JOURNAL OF MATERIALS SCIENCE 11 (1976) 1207–1214

Some observations on the micromorphology of deformed ABS and HIPS rubber-modified materials

P. BEAHAN, A. THOMAS, M. BEVIS

Department of Metallurgy and Materials Science, The University of Liverpool, UK

The distribution and micromorphology of crazes in deformed bulk and solvent cast thin films of ABS and HIPS have been characterized. A good correlation was shown to exist between the deformation structure in the two types of specimen. Some characteristic features of the micromorphology of the deformed matrix and rubber inclusions which are apparent in the permanently strained cast films are described, and some simple electron microscope studies with strained cast films which could lead to further insight of toughening mechanisms in rubber-modified polymers are proposed.

1. Introduction

The plastics ABS and HIPS are good examples of ways in which the mechanical properties of solids can be modified through a change in microstructure, in this case by the incorporation of elastomeric inclusions in the relatively brittle styrene-acrylonitrile copolymer (SAN) and polystyrene (PS) matrix materials respectively [1, 2]. The microstructures of deformed and undeformed ABS and HIPS materials have in the past been identified primarily by the transmission electron microscopy of thin sections of bulk specimens prepared by ultramicrotomy. The investigations by Matsuo and Kato and co-workers [1–6] are particularly notable ones and in these cases the osmium tetroxide staining technique for the rubber phase [3] was used for aiding the ultramicrotomy and for enhancing contrast in the transmission electron microscope.

The main advantage of a wide range of ABS and HIPS materials over the SAN and PS matrix materials is the improved toughness which results from the incorporation of an elastomeric second phase. The improved toughness characteristics have been attributed to the elastomeric phase acting as rubber bands holding newly formed fracture surfaces together [7] in much the same way as the highly oriented fibres within a craze maintain the integrity of a crazed specimen [8–11].

An alternative energy absorbing mechanism originating from experiments made by Bucknall and Smith [12] is based on the preferred nucleation and growth of crazes in the vicinity of the inclusions which act as stress concentrations. This basic feature of the latter model is now widely accepted. Explanations of how the size distribution of the inclusions affects the crazing characteristics and hence the tensile toughness of ABS materials have only recently been proposed by Grancio [13] following tensile experiments on a range of model ABS systems. Very little attention has, however, been paid to identifying the role of elastomeric inclusions in the deformation process other than their role as stress concentrations.

The objective of the research which led to the results presented in this paper was to evaluate techniques of microscopy which would allow more definite information to be gained about the mechanisms of plastic deformation in rubber modified polymers. The experimental techniques which were used to investigate the deformation structures in both thin films and bulk compression moulded specimens of ABS and HIPS materials are described in Section 2. The results of the first broad survey of the similarity between structures formed in bulk and thin films after straining are described. The results obtained give some insight into the way more detailed investigations based on thin film studies could be used to assist the development of the understanding of deformation processes in rubber modified polymers.

2. Experimental

Thin films of ABS and HIPS for electron microscopy studies were prepared by solvent casting and by ultramicrotomy of stained bulk specimens. The HIPS was a general purpose grade containing approximately 7% rubber, and the ABS was a medium impact grade containing 14% rubber.

The solvent-cast films were simply prepared by casting a 2% solution of the polymers in ethyl acetate onto electron microscope grids which were placed on clean glass slides. The 3 mm diameter grids which contained the cast thin films were floated off the glass slides by immersion in de-ionized water, and were then strained in a microtensile jig. The plastic deformation of the copper grids ensured that the applied strain on the polymer film was maintained during staining and during electron microscopy studies. The films were stained by immersion in a 1% solution of osmic acid for 3h.

Small blocks of the strained bulk materials were first trimmed and faced with an ultramicrotome. The faces of the blocks were taken from within 1 mm of the fracture surface and, therefore, represented volumes of the specimen which had undergone large strains prior to ultramicrotomy. After facing the blocks of bulk material were immersed in a 1% solution of osmic acid for a minimum of 3 weeks to ensure adequate staining Ultra thin sections of the order 60nm thick were prepared from the stained blocks and then collected on 200 mesh electron microscope grids. The films prepared by solvent casting and ultramicrotomy were examined at 100 kV in a transmission electron microscope.

