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The microstructure and deformation of model ABS compounds

Part 1 *Experimental techniques, and the effect of matrix molecular weight and rubber content*

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An investigation of the effect of matrix molecular weight and rubber content on the deformation of a range of ABS (polyacrylonitrile butadiene styrene) model materials supports the view that rubber particles are effective in initiating and stabilising crazes, and that the increase in failure strain with increasing rubber content is more pronounced in materials with a lower matrix molecular weight. Results obtained from transmission electron microscopy of ultramicrotomed sections prepared from previously strained bulk specimens indicate that neither matrix molecular weight nor rubber content as such are significantly important in controlling the contribution of shear yielding to the overall deformation behaviour.

1. Introduction

The understanding of the relationships between structure and properties of rubber modified glassy polymers is a complex problem because of the number of structural variables involved and evident from the summary of the manufacturing routes and polymer blend properties described by Bucknall [1]. The major structural variables for a polymer of given chemical composition and molecular weight characteristics are: (a) volume of rubber [2, 3], (b) volume fraction of the dispersed phase [4], (c) rubber particle size and size distribution [5–11], (d) degree of cross-linking of the rubber [4, 12] and (e) degree of grafting [13, 14].

The improved fracture resistance of rubber modified polymers depends on the rubber forming a discrete phase and developments in the manufacture of such materials allows the size and distribution of the rubber phase to be accurately controlled. However, the exact requirements of rubber particle size, size distribution and microstructure for optimum impact improvement have yet to be completely resolved due to the vast number of inter-related structural and chemical variables existing in these polymer systems.

The aims of the work described in this and the following paper was to use previously described techniques for microstructural characterisation [15] to investigate systematically the microstructure and mechanical properties of a range of model ABS compounds, and thereby enlarge on the understanding of factors which control the properties of ABS materials. In Part 1 the experimental techniques and study materials used in the investigation will be described together with the experimental results relating to the effect of matrix molecular weight and rubber content. The experimental results relating to the effect of rubber particle size and graft frequency and their interpretation are described in Part 2.

2. Study materials and experimental methods

2. 1. SAN and ABS model materials

A series of SAN (styrene acrylonitrile) and ABS model compounds with well defined molecular weight, rubber particle size and content and degree

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TABLE I Model SAN materials used and their molecular weight and composition characteristics.

SAN	$\bar{M}_N \times 10^{-3}$	Rubber content (wt %)
A	24	0
B	41	0
C	69	0, 10, 20, 30
D	88	0
E	108	0, 10, 20, 30

of grafting were supplied by Borg-Warner Chemicals. An analysis of the molecular structure was also supplied from data derived from the procedures discussed by Moore *et al.* [16]. The major steps of a typical procedure are : (a) infra-red analysis, (b) separation of graft polymer from non-grafted polymer by centrifugation, (c) ozonolysis of the graft phase to remove the graft phase from the rubber, and (d) analysis of rubber fragments, grafted and ungrafted polymer.

Twenty ABS model materials, containing 15% by weight of rubber, were used to study the effect of grafting. These comprised four well-defined rubber particle sizes, each with five increasing degrees of grafting. Rubber ratio in the polymerisation process and a constant rubber level was maintained by adding SAN resin with a number average molecular weight, $\bar{M}_N$, of 75 000. An analysis of these materials is shown in Table I of Part 2 [17].

The effect of matrix molecular weight on the tensile deformation of SAN and ABS was investigated with five SAN materials with a number average molecular weights, $\bar{M}_N$, varying from 24 000 to 108 000 (Table I). Two of these SAN materials, $\bar{M}_N$ = 69 000 and 108 000, were used as matrix materials for ABS systems containing 10%, 20% and 30% by weight of rubber.

