The Observation of Crazes in High-Impact Polystyrene by Electron Microscopy

INTRODUCTION

Much information on the microstructure of high-impact polystyrene (HIPS) can be gained from microscopy of ultrathin sections of the material. Bucknall and Smith,[1] for example, have taken optical micrographs of thin films of HIPS which show the crazed nature of the stressed material, and Staverman[2] has published micrographs of thin sections which show the structure of the "rubber" particles. In the present paper electron micrographs are presented that give information on the behavior of crazes in stress-whitened HIPS.

The material used in the present case was a copolymerized HIPS containing 6% polybutadiene and having an Izod impact strength of 1.2 ft lb/in. notch (1/4 in. bar). Specimens for the electron microscope were prepared both from the normal material and from samples that were stressed at various strain rates in an Instron tensile testing machine. The most satisfactory methods of preparation of samples for the microscope have been reviewed by Williams and Hudson.[3] The method adopted here was that of Kato[4] in which osmium tetroxide is used as the fixing and staining medium. Fortunately, a 1%

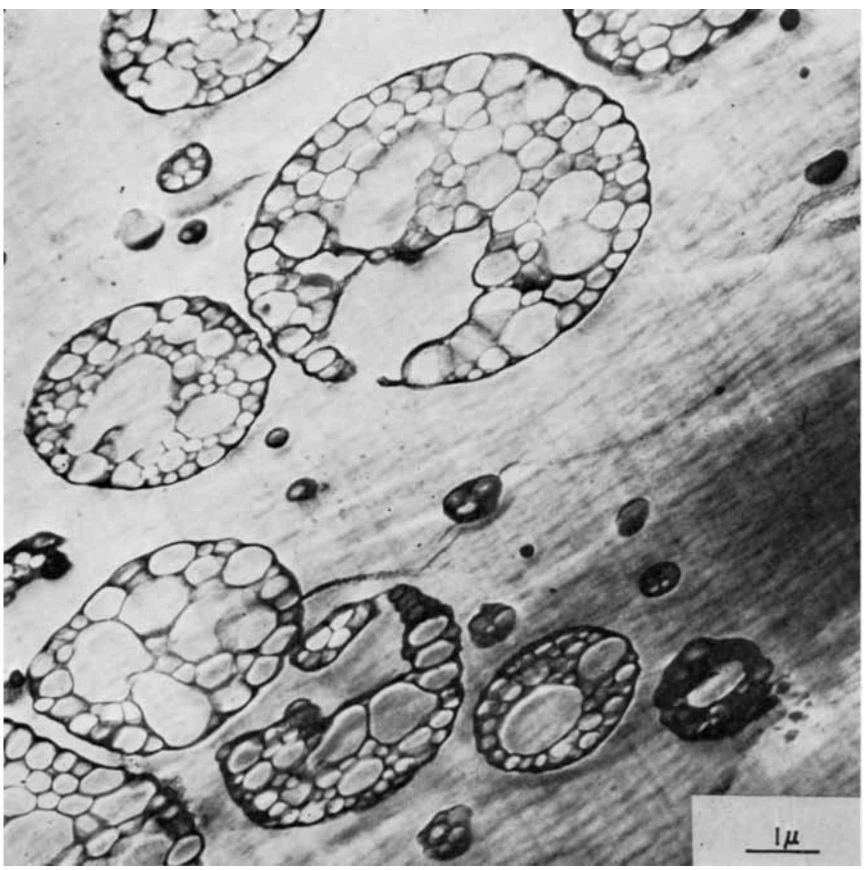

Fig. 1. Section of HIPS stained with OsO_4.