The experimental procedure based on solvent cast films provided a more straightforward alternative to the methods described by Kambour and co-workers [9. 10] for examining deformation morphologies in rubber-modified polymers. The main disadvantage of the latter method was the possibility of distortion of the true deformation microstructure arising from the high temperature sulphur-iodide eutectic craze filling technique. The main disadvantages of the solvent-cast thin film technique is associated with the uncertainty of the equivalence of the deformation processes in thin films and bulk specimens, arising from the difference in triaxial stress distribution, the dispersion of additives and the relative importance of specimen surface morphology in bulk and thin film specimens.

3. Experimental results and discussion

Thin sections of ABS and HIPS materials were prepared from compression moulded specimens using the techniques described in Section 2. Representative transmission electron micrographs of the micromorphology of the ABS and HIPS are shown in Fig. 1 and 2 respectively. The widely reported two phase structure of the elastomeric inclusions

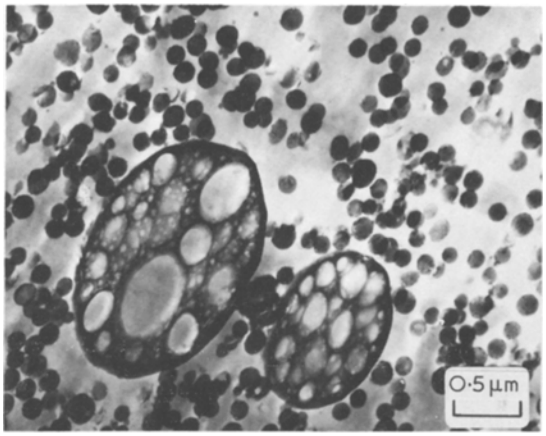


Figure 1 Transmission electron micrograph (TEM) of a stained thin section prepared by ultramicrotomy of an undeformed bulk specimen of ABS.

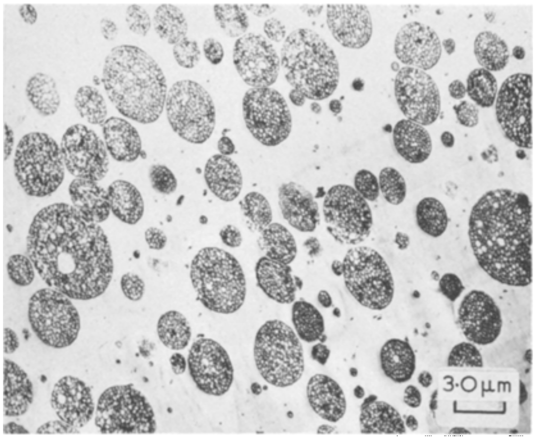


Figure 2 TEM of a stained thin section prepared by ultramicrotomy of an undeformed bulk specimen of HIPS.

are apparent in both sets of electron micrographs, the major difference being the diameters of the inclusions and the bimodal distribution in the ABS material used in the investigation. The diameters of these inclusions were approximately 0.1 and 0.5 to 1.5 μm for ABS and 0.5 to 5 μm for HIPS.

The solvent-cast films of ABS and HIPS were stained with osmium tetroxide prior to examination in the transmission electron microscope. Some typical examples of transmission electron micrographs obtained from ABS and HIPS are shown in Figs. 3 and 4. The main difference between these figures and those shown in Figs 1 and 2 is that the inclusions have not been sectioned. The internal cellular structure within the large inclusions in both ABS and HIPS is apparent and the densities and diameters of the inclusions are similar to those observed in the bulk specimens. The advantages of using thin films for studying the mechanisms of the growth and failure of crazes in amorphous polymers have been demonstrated in previous studies [11]. An important advantage of the thin film technique is that it allows the examination of specimens after deformation with no further preparation other than staining, as the deformed copper grid maintains the strain on the specimen throughout the electron microscope examination. These features are particularly important in films containing elastomeric inclusions because the relaxation of the rubber and associated crazes after deformation is minimized. The role of the inclusions in the toughening mechanisms can, therefore, be identified more readily. In the case of sections of bulk material prepared by ultramicrotomy a substantial amount of relaxation is unavoidable.

