Examination of failure in rubber toughened polystyrene

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Multiple craze formation is well-known to be an essential part of the toughening mechanism induced by appropriate incorporation of rubber particles into glassy matrices. Details of the craze structure of stress-whitened high impact polystyrene (HIPS) have been examined using transmission and scanning electron microscopy. In addition to the usual OsO_4 straining procedure for TEM, examination by SEM of surfaces created by fracturing at liquid nitrogen temperatures of previously crazed specimens proved useful. The results are discussed in the context of previous observations on craze structure and the relationship to formation of useful materials.

(Keywords: rubber; toughening; high impact polystyrene; crazing; electron microscopy)

INTRODUCTION

Electron microscopy has been a powerful tool for studying the nature of the rubber phase in high impact polystyrene (HIPS) and in other rubber toughened plastics. The use of electron microscopy requires the presence of contrast between the phases in a heterophase polymer such as HIPS. Osmium tetroxide staining is useful for making rubber particles visible and showing their internal morphology, and this staining also makes the crazes visible in a deformed sample[1-3]. A number of publications have shown that the crazes are associated with the rubber particles[1,4,5]. It was soon recognized that the extended crazes were not represented by such photomicrographs, because only the relaxed residual strain of the craze would remain visible on the removal of the load in a straining experiment. Accordingly, Kambour[6] used impregnation with a eutectic sulphur compound for fixing extended crazes. The subsequent sublimation of this compound permitted a microscopic examination of the fine structure of crazes. In 1976 Beahan, Thomas and Bevis showed extended crazes connecting rubber particles in cast films of HIPS by transmission electron microscopy (TEM)[7]. Recently, Kramer *et al.*[8,9] also used solvent cast thin sections of HIPS effectively in order to study the micromechanics of crazing by TEM. Michler[10,11] extended ultrathin sections of HIPS directly in a high energy transmission electron microscope for the study of craze micromechanics. Donald and Kramer[8] diluted the HIPS materials with PS so as to examine the deformation of individual rubber particles and their interaction with the matrix. Earlier, Schmitt[12] had studied PS extended HIPS by light microscopy to observe the stress whitening and particle separation from the matrix. Such techniques, however, have some limitations because of the absence of the interaction of the stress fields around the particles and crazes in the bulk of the material. This is particularly important in the study of polymers which contain more than the minimum critical volume fraction of the rubber phase for toughness.

The purpose of this paper is to report on a simple qualitative method for examining extended crazes in HIPS. Based on this method, it is also possible to examine damage caused to the rubber particle by extending the crazes short of failure. Another method is demonstrated for examining fracture surfaces, generated at liquid nitrogen temperature, of previously highly crazed and damaged bulk polymers using scanning electron microscopy (SEM).

A further purpose of this work was to utilize observations from these qualitative experiments to give some insights into the toughening of glassy polystyrene.

BACKGROUND

The early theories of rubber toughening of PS have previously been summarized[13], and more recently by Retting[14]. The early studies led to the proposal by Bucknall and Smith[5] that the rubber toughening of PS is primarily due to the crazing of PS initiated by discrete rubber particles. While the initiation and growth of crazes seem to have received considerable attention in the literature[8,10,15], the termination of crazes and the prevention of crack formation have not received equal consideration. These issues are best studied in an undiluted polymer where a high volume fraction of rubber phase is present and the various interactions are operative.

The need for good adhesion of the rubber particles to the PS matrix and the crosslinking of the rubber phase have been recognized as necessary requirements for a commercially useful HIPS[4]. Tough PS can be obtained also by mechanically blending an appropriate volume fraction of non-grafted polybutadiene rubber[16,17]. Limitations in some other properties of these blends make them less desirable as commercial products.

Schmitt[12] proposed that the separation between the rubber particle and the PS matrix in response to stress may play an important role in HIPS. He suggested that in

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the case of poor interfacial adhesion, separation may occur on cooling the polymer, due to a threefold difference in the coefficients of thermal expansion of the rubber and PS. On cooling, this difference places the rubber particle of HIPS in a triaxial tension. As a consequence, rubber particle separation from the matrix may occur due to applied stress, or the particle may be subject to internal damage in case of inadequate strength, e.g. due to lack of crosslinking. This stress condition of rubber particles was further treated by Beck *et al.*[18] It has also been shown that hole formation in ABS is often observed in stressed samples[19]. This hole formation may involve some dissipation of energy, but the holes may render them less effective for preventing a craze from initiating a catastrophic crack.