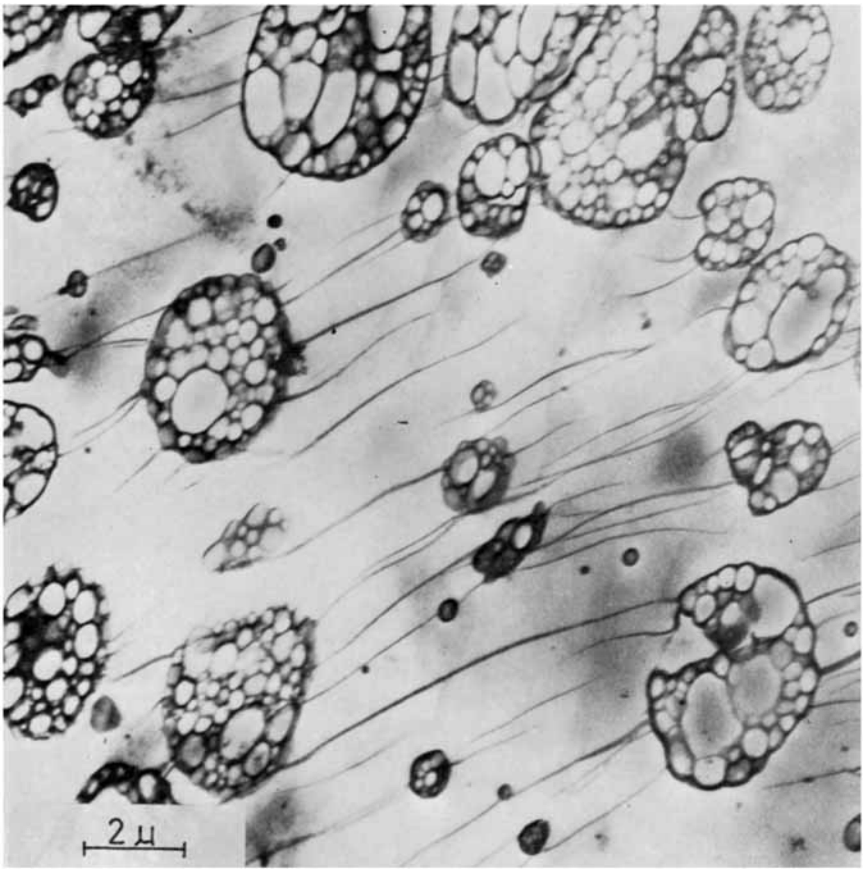

Fig. 2. Section of stressed HIPS showing crazes.

aqueous solution of osmium tetroxide will stain the craze planes in HIPS at the same time as staining and fixing the rubber component. Sample blocks for the ultramicrotome were cut both from the stress-whitened material and from normal material and treated in the staining solution. Thin sections were then cut from these blocks; for the stress-whitened specimens the cutting direction was at about 45° to the strain direction in the material.

After HIPS has been fractured, the path of the crack can be determined by cutting sections through the newly formed surface. These may be called "edge sections" and are of two types: unsupported and supported. Specimens were prepared as follows: For unsupported edge sections the microtome block was prepared from a tensile test piece so that the free fracture surface formed one edge of the cut face of the block and was cut in the ultramicrotome perpendicular to the free fracture surface. It was found, however, that the cutting action deformed the fracture edge so that particles closer than about 5 microns to the edge become badly distorted. Therefore, in order to examine particles closer to the edge than this, it is necessary to support the fracture surface. The method used to obtain supported edge sections was as follows: The free fracture surface was first coated with gold in vacuo and the gold-plated surface, together with 2 mm or so of the polymer, was sawn off and embedded in Araldite. After the Araldite had hardened, the block was trimmed so as to include a portion of the gold-covered fracture surface. The block was then fixed and hardened and sections were cut perpendicular to