2.2. Compression moulding and test specimens

Mechanically isotropic plaques of all the SAN and ABS materials were prepared by compression moulding. Granules of material were placed in a picture frame mould between stainless steel glazing plates and transferred to a hydraulic moulding press at a temperature of 200° C. The platens of the press were brought together and the mould was allowed to heat for ten minutes before applying pressure. A pressure of 4 MN m^{-2} was applied in stages of 1 MN m^{-2} which was released after each stage to allow air to escape from the mould. After a further 10 min period, the mould was allowed to cool slowly under pressure. The small amount of model materials available necessitated the use of a small picture frame mould, with dimensions of 2 mm x 60 mm x 80 mm. Tensile test specimens and ultramicrotomed sections were cut from the moulded plaques.

All tensile bars produced from compression and injection moulded plaques were prepared very carefully by hand to ensure that recorded differences in properties were due to material differences and not a reflection of the method of preparation. For the model ABS materials it was necessary to scale down the size of the specimens due to the limited amount of material available and so ASTM type V dimensions were used.

Tensile bars were prepared by securing rectangular strips of material, cut from the plaque, into a polishing jig of the required shape and dimensions. The material was cut to the approximate size of the jig using a jeweller's coping saw. The specimens were polished by hand using successively finer grades of carborundum paper; grades 180, 320, 400 and 600 respectively, and finished with "gamma" alumina paste. Tensile tests were carried out at 20° C and at a constant cross-head speed of 0.5 mm min^{-1}. The cross-sectional dimensions of the test pieces were measured prior to testing, and used to calculate engineering stress/engineering strain for all specimens and reproduced below.

2.3. Microscopical examination

The morphology of the bulk fracture surfaces was studied in reflected light illumination with a Reichert "Zetopan" light microscope. Scanning electron microscopy (SEM) was used to study fine structure surface details of bulk specimens. Prior to observation in the SEM the specimens were fixed onto aluminium studs and coated with a thin layer ($\simeq 10 \mu$m) of gold–palladium alloy, by vapour deposition in vacuo to reduce electrostatic charging and heat effects during electron bombardment.

The main problems encountered in the transmission electron microscopy studies were due to exposing ultra-thin specimens to the high energy electron beam and therefore considerable effort was made to avoid artefacts, particularly those associated with specimen preparation and electron beam damage, to ensure that the observed structures were typical of the bulk material. The sections of SAN and ABS materials were found to be reasonably stable in the electron beam provided

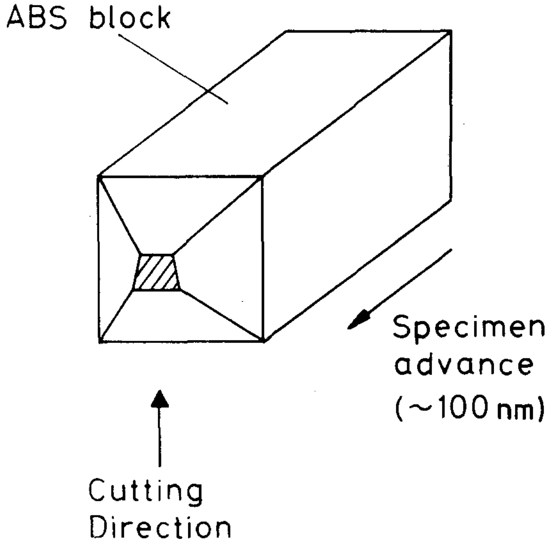

Figure 1 Schematic diagram of a trimmed specimen block used for ultramicrotomy, showing the trapezoidal shaped block face and the cutting and speciment advance directions.

that the incident electron beam was sufficiently de-focussed.

Thin specimens were prepared by ultramicrotomy and solvent casting. The advantages and limitations of these techniques are discussed in the following sections.

2.3.1. *Ultramicrotomy*

Ultra-thin (approximately 0.1 μm) specimens for transmission electron microscopy (TEM) observation were prepared from undeformed and deformed compression moulded specimens using a LKB Ultratone III ultramicrotome. Freshly prepared glass knives with a nominal bevel angle of 45° were produced with an LKB Type 780 1B knife maker. The thin sections were cut with a thermal advance setting of between 0.08 and 0.1 μm and were floated off the knife edge on a bath of distilled water. The specimens were then collected on 3 mm diameter copper grids.