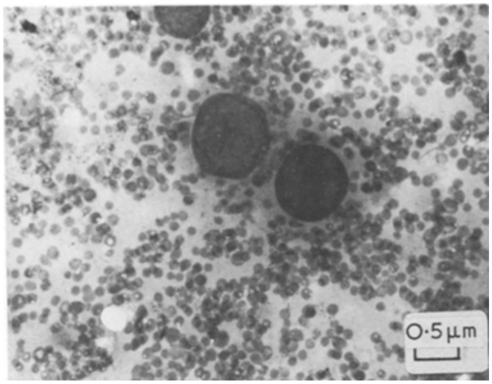


Figure 3 TEM of a stained solvent-cast film of ABS.

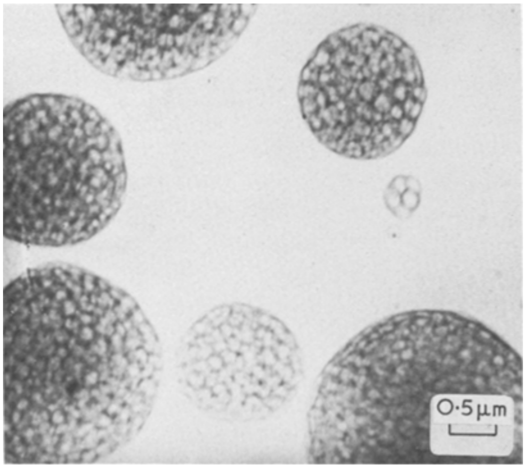


Figure 4 TEM of a stained solvent-cast film of HIPS.

Specimen size can affect the characteristic features of deformation processes and it is for this reason that the deformation morphology of both thin films and bulk specimens were studied. Earlier investigations [11] have shown that there is a good correlation between the micromorphology of crazes formed in bulk specimens and thin films of amorphous polystyrene, thus vindicating the use of the same techniques for the study of rubber-modified polymers which exhibit profuse crazing as the primary mode of plastic deformation.

3.1. Bulk studies

The thin sections of ABS and HIPS prepared by ultramicrotomy from stress-whitened regions adjacent to the fracture surface of tensile specimens were examined with a transmission electron microscope. Figs. 5 and 6 were typical of the electron micrographs of "stress whitened" ABS and HIPS respectively. The tensile axis (T.A.) used in the tensile testing of the bulk specimens and the cutting direction (C.D.) used in the ultramicrotomy of the sections are indicated on the micrographs. A considerable effort was made to minimize distortion in the specimens caused by the ultramicrotomy technique. To avoid any ambiguity as to the origin of the observed crazes the direction of cutting was always 30° to 60° away from the trace defined by the intersection of the plane normal to the tensile axis and the cutting surface.

The craze traces for both ABS and HIPS were predominantly normal to T.A. and, therefore, normal to the applied tensile stress axis. In the vicinity of the non-equatorial surfaces of the

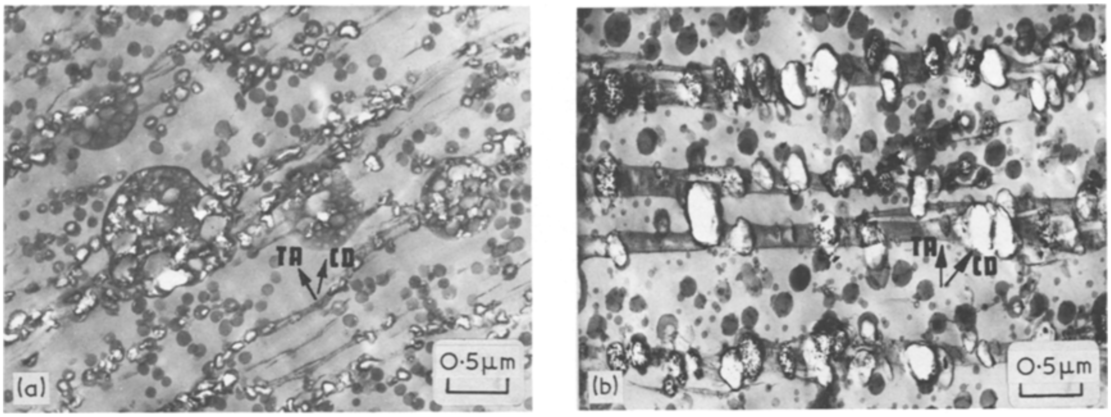


Figure 5 (a) TEM of thin film prepared by ultramicrotomy of bulk specimen of ABS after deformation and subsequent staining is osmic acid. T.A. and C. D. represent the tensile axis and the cutting direction respectively. (b) As (a), but for a different grade of ABS and a section prepared from a region of the specimen which had undergone large strains.