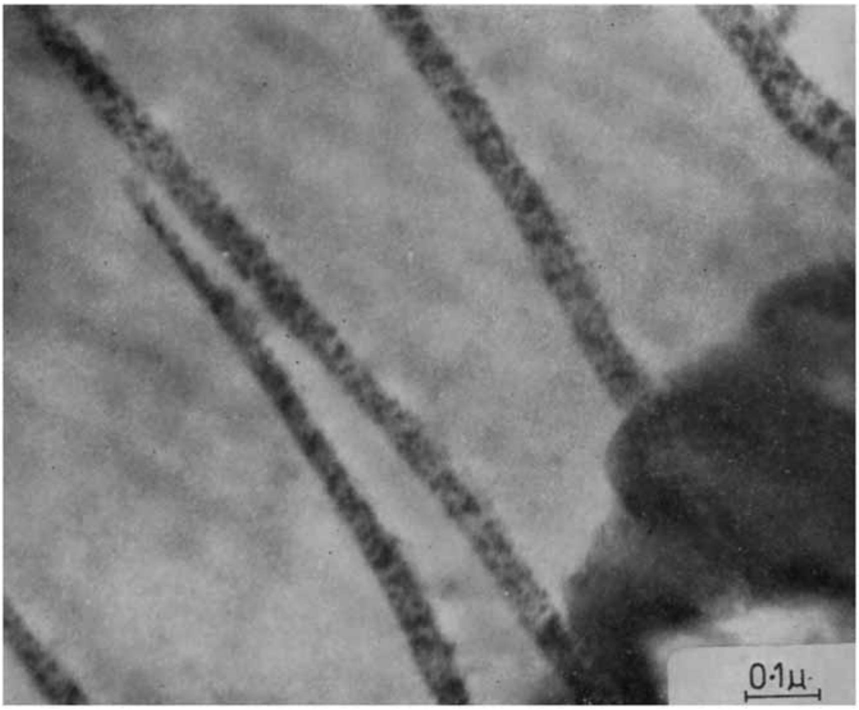

Fig. 3. High-magnification micrograph of stained crazes showing grainy appearance.

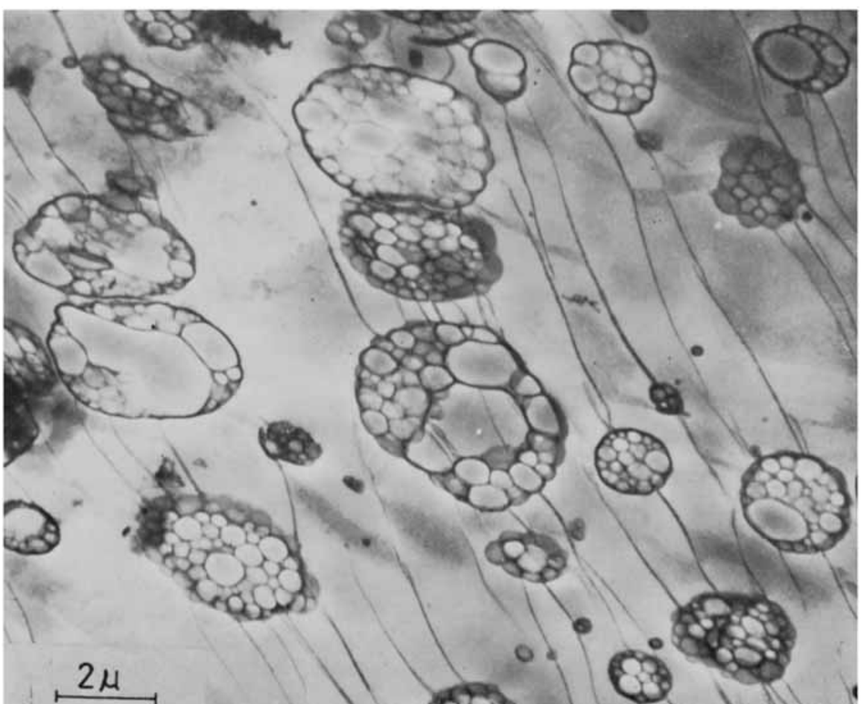

Fig. 4. Section of stressed HIPS showing craze apparently inside rubber particle.

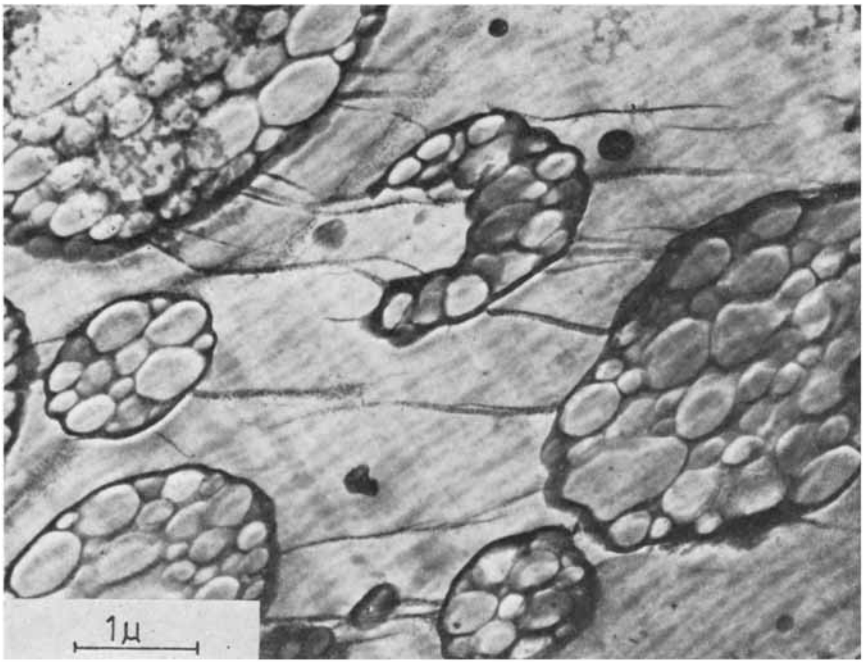

Fig. 5. Section of stressed HIPS with crazes inside arms of reentrant particle.

