Identification of Deformation Behavior in High-Thermal-Resistant Poly(acrylonitrile-butadiene-styrene) (ABS)

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ABSTRACT: Deformation mechanisms in postfractured high-thermal-resistant poly(acrylonitrile-butadiene-styrene) (ABS) were investigated using transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS). Although crazes were clearly identified by TEM, they were not detectable by SAXS. This was possibly due to a short distance between sample and imaging plate in the SAXS set-up and invisibility of craze fibril scattering from the postfractured samples. A rhomboid-shaped SAXS pattern was obtained from ABS samples with high ductility but with no crazes shown in the TEM micrographs. It is believed that the rhomboid-shaped SAXS pattern was generated from matrix shear yielding. The results show that a combination of TEM and SAXS enable us to distinguish crazing and shear yielding in the postfractured ABS.
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Key words: TEM; SAXS; crazing; shear yielding; ABS

INTRODUCTION

In our previous work on a high-thermal-resistant poly(acrylonitrile-butadiene-styrene) (ABS),[1] extensive elongation was observed from tensile specimens, but very few crazes were found from transmission electron microscopy (TEM). It was concluded that the extensive elongation was due to rubber particle cavitation and matrix shear yielding, not crazing. A similar conclusion was drawn from tensile testing of high-impact polystyrene.[2] However, the TEM work could only observe the matrix shear yielding through rubber particle deformation near the fracture surface and matrix drawing on the fracture surface. Shear yielding in the bulk material was not visible, because of lack of contrast in the TEM micrographs.

This work revisits the above TEM study, and attempts to obtain direct evidence on the involvement of shear yielding in the high-thermal-resistant ABS. The experimental technique used was small-angle X-ray scattering (SAXS). This technique has been extensively used for the study of craze formation in glassy polymers. It was reported that SAXS pattern for crazes consists of a pair of intense streaks normal to the craze plane (named anomalous streak) and a second pair of less intense streaks parallel to the craze plane.[3]

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Table I ABS Blends Used in This Study

	g1-28	g2-28	g5-28
Blend ratio (ABS/SMI/SAN_{add})	36 : 20 : 44	45 : 20 : 35	40 : 40 : 20
Blend ratio in matrix (SMI/SAN)	1 : 3	1 : 3	1 : 1
Blend composition			
SMI	SMI55	SMI55	SMI55
SAN_{add}	SAN28	SAN28	SAN28
Ordinary ABS	ABS-g1	ABS-g2	ABS-g5

The streaks parallel to the craze plane are related to the craze fibril diameter, but not visible when the specimen is unloaded with a small compressive force normal to the craze plane.

In situ SAXS measurement during tensile testing was reported by Okamoto et al.[4] on high-impact polystyrene. SAXS pattern for the shear yielding consists of a pair of streaks in the direction of tensile stress. These are smaller and sharper than the anomalous streaks for crazing. No TEM was conducted in that study to clarify whether crazing also existed in the specimen in which shear yielding was detected by SAXS. It should be noted that intensity difference between the two pairs of streaks for the crazing in the above study is opposite to that reported by Brown and Kramer.[3] The former showed strong craze fibril scattering, whereas the latter showed strong anomalous scattering.

In this work, TEM and SAXS were used to distinguish crazing and shear yielding in the high-thermal-resistant ABS. TEM was expected to identify crazing, and SAXS shear yielding.

EXPERIMENTAL

Materials

Three high-thermal-resistant ABS specimens were used in the study (named g1-28, g2-28, and g5-28). The constituents of the ABSs are "ordinary" ABS, poly(styrene-*co*-acrylonitrile) (SAN, named SAN_{add} to distinguish it from SAN in the ordinary ABS, named SAN_{ABS}) and poly(styrene-*N*-phenyl-male-imide) (SMI). The g1, g2, and g5 refer to the ordinary ABS used, and 28 to the SAN_{add} (SAN28). The g1-28 and g2-28 are the same as those named #1 and #3 in the previous publication,[1] each of which contains 20 wt % SMI. The third ABS (g5-28) contains 40 wt % SMI, thus showing much lower ductility than the first two ABSs. Blend ratio and composition of the 3 ABSs are given in Table I, and details of their constituents in Table II.