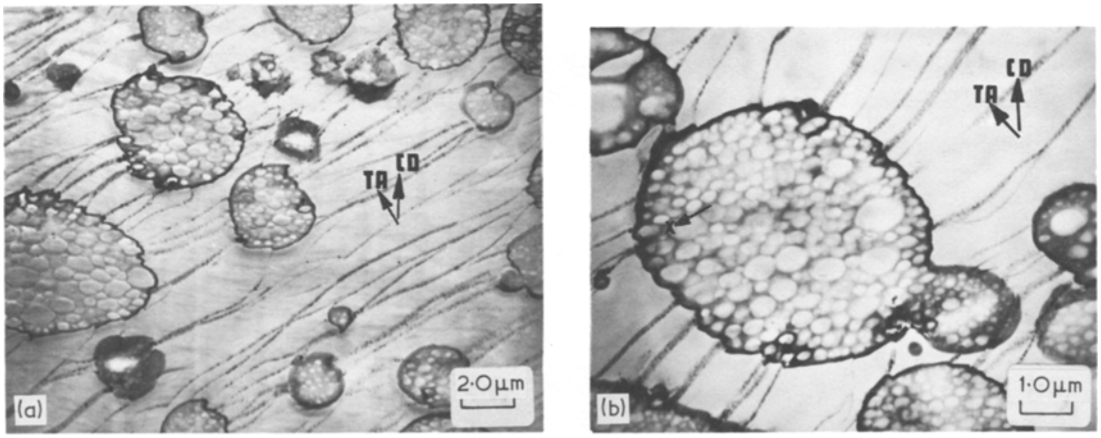


Figure 6 (a) and (b) TEMs of thin films of HIPS prepared by ultramicrotomy of bulk specimens after deformation and staining.

large inclusions the crazes were curvilinear. In these regions there is a substantial modification of the orientations of the minor principal trajectories away from an orientation normal to the applied tensile stress axis. The resultant distribution of crazes is consistent with the observation of the shapes of crazes observed in unmodified amorphous thermoplastics in the vicinity of a stress bias, where crazes have been shown to grow along the minor principal stress trajectories [14]. The effect described above is more apparent in HIPS and this represents one of the main differences between the deformation morphology of HIPS and ABS sections prepared by ultramicrotomy from bulk specimens after straining. In the most highly strained regions of a HIPS specimen the crazes appear to emanate from the inclusions at roughly equal intervals over the whole circumference, including the poles. The crazes in the ABS emanate predominantly from the equatorial regions of the inclusions and are, therefore, planar in shape.

The substantial contraction of the bulk specimens which occurs after fracture is reflected in the formation of notches at matrix-inclusion interfaces. This effect was attributed to the contraction of the elastomeric inclusions in the cross-sections defined by the thick crazes which form in the vicinity of the fracture surface prior to catastrophic failure. This effect was more pronounced in the thin sections cut from regions near to the fracture surface. "Stress whitening" was most pronounced in such regions and it is reasonable to assume that the maximum thickness of the crazes formed is also greater than those formed elsewhere. The bands of dark contrast which were apparent within the inclusions at positions where matrix crazes intercept them represent regions of preferential staining. This effect could be indicative of substantial drawing and probably cavitation within the inclusion. This hypothesis was verified by the results of cast thin film studies which are described below.

The small inclusions which lie in the craze bands in the ABS sections can exhibit a different morphology from those which lie outside as illustrated in Fig. 6. The morphology of the rubber which is contained within a craze band in both large and small inclusions exhibited the same morphology. This observation indicated that the cutting conditions used in ultramicrotomy gave rise to a morphology which was sensitive to the differences in the structure of the inclusions lying inside and outside of craze bands. The difference in craze morphology will be shown to correlate well with the very clear difference in the morphology of the rubber inclusions which lie inside and outside of the craze bands formed by straining cast thin films.