Certain conditions were found to be of critical importance for the preparation of good quality sections:

(a) For cutting the thinnest possible sections, the specimen block face was trimmed down to a trapezoidal shape less than 1 mm in width as illustrated in Fig. 1. This combination in the block face of small area and tapered sides virtually eliminated "chatter" marks (periodic variations in section thickness) caused by specimen vibration as a result of impact with the knife edge [18].

(b) A slow cutting speed was found to be necessary for preparing good sections. A cutting speed of 2 mm sec^{-1} was used throughout.

(c) The trimmed specimens of ABS were treated with osmium tetroxide in aqueous solution for two days before final sectioning, according to the method developed by Kato [19–21]. The osmium tetroxide technique has a two fold purpose; firstly, to harden the rubber phase sufficiently to enable thin sections to be cut and secondly, to give the necessary contrast in the TEM. The osmium tetroxide usually only penetrates 5 to 10 μm into the surface of the specimen block and therefore the treated block must be very carefully aligned in the instrument so that good quality sections can be cut immediately. Poor specimen alignment may result in the stained layer being removed on the first cutting stroke.

In order to examine the deformation behaviour of ABS materials, thin sections were cut from stress whitened areas of compression moulded tensile specimens close to the fracture surface, at a known angle of approximately 50° from the tensile axis so that any artefacts arising from the sectioning procedure could be established.

Ultramicrotomy allows the deformation mechanisms operating in bulk materials to be studied in considerable depth in the TEM. The main limitation of the technique is that the bulk tensile specimens, from which the sections are prepared, undergo a significant amount of relaxation after failure which can mask some of the fine microstructural detail. Therefore, the study of deformation in ultramicrotomed sections has been supplemented using solvent case thin films [15].

2.3.2. *Solvent cast thin films*

Granules of SAN and ABS materials cut from compression moulded plaques were dissolved in ethyl acetate to form an approximately one weight per cent solution. The solution was poured over electron microscope grids, supported on a glass slide and the solvent was allowed to evaporate. A thin layer of polymer, approximately 0.1 μm thick, remained embedded on the grids. The grids were then removed from the glass slide by immersing in distilled water. The specimens were deformed in a specially constructed microstraining stage, and since the copper grid deformed plastically the applied strain in the thin film was retained. The ABS specimens were stained with osmium tetroxide prior to TEM examination to give the necessary contrast. The solvent casting technique provides a straightforward and rapid method of studying the tensile deformation of amorphous polymers since the supporting grid deforms plastically and the applied strain is retained. This feature is particularly important in films containing elastomeric inclusions because the relaxation of the rubber and associated crazes after deformation is minimized. The role of the rubber inclusion in the toughening mechanisms can therefore be identified more readily. The main disadvantages of the solvent casting technique are associated with the uncertainty of the equivalence of the deformation processes in thin films and bulk specimens arising from differences in triaxial thermal contraction effects and the dispersion of additives. Additionally, more intrinsic parameters, such as the type of solvent and rate of evaporation may influence the deformation of the thin films. Therefore, the deformation morphology of both solvent cast thin films and ultramicrotomed sections cut from bulk specimens were studied. The two techniques may be considered to be complementary.

3. Experimental results: the effect of matrix molecular weight and rubber content

The effect of molecular weight of SAN was examined in a series of model polymers with $\bar{M}_N$ varying from 24 000 to 108 000 as listed in Table I. Tapered tensile specimens prepared from compression moulded plaques were tested in tension with a constant cross-head speed of 0.5 mm min^{-1}. The low molecular weight SAN ($\bar{M}_N$ = 24 000) was found to be very fragile and all specimens shattered during clamping in the Instron jaws and consequently a value of tensile strength could not be obtained. A plot of fracture stress against molecular weight is shown in Fig. 2. The failure stress increased linearly with increasing molecular weight although the pronounced weakness of SAN with $\bar{M}_N$ = 24 000 suggested that the curve would fall off dramatically in the region of $\bar{M}_N$ = 40 000. The overall effect of molecular weight on fracture stress of SAN was similar to the results obtained by Fellers *et al.* [22] and Haward and Mann [3] for polystyrene, although for polystyrene the critical value of $\bar{M}_N$ below which specimens became very brittle was significantly higher and of the order of 7×10^4.