While crazing is without doubt the principal mechanism of energy absorption in rubber toughened polystyrene[8,10], other possible mechanisms should continue to be explored.

EXPERIMENTAL

Materials used

Compression moulded specimens of Styron 456 (Dow) were used for the examination of crazing, while injection mouldings of HIPS 825E (Cosden) were used for the examination of fracture surfaces.

Extended craze structure and particle damage

The following method was used to develop extended crazes in HIPS prior to fracture. Moulded samples were first craze-whitened by stress application in an Instron. These specimens were then bent into a 'U' shape, and the two ends were fastened together so that a minimum of deformation recovery of the sample would take place. The specimen was then immediately exposed to a 4% OsO_4 solution in water for staining. After staining for 24 h, the specimens retained their 'U' shape without restraints. Sections were cut using a microtome with a diamond knife and were from 0.06 to 0.1 μm in thickness. Specimens for viewing in the TEM were obtained both perpendicular and parallel to the apparent principal stress (from Instron) near the surface of the most extended portion of the bent specimen. These sections were viewed both by TEM and SEM using standard methods.

Fracture surfaces of highly stress damaged specimens

Craze-whitened specimens were obtained by various means, e.g. from a stress–strain experiment and by manual flexing. These samples were cooled in liquid N_2 for about 1 h followed by fracture in an Izod impact tester. Fracture surfaces were coated by Pd–Au vapour deposition and viewed in a JEOL SEM.

Crazes associated with a crack

An Izod impact tester was used to obtain partial crack propagation, by adjusting the hammer height for a partial break of a notched specimen. The partially cracked specimen (still in one piece) was stained in a 4%OsO_4 solution. The microtoming was carried out to include the crack tip.

RESULTS AND DISCUSSION

Crazes in strained HIPS are known to be numerous and several of the crazes may be associated with a single rubber particle[1,4,15,19]. *Figures 1* and *2* show crazes in a commercial HIPS obtained by the usual technique of OsO_4 staining of stress-whitened section without an attempt to keep crazes in their extended state. *Figure 1* shows crazes in a cross-section of a 1.27 × 0.31 cm compression moulded specimen which was pulled in an Instron at 1.27 cm min^{-1} up to the point of failure. The crazed section was obtained from the centre of the specimen, showing many short crazes and indicating the locus of initiation at the rubber particles. It is obvious that multiple crazes initiated from some particles. Several reasons for the existence of such multiple craze initiations have been suggested in literature. They are: (1) multiple stress concentration areas on particles with 'raspberry surface'[10], (2) stress-field interactions in polymers with a