Specimens used in the study were taken from dumbbell specimens fractured in tensile tests. The dumbbell specimens were prepared by blend-

Table II Constituents of the ABS Blends

	g1-28	g2-28	g5-28
SMI	SMI55	SMI55	SMI55
M_w of SMI	171,000	171,000	171,000
SAN_{add}	SAN28	SAN28	SAN28
M_w of SAN_{add}	120,000	120,000	120,000
AN content (wt %)	28	28	28
Ordinary ABS	ABS-g1	ABS-g2	ABS-g5
Bd/SAN_{ABS}	50 : 50	40 : 60	50 : 50
Rubber particle structure	Homogeneous	Salami	Salami
Rubber particle size	0.1 + 0.5 μm (bimodal)	0.5 μm	0.3 μm
SAN_{ABS}	SAN23	SAN23	SAN23
M_w of SAN_{ABS}	89,000	129,000	65,000
AN content (wt %)	23	23	23

Bd, butadiene; AN, acrylonitrile.

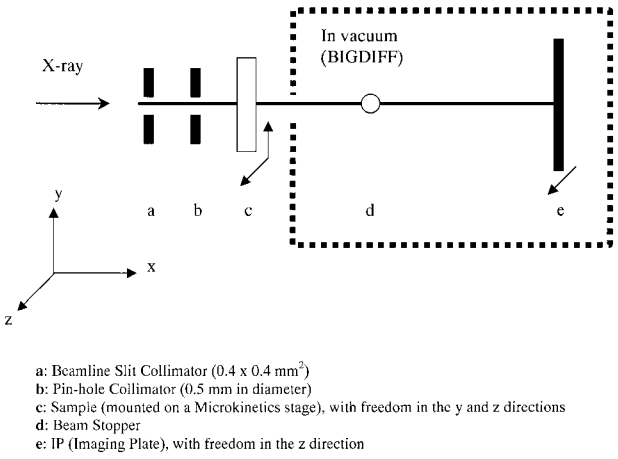

Figure 1 SAXS set-up. Freedom of movement is indicated by the arrows under the components. Sample was placed to align extension deformation with the z-direction.

ing the ordinary ABS, SAN_{add}, and SMI using first, a twin screw extruder, and then an injection molding machine. Details of the dumbbell specimen preparation are available elsewhere.[1,6]

TEM samples were prepared using a near-fracture-surface sectioning technique[7] to examine deformation behavior immediately beneath the fracture surface. SAXS samples were strips 0.5-mm thick and 3.3-mm wide that were sliced from the tested specimens along the gauge length direction using a slow cutter (Leco VC-50).

TEM

A transmission electron microscope (Joel 2000 EX TEM) operated at 200 KeV was used for the TEM examination. The images were recorded in negatives (SQ163; Kodak), and then scanned into digital files using a high-resolution negative scanner (Polaroid SprintScanner 45) with a resolution of 16 μm.

SAXS

The SAXS experiment was conducted at a wavelength of 1.5 Å using a tuned channel cut monochromator in the Photon Factory, Tsukuba, Japan. The sample was mounted on one jaw of a tensometer on a Microkinetics stage which was situated in front of the vacuum diffractometer (BIGDIFF), available at BL-20B in the Photon Factory.

The set-up is shown in Figure 1. With the beam in the x-direction, primary positioning of the sample was effected by movement in the y-z plane. A 0.5-mm diameter pinhole was mounted on the body of the tensometer close to the sample. Further collimation was provided by a slit system (0.4 $\times$ 0.4 mm) situated about 300 mm closer to the source, and the primary beamline slits were closed down to reduce the incident beam by 20%. An imaging plate (IP) was mounted in the BIGDIFF to be symmetrical about the incident beam and was shielded from this beam by a beam stoper about 200 mm from the IP position. The distance from the IP to the specimen was 1783 mm. The IP cassette was movable during the experiment to record four SAXS patterns in one IP: (i) with the sample out of the beam; (ii) in the deformation zone, with the center of the beam being on the fracture edge; (iii) in a region of 0.6 mm from the fracture edge; and (iv) in a region far from the fracture edge (3.6 mm). Positions of the beam on the sample are depicted in Figure 2. The sample was moved into the beam in the z-direction using the tensometer.

SAXS patterns presented in this report were converted to eight levels of brightness using image process software (Photoshop, Version 5, Posterise command), to highlight the contour shape of the diffraction pattern. An example of the effect is given in Figure 3.

The X-ray exposure time was determined by conducting a preliminary study on a g5-28 specimen. This ABS, as shown in Results and Discussion, contains extensive crazing in the matrix. It was believed that its SAXS pattern should represent craze deformation. This has been well documented in the literature. The X-ray exposure time was determined to avoid overexposure, which would result in an artificial line on the IP. This would occur across the IP's width; that is, along the z-direction in Figure 1.