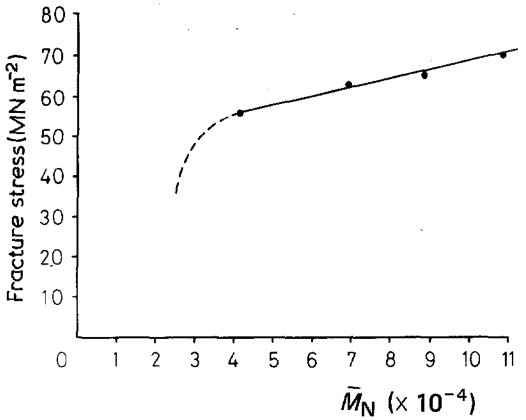

Figure 2 Plot of fracture stress versus number average molecular weight ($\bar{M}_N$) of SAN.

There was no evidence of large numbers of crazes forming before failure of the SAN materials but the fracture surfaces of specimens with $\bar{M}_N \geqslant 40 \times 10^3$ were found to contain mirror regions and associated patch microstructures which indicated craze controlled fracture [23]. The extent of the mirror regions was found to increase with increasing molecular weight.

Two of these model SAN materials, $\bar{M}_N = 69 \times 10^3$ and 108×10^3, were used as matrix materials for ABS polymers and containing 10%, 20% and 30% by weight of rubber. The microstructures of the ABS polymers were examined in ultramicrotomed sections using the TEM. Typical examples of the microstructures of ABS specimens containing 10% and 30% rubber content are shown in Fig. 3. The elastomeric phase consisted of a reasonably uniform dispersion of rubber particles and a well defined particle size with an average diameter of 0.3 μm.

Dumbell shaped ASTM type V tensile specimens were prepared from compression moulded plaques and tested at a constant cross-head speed of 0.5 mm min^{-1}. The yield stress and elongation to failure for each of the six ABS materials are shown in Fig. 4. In materials having a constant matrix molecular weight, the yield stress decreased and strain to failure increased with increasing rubber content. The increase in failure strain with increasing rubber content was more pronounced for ABS specimens containing low matrix molecular weight.

Deformation morphologies were studied in ultramicrotomed sections prepared from stress whitened areas close to the fracture surface. Typical examples of transmission electron micro-

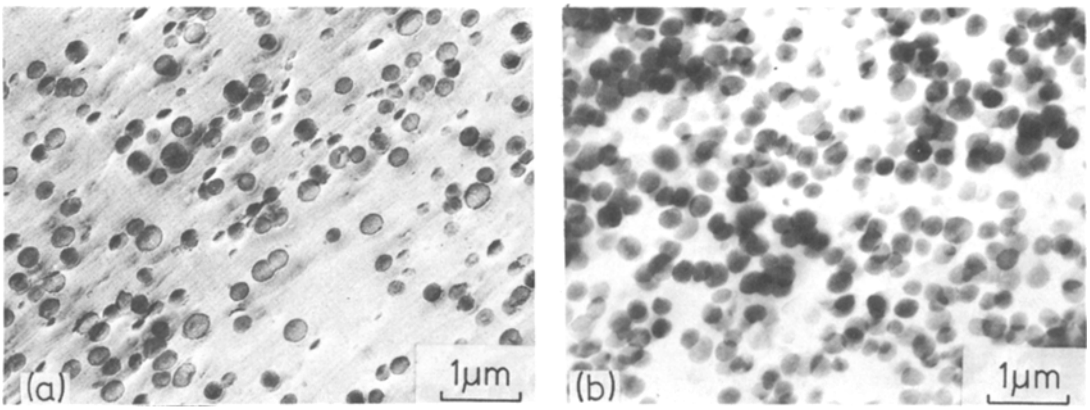

Figure 3 Typical transmission electron micrographs of the microstructure of ABS model compounds containing (a) 10% and (b) 30% rubber contents respectively (matrix $\bar{M}_N = 69 \times 10^3$).

graphs of sections of ABS specimens with matrix $\bar{M}_N = 69 \times 10^3$ and 10% and 30% rubber content are shown in Fig. 5. In all cases craze remnants were observed normal to the applied tensile axis and the predominant deformation mode was considered to be crazing. Similar microstructures were also observed in ABS specimens with matrix $\bar{M}_N = 108 \times 10^3$.