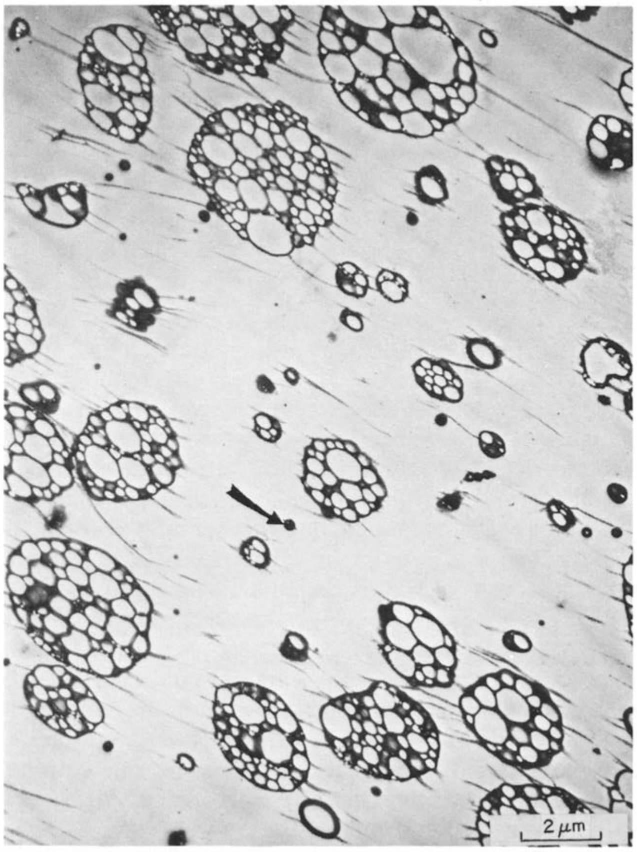

Figure 1 Crazes in the centre of HIPS test bar, pulled to failure at 1.27 cm min^{-1}. Arrow shows craze initiation at a small rubber particle

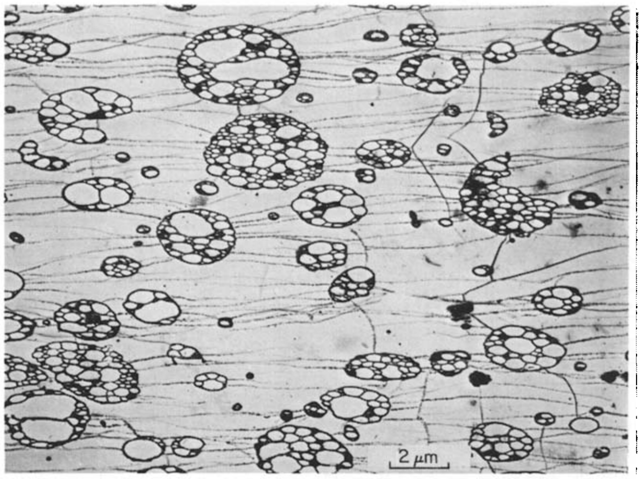

Figure 2 Crazes near the surface (~ 10 μm) of HIPS test bar, pulled to failure at 1.27 cm min^{-1}

high volume fraction of particles[10], and (3) particle separation from the matrix polymer[12,20].

Figure 2 shows crazes from a similar experiment, in a section about 10 μm from the outer surface of the specimen. In this case, an unusually high concentration of crazes is observed with initiation around most of the particles. It is noticed that craze initiation also occurs on particles which are well below 1 μm in diameter. In fact, *Figure 1* has one particle in the left centre of the photomicrograph which is about 0.2 μm and shows a distinct initiation of a craze.

It may be concluded that in commercial HIPS, the complex stress field near the surface of the sample causes a very high concentration of multidirectional crazes. This high concentration of interacting crazes near the surface implies that the crack initiation is delayed because of the energy absorbing property of crazes. Further, the initiation of crazes does not seem to be limited to some critical size of particles in this polymer. Serial sectioning of crazed areas was carried out in an attempt to explore the origin of crazes at maximum stress concentration of the equator of rubber particles and the location of the termination of crazes. The best result from these experiments is shown in *Figure 3*. It is apparent that crazes were made visible only to a limited extent in the plane of the section, and that the craze growth path is not easily visualized in three-dimensions. It is, however, observed that closely neighbouring particles do share a common craze, indicating that termination at a rubber particle has taken place. Kramer[21] has suggested that there is no mechanism for craze termination by rubber particles, in which case crazes in a polymer with a high volume fraction of the rubber phase must propagate in a tortuous path. It is likely, however, that significant craze stoppage occurs by mutual termination. Mutual termination of crazes may also be noted in *Figure 6*.

The apparent randomness and interactions of crazes are further shown in *Figure 4*, where the crazes of a partially broken notched Izod specimen are shown. It is apparent that an extremely complex stress field has developed, resulting from notching, stress directions and speed. On careful examination of *Figure 4* it is obvious that most of the particles, including the smallest ones, are associated with numerous crazes. Also, the fracture surface contains severed rubber particles and the highest concentration of craze matter. Also it is noted that distortion of rubber particles only occurs with the growth of the crack. It may be concluded that polymers which depend on a crazing mechanism for toughening must develop a high volume fraction of craze matter in a stressed region[22]. In fact, the inability to form such a high concentration of crazes by voids or glass beads in a brittle matrix is one of the reasons for their lack of toughness. Of course, the absence of the contribution of the rubber phase in terminating crazes may be another reason for the brittleness of foams and glass bead reinforced PS.