The thickness of the crazes observed in the sections prepared by ultramicrotomy from regions near to the fracture surface were much less than the thickness of crazes formed in bulk specimens of polystyrene. This difference is due primarily to the contraction of the crazes after ultramicrotomy, the reason used to explain the notches in the inclusion surface at points of craze-inclusion intersections. The thickness of crazes formed in bulk polystyrene is believed to be predominantly in the range 1 to 3 μm [15] as determined from measurement of fracture surface features in craze controlled fracture.

3.2. Thin film studies

Solvent cast films of ABS and HIPS which had been strained to produce crazing were examined in the transmission electron microscope. The cast films had undergone large strains in the range of 20 to 100% which could be considered as a reasonable simulation of local strains experienced by regions of the bulk specimens from which ultramicrotomed films were prepared, that is, regions near to the fracture surface. Figs. 7 and 8 are typical examples of the resultant deformation structures in cast films of ABS and HIPS respectively. A comparison of Fig. 7 with Figs. 5 and 6 shows that the craze distributions are broadly similar in the films prepared by solvent casting and the ultramicrotomy of bulk specimens. This result indicates that it is not unreasonable to use cast thin film studies as a means of investigating the deformation morphology of rubber-modified polymers, provided that it is realized the dimensions and method of preparation of the thin solvent cast films may influence the fine detail of the observed deformation morphologies.

Figs. 5 and 7 show that there can be a significant difference between the morphology of the small rubber inclusions in different parts of a test specimen. The small inclusions within the craze bands have undergone large elongations parallel to the tensile axis, this is illustrated most clearly in Fig. 7 and is shown in the schematic diagram of Fig. 9a. In contrast the small inclusions outside of the craze bands have undergone no measurable elongation parallel to the tensile axis.

The large inclusions in both ABS and HIPS films can undergo substantial elongations, but this is confined primarily to the cross-sections of the

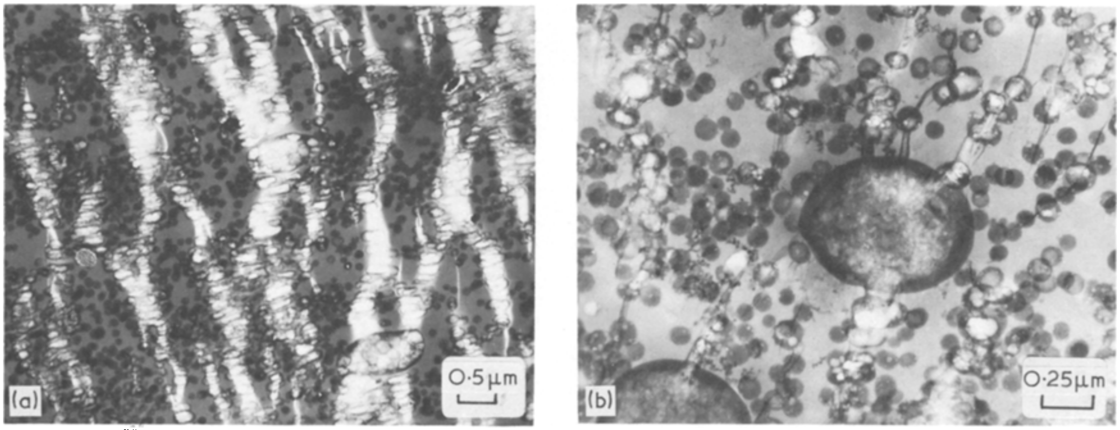


Figure 7 (a) and (b) TEMs of thin solvent-cast films of ABS embedded in electron microscope grids after small and large strains respectively and subsequent staining.