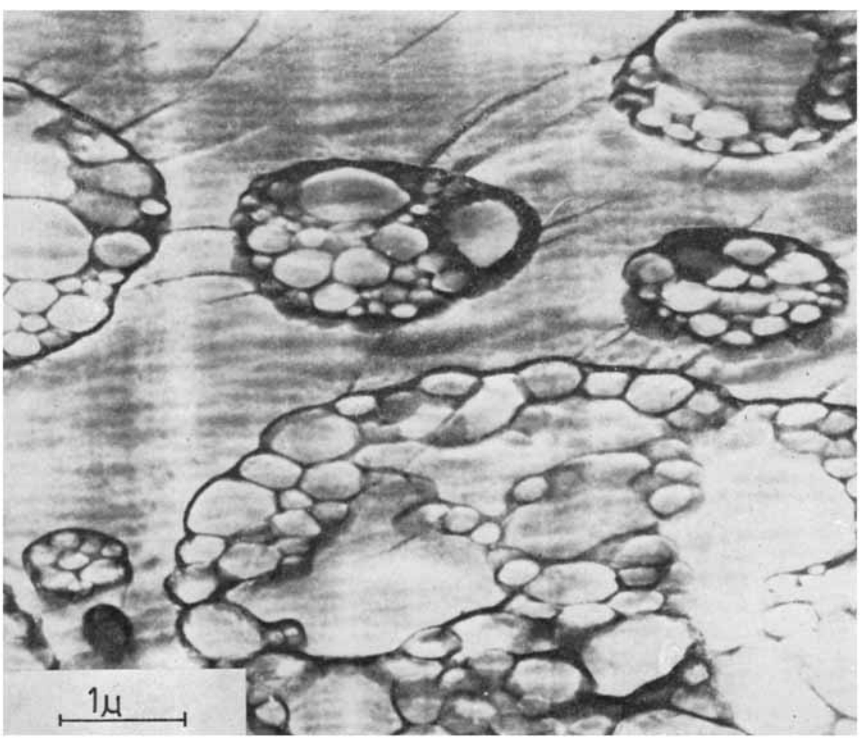

Fig. 6. Section of HIPS which had been stressed quickly. Crazes have not had time to develop fully.