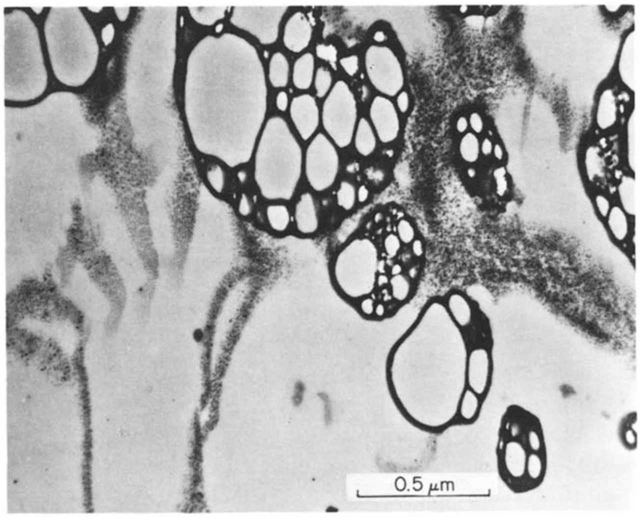

Figure 3 Serially sectioned pre-crazed sample used in *Figure 2* HIPS showing craze planes

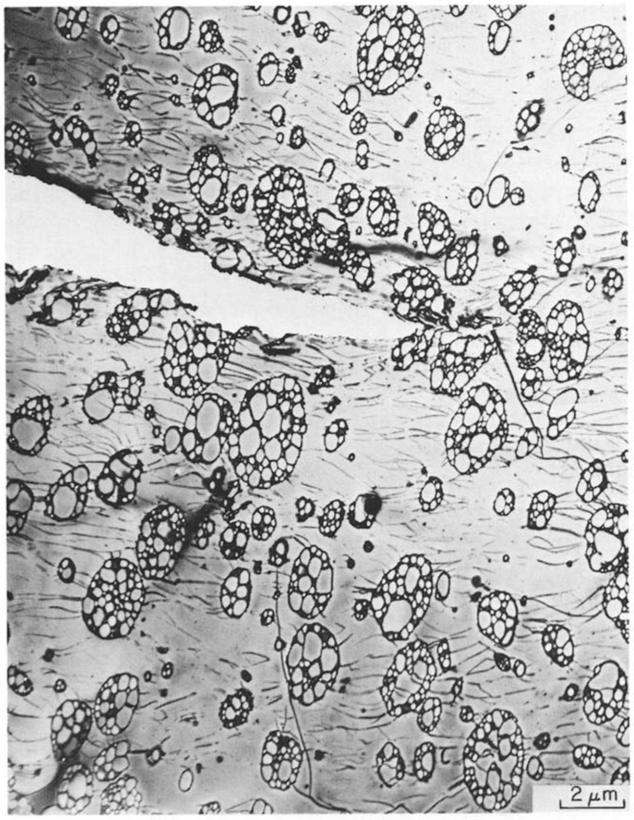

Figure 4 Crack tip of a partially broken Izod specimen of HIPS

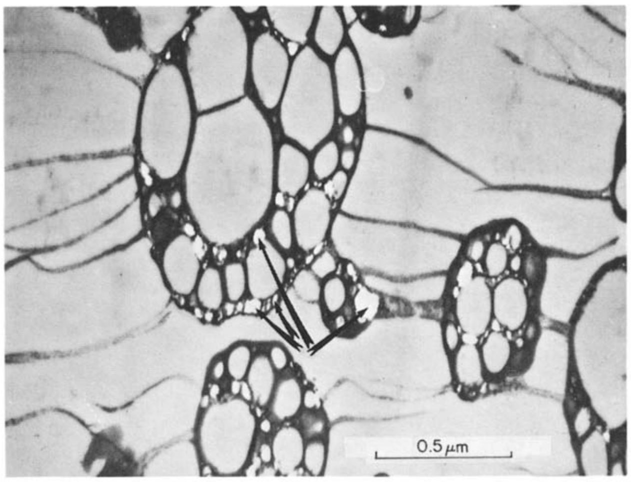

Figure 5 Failure in rubber membranes of the particle. Craze damaged HIPS specimen was OsO_4 stained in a 'U' shape