The fracture surfaces of all ABS specimens contained features typical of ductile fracture, i.e. slow and fast crack-growth regions. The extent of the slow crack-growth region increased with increasing rubber content. Representative scanning electron micrographs of the slow crack-growth regions of specimens with 10% and 30% rubber contents are shown in Fig. 6. In the slow crack-growth region of specimens with low rubber content the fracture surface morphology included a uniform dispersion of secondary fracture features which were approximately similar in diameter to the size of rubber particles observed in ultra-microtomed sections. In contrast, the morphology of the slow crack-growth region of specimens with high rubber content contained a highly drawn, fibrillar structure and little indication of individual inclusions.

4. Discussion: The effect of matrix molecular weight and rubber content

The fracture stress of the series of SAN copolymers was found to decrease linearly with decreasing molecular weight until a critical value of $\bar{M}_N$ ($= M_0$) is lower and the fracture stress at this value ($= \sigma_0$) is higher than for polystyrene. For example, values obtained by Fellers and Kee [22] for polystyrene are approximately $M_0 = 70000$ and $\sigma_0 = 35\,\text{MN}\,\text{m}^{-2}$, compared with M_0 between 24000 and 40000 and $\sigma_0 = 50\,\text{MN}\,\text{m}^{-2}$ for the SAN materials used in the present study. Gent and Thomas [24] have stated that M_0 can be regarded as the molecular weight at which the onset of a pronounced increase in tensile strength

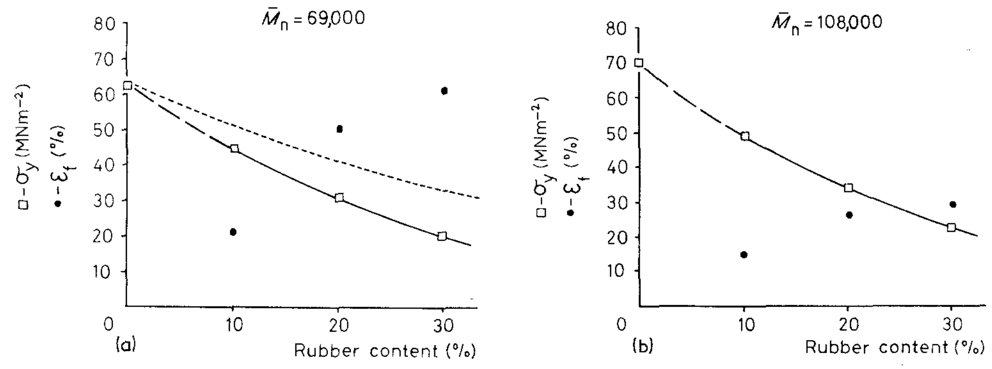

Figure 4 Plot of yield stress, σ_y, and failure strain, ϵ_f, against rubber content for ABS compounds with (a) matrix $\bar{M}_N = 69 \times 10^3$ (---- indicates values of yield stress bases on the effective cross-sectional area of matrix material in the ABS specimens), and (b) with matrix $\bar{M}_N = 108 \times 10^3$.