SAXS patterns from the g5-28 specimen, with exposure time ranging from 15 to 60 s, are shown

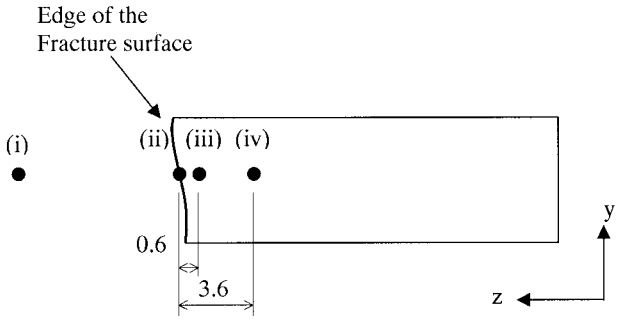

Figure 2 Positions of beam spot on the polymer sample.

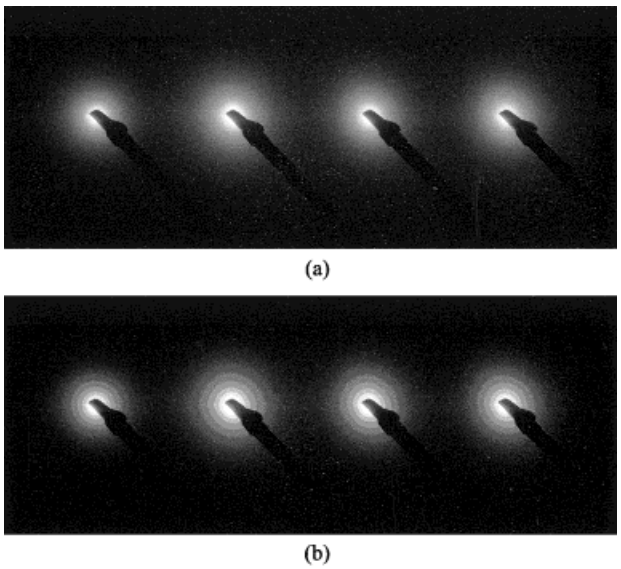

Figure 3 SAXS pattern (a) before and (b) after the use of posterize command in Photoshop (Version 5).

in Figure 4. The patterns indicate that the artificial line starts being visible at 60 s, indicated by white arrows in Figure 4(C). Therefore, an exposure time of 30 s was selected for the study. The exposure time should be short enough to avoid generating the horizontal line, even with possible variation of the beam intensity during the experiment.

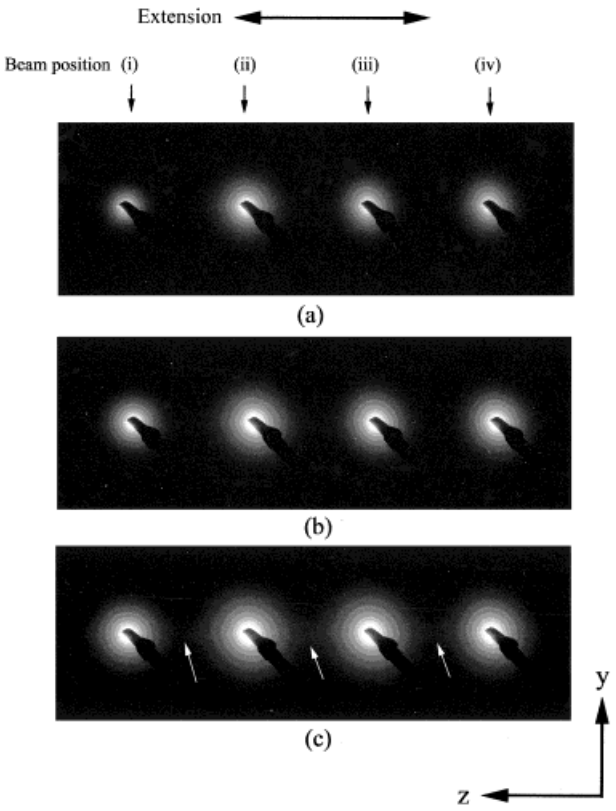

Figure 4 SAXS patterns of g5-28 after tensile fracture, collected at various exposure time (a) 15 s, (b) 30 s, and (c) 60 s.