Figure 5 gives the result of an attempt to show extended crazes from the examination of the 'U'-shaped craze damaged specimen. It is observed that the craze widths are much smaller than expected, particularly in comparison to stretched films made by solvent casting[7,8]. The relatively small particles of less than 1 μm show multiple crazes per particle as previously discussed. Also, it may be observed that the particles of 0.1–0.2 μm in diameter may participate in craze initiation and termination for specimens extended nearly to failure. Another significant feature shown, is failure within the rubber particle membranes. Holes are formed without penetration into the PS phase of the matrix or within the rubber particle. Within these holes some drawn rubber filaments may be seen but they are much larger in diameter than the craze fibrils of PS. Some crazing within the PS occlusions may be observed (see also *Figure 4*). Such failure within rubber membranes was also shown by Kramer. It may be suggested that the stability of extended crazes is apparently enhanced by the graft material as part of the craze–rubber particle interface. Also, it is noted that a small particle has developed a void between the particle and the craze. One may speculate that the ultimate failure path involving rubber particles may be determined by the hole-filled membranes of rubber either along the surface membrane of the particle or through a more tortuous path through the particle. Also the lack of significant elongation or distortion of particles in a fracture can be seen.

Figure 6 shows a more highly damaged craze structure by this technique. Both incipient craze and failure within the rubber membranes are apparent. From this photomicrograph the possibility of craze termination by combination by be visualized. Also, it may be speculated that for high rubber phase volume fractions, combination may be the predominant mechanism of craze termination. *Figure 7* shows a SEM photomicrograph of another highly extended craze structure, obtained from the 'U'-shaped specimen. The fibrils of the crazes seem to have been eliminated to a large extent, either during stressing, in the process of sample preparation or during microscopy. However, the damage to the rubber particles, as well as the high concentration of crazes, are clearly noticed and are consistent with previously shown photomicrographs. This view also indicates the possibility of craze stoppage by combination.

The craze structure of HIPS which has been previously stress-whitened can also be revealed by SEM examination of subsequently created fracture surfaces as seen in *Figure 8*. For comparison purposes, *Figure 8a* shows a fracture surface obtained at room temperature in an Izod impact tester for a HIPS specimen which had not been previously strained, while *Figure 8b* shows a featureless brittle fracture surface obtained in a similar manner except that the sample was cooled to liquid N_2 temperature prior to breaking. *Figures 8c* and *8d* were obtained for specimens which had been crazed at room temperatures prior to creating the fracture surfaces by breaking them at liquid N_2 temperature using an Izod impact tester. The material shown in *Figure 8c* was crazed by 5% extension in an Instron while that in *Figure 8d* was, in addition, further damaged by multiple bending of the stress-whitened material. In *Figure 8c* several rubber particles are visible as well as an extensive amount of craze matter in the matrix. Some deviation from an expected relatively planar surface is also noted. Also, it appears that the severed rubber particles show separation from the matrix. This separation was shown in large particles by Schmitt[12] in his early work on the toughening mechanisms of PS. *Figure 8d* shows this separation much more clearly, indicating that this contribution to the failure mechanism is, indeed, possible for commercial HIPS. If this phase separation occurs early in the deformation process, a new population of crazes may be initiated in the region between the equator and the pole (45°)[20]. The significance of this contribution to the craze initiation or further energy absorption remains to be studied in the future. Finally, the fracture surface in *Figure 8d* seems to be consistent with the multidirectionality of crazes shown previously.