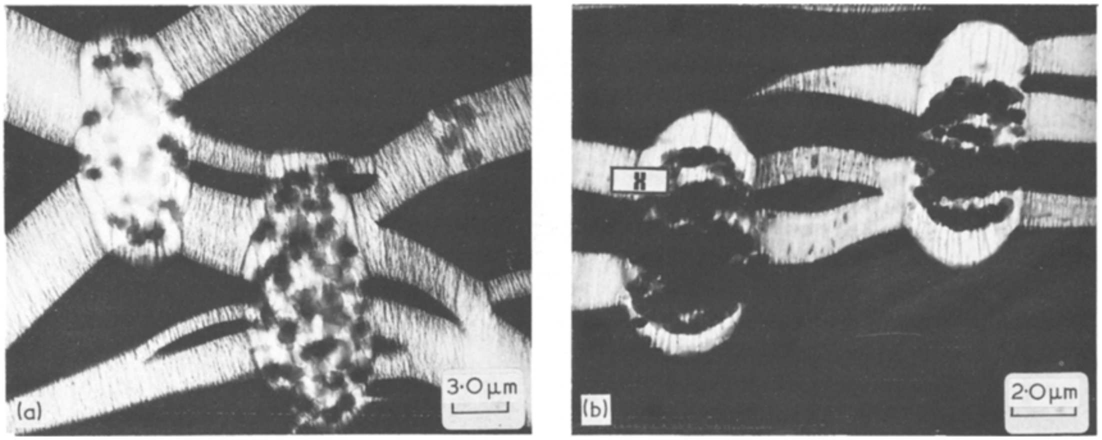


Figure 8 (a) and (b) TEMs of thin solvent-cast films of HIPS after straining and staining.

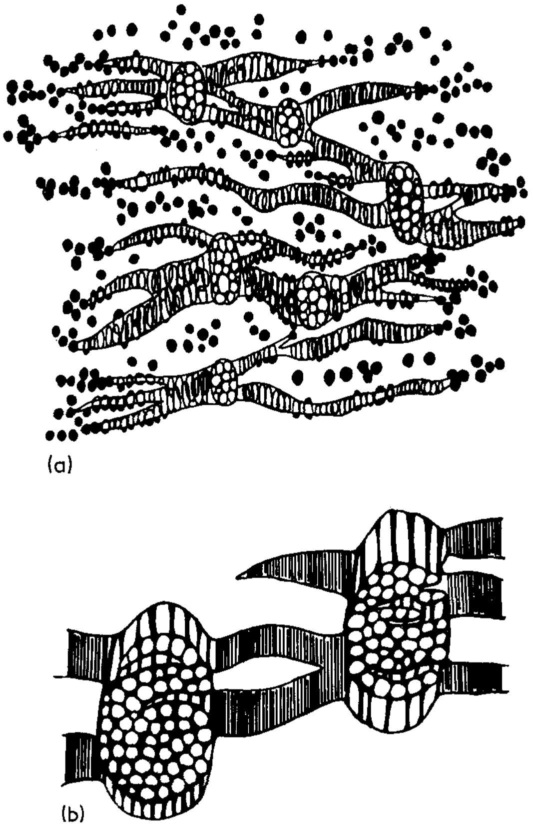


Figure 9 (a) and (b) Schematic diagrams representing the deformation morphology and the changes in shape of the rubber inclusion after deformation of ABS and HIPS respectively.

inclusions described by the crazes formed in the matrix material. Comparison of Fig. 6b and 8b shows that the enhanced contrast observed within rubber inclusions in bulk specimens, for example at position X in Fig. 6b, is consistent with the observation that the inclusions in the solvent cast films undergo large strains as represented by X in Fig. 8b.

The crazes formed in the rubber-modified films exhibit a fibre microstructure similar to that observed in crazed solvent cast films of the matrix polymers. Figs. 10a and b are transmission electron micrographs of crazes formed in grades of styrene acrylonitrile (SAN) and polystyrene (PS) which were very similar to the SAN and PS components of the ABS and HIPS materials used in the investigation described in this paper. The crazes exhibit all of the main characteristics of crazes reported in earlier investigations [11]. One particularly important characteristic which must be referred to here is the difference in the maximum widths of the crazes observed in SAN and PS matrix materials. In the materials used in the present investigation the craze widths in the SAN and PS did not exceed 1.0 and 4μm respectively.

The crazes in both ABS and HIPS propagate from the matrix into the rubber inclusions. The fibre structures formed within the large inclusions and shown in Figs. 8a and b are not fibres of matrix and PS, but fibres of the rubber phase. Fibrillation occurs within the large inclusions throughout the volume defined by the cross-sectional area of the inclusion and the thickness of the matrix craze, and accounts for the change in volume of the rubber inclusion which is determined by the matrix craze strain. There is a definite difference in contrast of the fibres formed within the large inclusions and within the matrix crazes but, other than delineation of the matrix craze/rubber interface and the preferred orientation of fibres in the matrix, this is not readily apparent in the reproduction from electron microscope recording plates shown in Fig. 8.