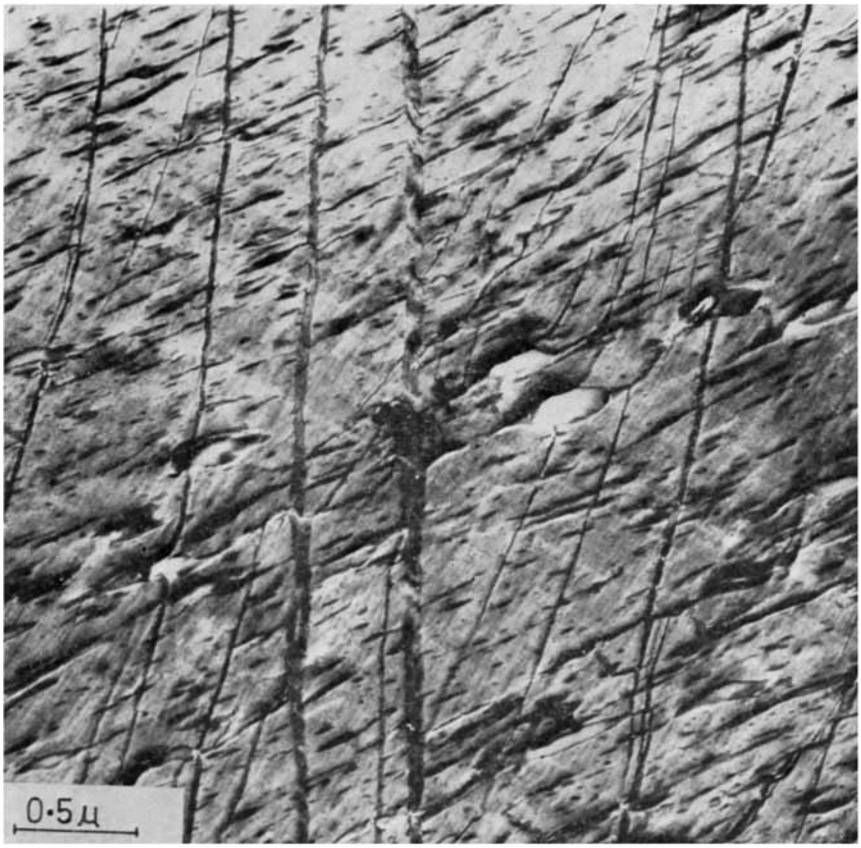

Fig. 7. Section of HIPS with "solid" rubber particles showing how crazes are unaffected by presence of rubber.

the fracture surface. The gold interface was necessary because otherwise the Araldite affected the polystyrene in such a way as to make interpretation difficult. (Since the work reported here was completed, Kato[5] has published micrographs of edge sections using an "oily black ink" as a support medium.)

RESULTS AND DISCUSSION

Figure 1 is a micrograph of a section of the unstressed HIPS and shows the very open, swollen nature of the rubber particles. This structure is well known. If this material is strained, it shows a marked yield point and stress-whitening becomes evident. Figure 2 is a micrograph of a sample of HIPS that has been stressed in an Instron. This micrograph shows craze planes as well as the usual rubber particles. At high magnification (Fig. 3), the craze planes appear to be grainy, a feature that might be expected if the osmium stain is resident only in the voids of the crazes.[6] It will be noticed in Figure 2 that the crazes seem to join the rubber particles but not to enter them. This is a general feature revealed in micrographs of stress-whitened HIPS. Occasionally, however, crazes are observed inside (Fig. 4), but it is thought that this is not true "entry" of the crazes inside the particles. Figure 5 shows that what appears in Figure 4 is probably a section through the limbs of a reentrant particle which happens to have a craze plane incident at this point.

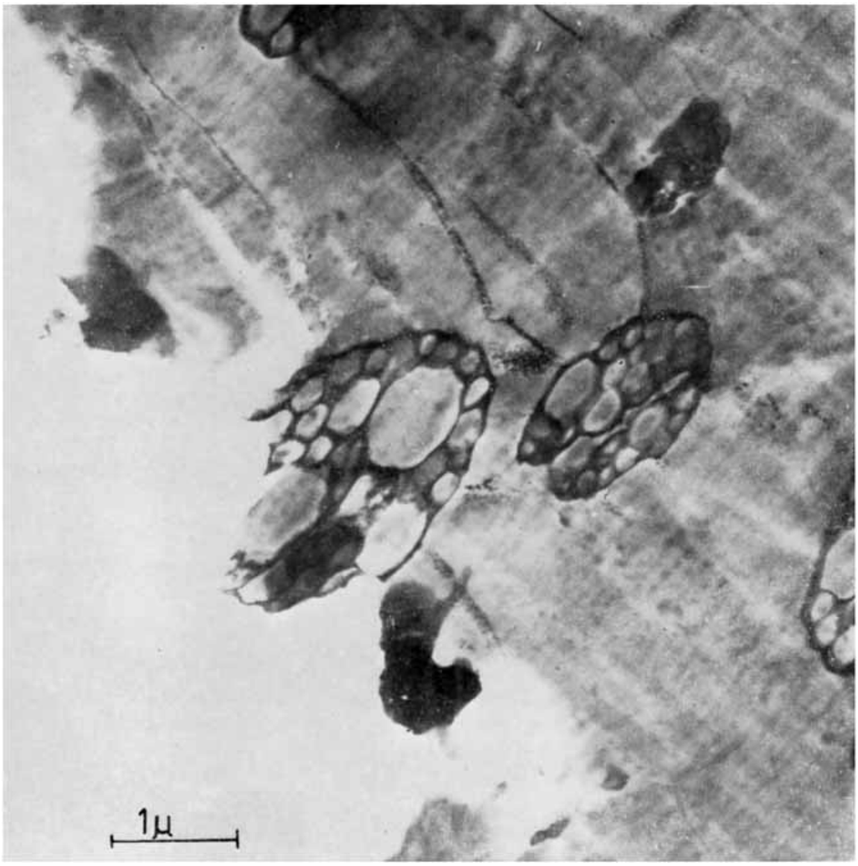

Fig. 8. Unsupported edge section of fractured HIPS. Fracture has run round included polystyrene particle and not through it.