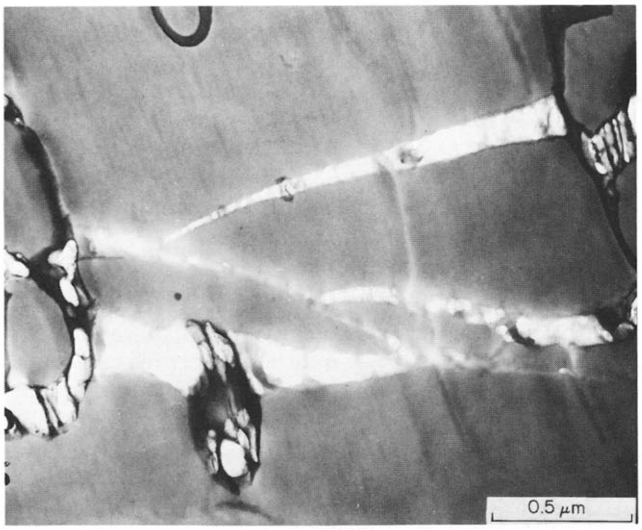

Figure 6 Highly extended crazes and holes in the rubber membranes of the particle: OsO_4 stained in a 'U' shape

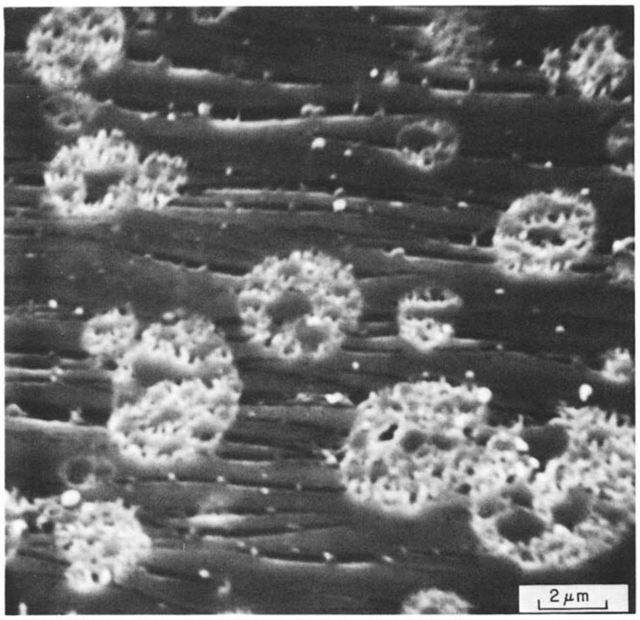

Figure 7 SEM photomicrograph of a highly damaged HIPS: OsO_4 stained in a 'U' shape

CONCLUSIONS

Two methods for the examination of crazed HIPS have been outlined. One method involves the examination of extended crazes and partially failed rubber particles by TEM and SEM. The other uses an SEM method for examining fracture surfaces of previously craze damaged specimens broken at liquid nitrogen temperatures. The results from the use of these methods indicate that (1) a high concentration of crazes exists prior to failure of HIPS, many of these crazes eminate from single particles; (2) the direction of many crazes deviates from the expected