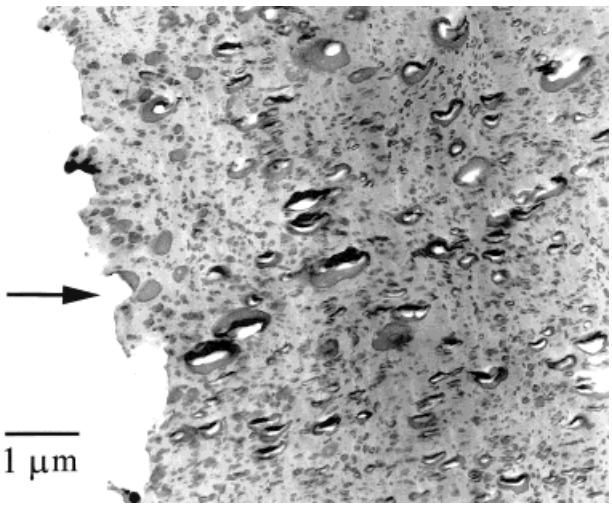

Figure 5 TEM micrograph of g1-28. The black arrow indicates the edge of the fracture surface, and the white arrow the stress direction.

RESULTS AND DISCUSSION

TEM micrographs for the three ABSs in regions beneath the fracture surface are shown in Figures 5–7. Figure 6 is the same micrograph that was

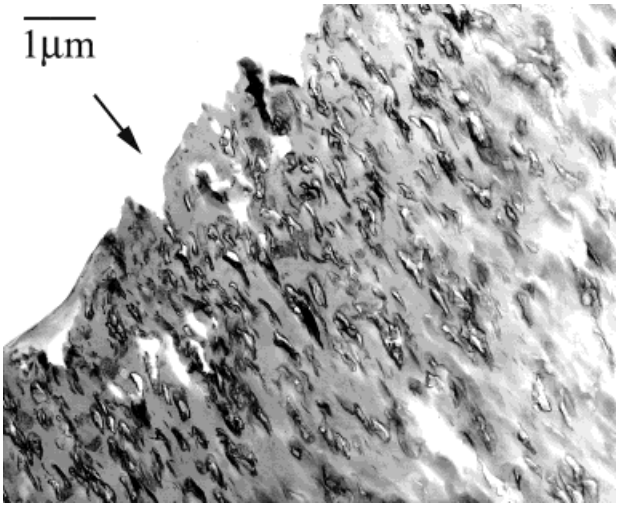

Figure 6 TEM micrograph of g2-28. The black arrow indicates the edge of the fracture surface, and the white arrow the stress direction.

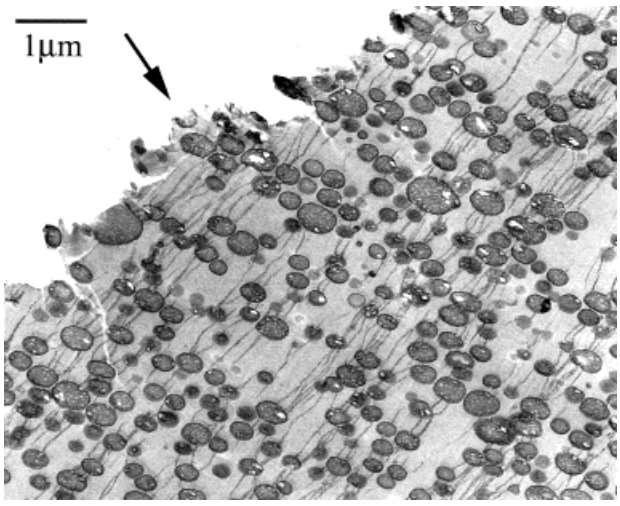

Figure 7 TEM micrograph of g5-28. The black arrow indicates the edge of the fracture surface, and the white arrow the stress direction.

reported in the previous publication.[1] Figures 5 and 6 show lack of crazing in the ABSs, despite extensive elongation before fracture (with elongation of 7.5 and 22.3 mm, respectively, for a gauge length of 65 mm). However, Figure 7, from g5-28 which has high SMI content thus a much brittle matrix, shows extensive crazing.

SAXS patterns from the three ABS specimens are given in Figure 8. It should be noted that because of extensive elongation of g1-28 and g2-28, beam positions (ii) to (iv) were all from the deformed whitening zone, but only positions (ii) and (iii) of g5-28 were from the deformed region. Shapes of these SAXS patterns fall into two categories: rhomboid and circular. The former was obtained from g1-28 and g2-28 of which TEM micrographs do not show extensive matrix crazing, whereas the latter are from either g5-28 or undeformed region.