The specimens shown in Figures 2 to 5 were pulled on the Instron at a speed of 0.05 in./min to allow maximum craze plane development. Figure 6, however, is a micrograph of the same material pulled as fast as the Instron would allow, that is, 50 cm/min. Here, the craze planes can be seen but they have not had sufficient time to develop to the same extent as in Figures 2 to 5.

It seems possible that the polystyrene particles inside the rubber may act as reinforcing particles. If this were so, then one might expect a HIPS without them, i.e., with totally rubber particles, to be relatively weak. It is not possible, of course, to prepare two HIPS samples so that both have the same particle size and rubber content but only one has swollen particles. Figure 7, however, shows a section of a HIPS with solid, but small, particles. It can be seen that the well-developed craze planes pass unhindered through the rubbery phase.[2]

If, on fracture, the advancing crack front follows a craze plane, one would expect it to travel round and not through the polystyrene particles embedded in the rubber since there are no craze planes in these polystyrene particles. Figure 8 is a micrograph of an unsupported edge section and shows how the crack has been diverted round the included polystyrene particles, and Figure 9 is a micrograph of a supported edge section showing a similar situation. The thick black line round the HIPS is the layer of evaporated gold. Sometimes, of course, the crack goes round the outside of the rubber particles as can be

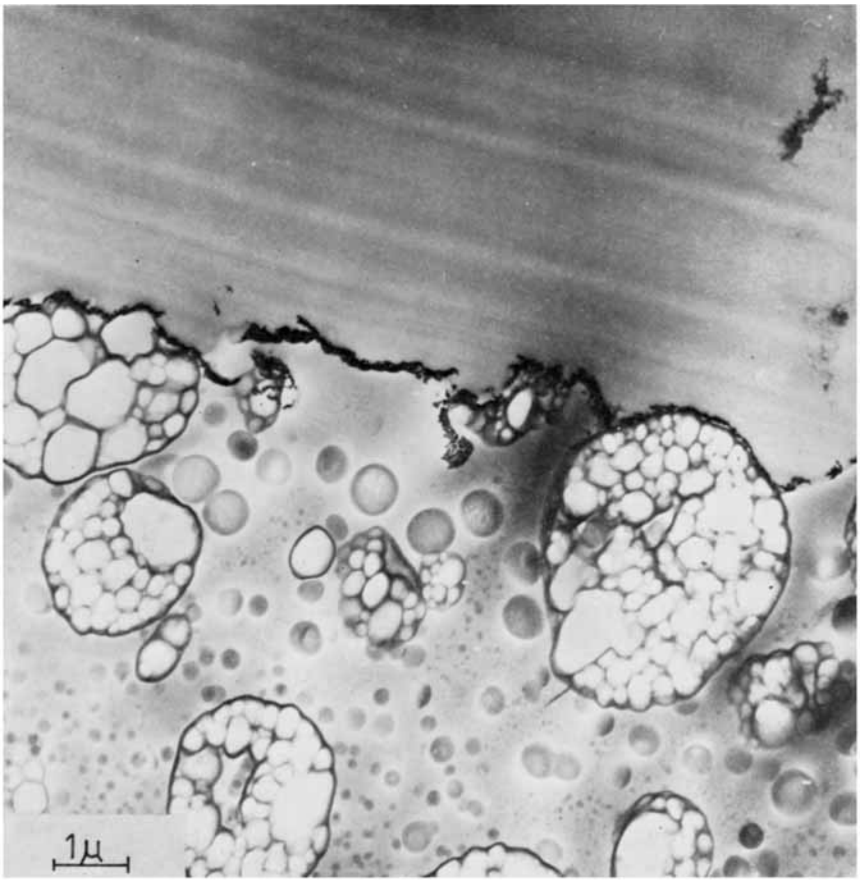

Fig. 9. Supported edge section of HIPS showing, at left, how fracture ran round included polystyrene particles. Effect of Araldite on polystyrene can also be seen.

seen in Figure 9, but when a crack goes through a rubber particle it generally follows the elastomeric phase.

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