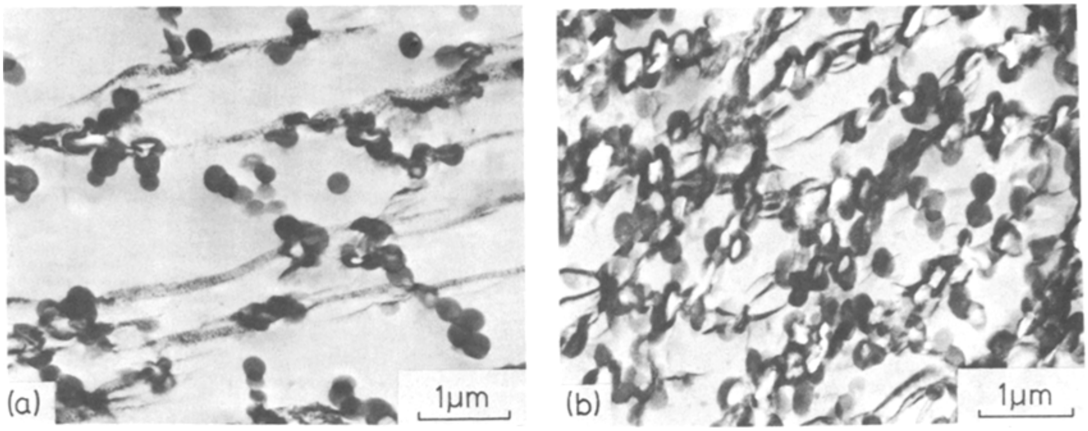

Figure 5 Transmission electron micrographs of ultramicrotomed sections prepared from stress whitened regions of ABS specimens with matrix $\bar{M}_N = 69 \times 10^3$ and (a) 10% and (b) 30% rubber content respectively.

occurs as the molecular weight is increased. These authors found a close correlation between M_0 and the molecular weight at which an entanglement network in the polymer is first apparent. This transition from a brittle material to a material with high tensile strength, with increasing molecular weight, causes a dramatic change in the fracture surface morphology of polystyrene from a glass-like fracture surface to a morphology typical of craze-controlled fracture [25, 26] and this also appears to be the case for SAN.

The differences in M_0 and σ_0 between polystyrene and SAN are most likely related to the presence of polar acrylonitrile groups in SAN which increase molecular chain interactions and therefore increase the resistance of the polymer to craze formation so that higher stresses are required to produce crazes. Additionally, crazes in SAN are generally significantly narrower than those in polystyrene [27, 28] and this may reduce the critical molecular weight requirement to produce stable crazes.

The effect of matrix molecular weight and rubber content on the microstructure and tensile deformation was investigated in a series of ABS polymers with three rubber contents (10%, 20% and 30% by weight), containing a well defined particle size with an average diameter of 0.3 μm, and two matrix molecular weights, namely $\bar{M}_N$ = 69 000 and 108 000. Thus the ABS materials

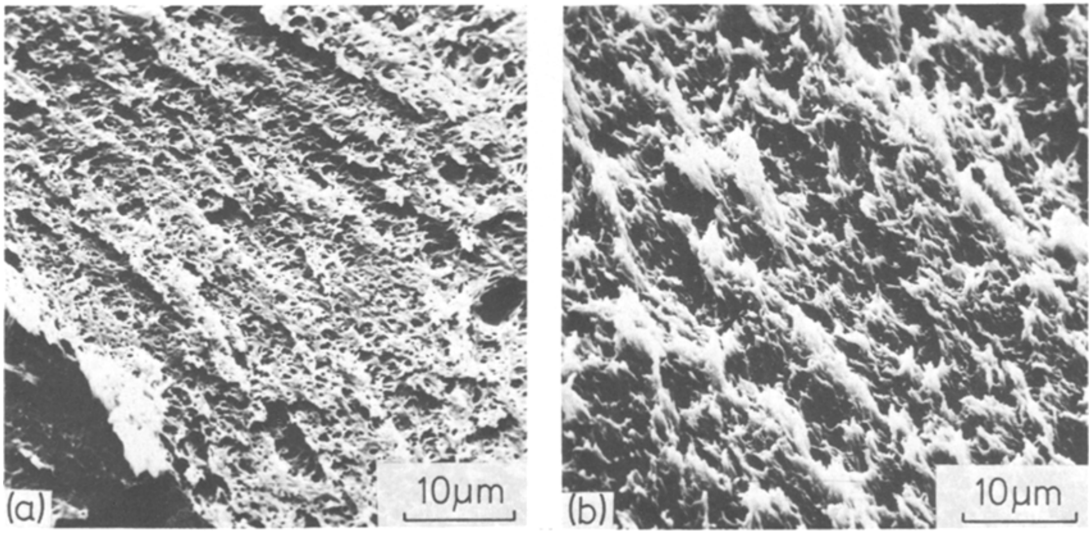

Figure 6 Typical scanning electron micrographs of the regions of slow crack growth on the fracture surfaces of ABS specimens containing (a) 10% and (b) 30% rubber contents respectively (matrix $\bar{M}_N = 69 \times 10^3$).