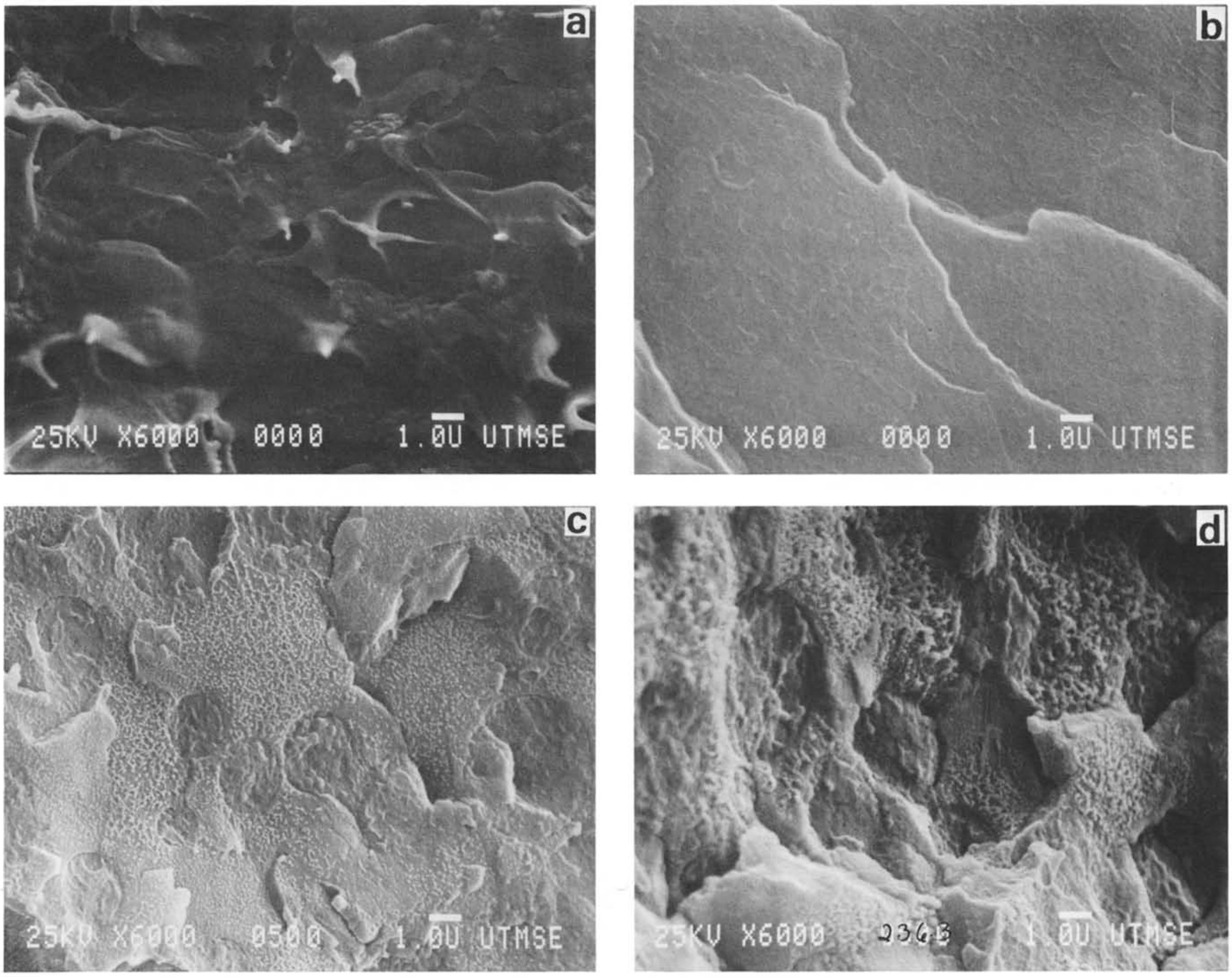

Figure 8 SEM photomicrographs of HIPS fracture surfaces. (a) Fractured in an Izod tester at room temperature. (b) Fractured in an Izod tester at liquid nitrogen temperature. (c) Previously extended 5% specimen fractured at liquid nitrogen temperature. (d) Extended 5% specimen, followed by bending of the stress-whitened portion to further promote structural damage. Fractured at liquid nitrogen temperature

direction, perpendicular to the principal stress; (3) separation of particles from the matrix polymer can be observed on fracture surfaces of previously craze damaged specimens; (4) the presence of a high volume fraction of rubber particles appears to be of importance in establishing an environment for the development of a high concentration of crazes and it may be crucial for the prevention of an early initiation of cracks leading to fracture.

The importance of the presence of a high volume fraction of the rubber particle phase in HIPS should be emphasized for future studies on toughening of glassy polymers. It is well recognized that below a critical rubber volume concentration, the polymer remains quite brittle, particularly when tested at low temperatures[16,17]. It is also known that prestressing the specimens of ABS[23] below the craze-initiation stress levels gives rise to significant embrittlement and often ultimate failure in the absence of stress-whitening. Also, it is the experience of the authors that failure in some commercial mouldings of HIPS often occurs with no stress-whitening in the area of failure. Accordingly, it seems particularly important to continue to devise methods for the study of failure in rubber toughened plastics. Use of undiluted bulk specimens, indicates that the high volume fraction of the rubber phase is responsible for the apparently complex stress fields and craze interactions, leading to the desired tough polymers.

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