The regions of dark contrast which can be seen within the highly strained parts of the large rubber inclusions in HIPS arises from undeformed PS contained within the multiphase domains prior to deformation. The strain imposed on the inclusions by the adjacent matrix crazes is accommodated almost entirely by the rubber phase, leaving the polystyrene particles undeformed as shown schematically in Fig. 9b. In HIPS the styrene particles contained within the rubber inclusions are approximately 0.1 μm diameter and account for the dark contrast relative to that given by the highly fibrillated rubber.

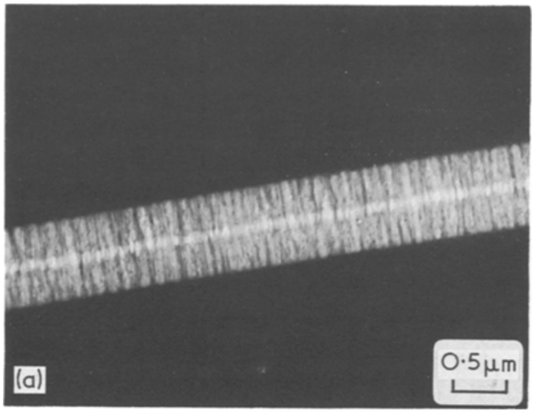
When matrix crazes propagate into or from the rubber inclusions at positions near to the poles of the inclusions the strains imposed by the matrix crazes are accommodated entirely by the rubber surface layer of the inclusion. The "crazed" rubber phase is then free of polystyrene particles. These are then the optimum conditions for examining the structure of the rubber fibres and the integrity of the matrix-inclusion interface. Similar considerations clearly apply to ABS materials.

The crazes formed in both ABS and HIPS tend to define bands which follow paths approximately normal to the applied strain axis, but whose local orientations are such as to maximize the density of rubber inclusions contained with a craze band. Crazes nucleate preferentially in the vicinity of large inclusions, which is in part due to the larger volume of material adjacent to these inclusions which is at an elevated stress relative to the average tensile stress. Once crazes have been nucleated they tend to propagate into inclusions, the captive cross-section of a rubber inclusion being greater than its maximum cross-sectional area. The matrix crazes propagate through the large inclusions and in the case of ABS they envelope the small ones. This occurs because crazes grow along paths defined by curvilinear minor principal stress trajectories in regions where major principal stresses are high.

4. Conclusions

A good correlation between the deformation morphologies found at large strains in bulk specimens and solvent cast thin films of ABS and HIPS has been demonstrated, at least at the level of micromorphological detail considered in Section 3 and subject to the limitations referred to in Section 2. The experimental procedure which is based on the transmission electron microscopy of permanently strained cast films, should prove to be equally useful in the study of films containing rigid inclusions such as ceraplasts [16].

The correlation between bulk and thin film studies in ABS and HIPS is sufficiently good to allow some observations arising from the thin film studies to be used as a basis for further electron microscopy, which could lead to a more complete understanding of toughening mechan-



