an indication that the fingers (fine lines) are crazes. We believe that the major principal stress is responsible for the fibre extension within the craze. In *Figure 8b* we construct the finger zone shape by letting crazes lie along the gradient of the hydrostatic tension field and cutting them off at a critical angle θ_c, which is defined as the angle between the direction of the gradient field and the direction of major principal stress. The critical angle is $39° \pm 1°$ as estimated from *Figure 2b*. The craze path stops growing if the angle $\theta \leqslant \theta_c$. So the critical angle criterion gives a boundary within which the craze develops along the gradient of the hydrostatic tension field, and outside this boundary the craze cannot grow.

Craze propagation and breakdown

Figure 9 shows the traces of crazing paths in ABS from TEM micrographs. The crazing paths have a tree-like structure. It is obvious that the craze tip advance is unstable. We have demonstrated that the structure of the crazing path is a fractal and that the instability of the craze propagation path is similar to viscous fingering systems[15,16]. The rubber particles act as random obstacles that cause the crazing path to terminate, to branch or to change direction.

The cavitation inside the small rubber particles is closely associated with the crazing paths. From *Figure 6*, in the area of the finger zone (but away from the crack tip) there are many cavitated small particles, which are generally found on the crazing paths. From *Figure 7*, in the area near the crack tip there is a tremendous amount of crazes and cavitation in the small rubber particles. But it is surprising that some of the small particles are not

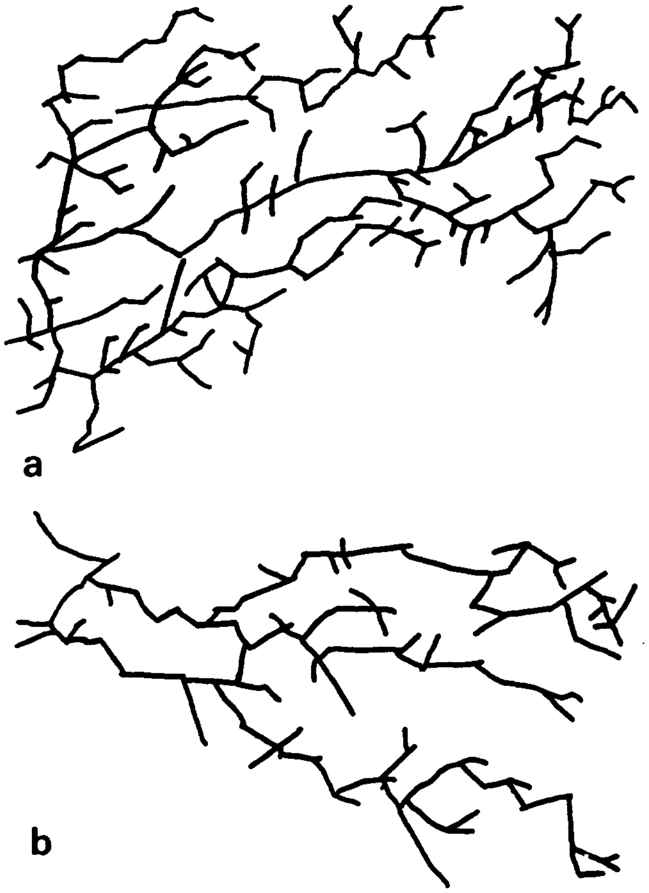

Figure 9 The traced crazing paths from TEM micrographs: (a) 25% rubber; (b) 17.5% rubber

deformed at all in the crack tip area. We suggest that those small rubber particles on the crazing path easily form cavities at high strain. The particles that are not on the crazing paths are less likely to form holes since they are not subject to the stress field of the crazes. So the structure of crazing paths is related to the fracture toughness of the material because of both the energy dissipated into initial craze formation and that needed for the small rubber particle cavitation at a later stage.

CONCLUSIONS

The plastic zone in front of a mode I crack in ABS polymer has two distinct parts. A homogeneous cardioid zone assumes a shape that follows a contour of a critical hydrostatic tension criterion. The irregular finger zone shape is determined by the gradient of the hydrostatic tension field and a critical angle between the direction of the gradient field and the direction of the major principal stress. The cardioid zone encloses the area in which cavitation appears in the larger particles. The finger zone consists of tree-like crazing paths, which are associated with cavitated small rubber particles.

The cavitation and the craze make the major contributions to the fracture toughness of the ABS material. The small rubber particles on the crazing paths cause the craze to propagate diversely through the matrix and cavitate themselves at high strain.

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