Two obvious conclusions can be drawn from the SAXS results: (i) the SAXS pattern for crazing, g5-28, is not different than that from an undeformed region, and (ii) dominant deformation mechanism is similar for g1-28 and g2-28, but different than that of g5-28. The first conclusion seems to be different than that drawn by Brown and Kramer,[3] who noted that a pair of streaks, corresponding to craze fibril scattering, should be visible on the SAXS pattern in the direction parallel to the craze plane. However, maximum intensity of the streaks in their results is at a position with 2θ around 5 mrad. In our set-up, this corresponds to a position of around 8 mm from the central beam spot in the y-direction, which is still covered by the beam stopper. As a result, fibril scattering is unlikely to be visible using our SAXS set-up. This means that the SAXS pattern for g5-28 is no different than that from an undeformed specimen.

The streaks for the craze fibril scattering may also be invisible if the specimens were subjected to a small compressive force normal to the craze plan.[3] As our SAXS samples were prepared by cutting the fractured specimens into strips, a compressive force may have been applied unintentionally during the specimen preparation, that may have made the fibril scattering streaks disappear from the SAXS pattern.

The rhomboid-shaped SAXS pattern for g1-28 and g2-28, compared with the circular shape for g5-28, indicates that the deformation mechanism involved is not crazing. The only other deformation mechanism that has been reported for ABS is shear yielding.[8,9] Because the TEM micrographs

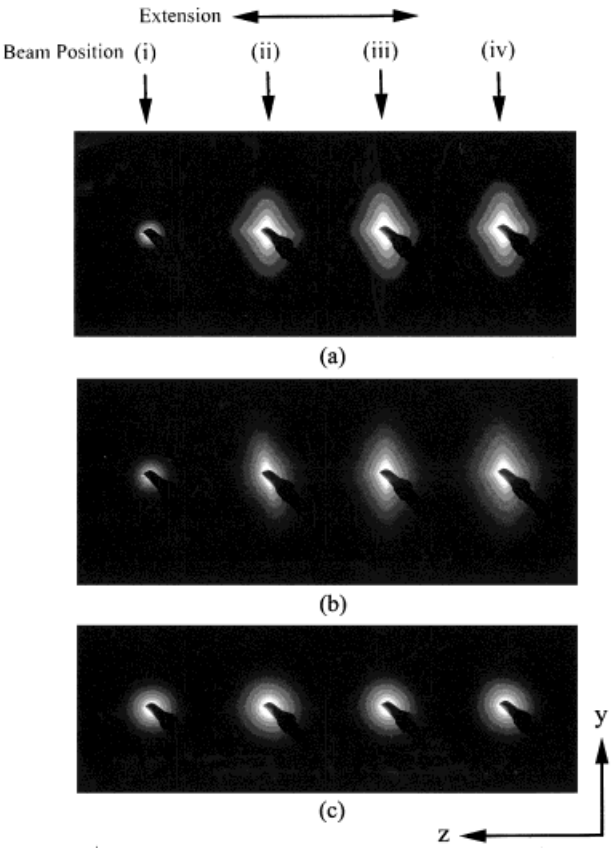

Figure 8 SAXS patterns from (a) g1-28, (b) g2-28 [same as Fig. 4(b)], and (c) g5-28. The specimens were tensile fractured before the examination. X-ray exposure time was 30 s.

do not show evidence for crazing in these ABSs, we believe that the rhomboid-shaped SAXS pattern represents shear yielding. To our knowledge, such a SAXS pattern for ABS has not been reported previously.

The rhomboid-shaped SAXS pattern for shear yielding is different than that reported by Okamoto et al.[4] They suggested that the SAXS pattern for shear yielding should consist of a pair of streaks in the direction of tensile stress. It is possible that the rhomboid-shaped SAXS pattern was due to unloading of the specimens. Under loading, the SAXS pattern might be sharper, to be similar to that reported by Okamoto et al.[4] However, further experiments are needed to elucidate the reason why a difference exists.

CONCLUSIONS

The matrix deformation behavior of three high-temperature-resistant ABS specimens were investigated using TEM and SAXS analyses of the fractured specimens. It was found that crazing could be identifiable by TEM, but not by SAXS using the existing X-ray beam-stopper. This arises from the fact that there is only a short distance between the sample and imaging plate and a possible compressive force introduced during sample preparation. A distinct rhomboid-shaped SAXS pattern was obtained from samples with shear yielding which cannot be observed by TEM. The SAXS pattern facilitates the identification of shear yielding.

This study shows that a postfracture analysis of using TEM and SAXS enables identification of crazing and shear yielding in the ABS. This gives a simple alternative to real-time SAXS measurement during tensile testing that has been used in the past.

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