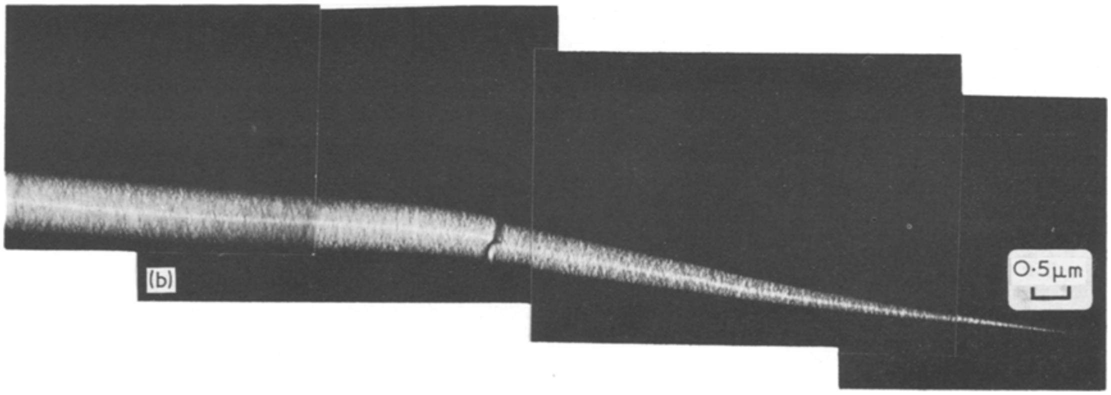


Figure 10 (a) and (b) TEMs of crazes formed in styrene acrylonitrile (SAN) and polystyrene (PS) which were very similar to the SAN and PS components of the ABS and HIPS materials shown in Figs. 1 and 2.

isms in rubber-modified polymers. The fibre morphology of the deformed rubber phase, the matrix crazes and the fibre structure at the interface between the rubber inclusion and the matrix polymer can be characterized by transmission electron microscopy of strained cast films, thus allowing the characterization of changes in micromorphology caused by changes in the composition and molecular structure of the matrix material or the inclusion, the grafting between the two phases, or the distribution and concentration of additives. Some experiments of this nature have already been carried out, for the concentration of lubricants has recently been shown to have a marked effect on the distribution of crazes and also the micromorphology of crazes and the fracture surfaces of bulk specimens in crystal polystyrene [17].

One very obvious result reported in Section 3 was the observed dependence of the widths of crazes on the type of matrix material. The characteristic widths of the matrix crazes; which are determined by the matrix polymer and altered by the styrene–acrylonitrile ratio in ABS materials for example, could be important in deciding the optimum sizes and dispersions of both small and large rubber inclusions for a given matrix material. For example, the number of crazes which can develop from one large rubber inclusion must be related to the ratio of the craze thickness to the diameter of the inclusion. In addition the ability of a small rubber inclusion to retain its integrity or to completely bridge the two interfaces of a matrix craze as shown in Fig. 9a, must also be related to the ratio of the craze width to the diameter of the inclusion for any one system. Both factors relate to the toughening mechanisms in brittle plastics, the former determines the volume fraction of crazes associated with each large inclusion and the latter determines the ability of a craze to withstand the high strains which occur prior to fracture.

Acknowledgement

The authors are indebted to the Science Research Council for financial support.

References

1. M. MATSUO, C. NOZAKI and Y. JYO, *Polymer Eng. Sci.* **9** (1969) 197.
2. M. MATSUO, A. UEDA and Y. KONDON, *ibid* **10** (1970) 253.
3. K. KATO, *Polymer Letters* **4** (1966) 35.
4. *Idem, Polymer London* **8** (1967) 33.
5. *Idem, Polymer Eng. Sci.* **7** (1967) 38.
6. Idem, *Kolloid Z.u.Z. Polymere* **220** (1967) 24.
7. E. H. MERTZ, G. C. CLAVER and M. J. BAER, *J. Polymer Sci.* **A1 4** (1966) 1595.
8. O. K. SPURR and W. D. NIEGISH, *J. Appl. Polymer Sci.* **6** (1962) 585.
9. R. P. KAMBOUR and A. S. HOLIK, *J. Polymer Sci.* **A-2** (1969) 7.
10. R. P. KAMBOUR and D. R. RUSSELL, *Polymer* **12** (1971) 237.
11. P. BEAHAN, M. BEVIS and D. HULL, *Proc. Roy. Soc. London.* **A343** (1975) 525.
12. C. B. BUCKNALL and R. R. SMITH, *Polymer* **6** (1965) 437.
13. M. R. GRANCIO, *Polymer Eng. Sci.* **12** (3) (1972) 213.
14. S. STERNSTEIN, L. ONGCHIN and A. SILVERMAN, *Appl. Polymer Symp.* **7** (1969) 175.
15. J. MURRAY and D. HULL, *J. Polymer Sci. A-2* **8** (1970) 1521.
16. R. A. HAUSSLEIN and G. J. FALLICK, *Appl. Polymer Symp.* **11** (1969) 119.
17. D. L. G. LAINCHBURY and M. BEVIS, *J. Mater. Sci.* to be published.

Received 29 December 1975 and accepted 13 January 1976.