used had a matrix molecular weight significantly higher than M_0 determined previously, and in terms of suitable mechanical properties could therefore be used in a way which related to commercial practice.

For ABS materials with constant matrix molcular weight, the yield stress decreased substantially with increasing rubber content, in agreement with previous studies [3, 29]. There are several different ways in which the rubber content can affect the yield stress of ABS polymers. Firstly, the addition of rubber to SAN results in a reduction of volume fraction of the load-bearing matrix material. An estimate of this effect has been made by modifying the values of yield stress in terms of the reduction in matrix cross-sectional area, and the result is included in Fig. 4a. It is clear from this result that the reduction in matrix cross-section can only account for a small proportion of the drop in yield stress. The major effect of rubber content on the yield stress is most likely to be due to the concentration of stress in the neighbourhood of the equators of inclusions allowing crazes to form at a lower applied stress. This lowering of craze initiation stress has been convincingly demonstrated by Matsuo *et al.* [30] in a series of experiments on the crazing behaviour of polystyrene specimens containing two 3 mm rubber spheres with varying interparticle spacings. By decreasing the interparticle spacing, which is equivalent to increasing the rubber content, these authors found that stress concentrations rose in the region between the particles so that crazes formed preferentially in this region. Matsuo *et al.* found that the stress fields did not overlap significantly unless the particles were less than $0.9R$ apart, where R is the radius of the particle. A theoretical model developed by Broutman and Panizza [31] indicates that the stress concentration factor increases sharply in the region of 35 to 40%, by volume, of rubber (approximately 30 to 35% by weight) which is probably due to overlapping stress concentrations as the interparticle spacing decreases. However, in a real polymer local variations in the distribution of rubber may reduce this value thereby enhancing craze formation and yielding at lower rubber contents than predicted.

It is well known that increasing the rubber content leads to an increase in failure strain since a material with a high rubber content will initiate more crazes and these will be stabilised by an increased number of surrounding inclusions. However, relatively little attention has been given to the effect of matrix molecular weight other than the deleterious effect of low molecular weight tails [4, 32]. In the present study it was found that the increase in failure strain with increasing rubber content was more pronounced in materials with a lower matrix molecular weight. These results were gained from only five test specimens of each composition, however, the good reproducibility of the tensile tests indicate that the effect is well-founded. It would be reasonable to expect the molecular weight of the matrix to be important in controlling the mechanical properties of rubber modified materials since it is well established that molecular weight influences the size of crazes in glassy polymers. For example, Fellers and Kee [22] observed that crazes in polystyrene with a high molecular weight tended to be long and thin, whereas in low molecular weight materials crazes were short and coarse. Bragaw [33] has reported that the relative dimensions of craze thickness and rubber particle diameters are important in controlling the properties of rubber modifed polymers. However, in the present study very few crazes were observed in the unmodified matrix material during testing, partly due to the geometry of the tensile test specimens and also because of the difference in crazing behaviour of SAN, which therefore precludes further definite comment on the application of the previously reported models to ABS compounds. Nevertheless, the results suggest that an excessively high matrix molecular weight reduces, or possibly a lower matrix molecular weight increases, the efficiency of rubber in toughening ABS polymers.

The deformation behaviour of these model ABS materials was examined in ultra-thin specimens prepared from stress-whitened areas close to the fracture surfaces. In all cases the predominant deformation mechanism was found to be crazing. This result was based on two types of observation. Firstly, crazes were readily identifiable in the electron microscope. Secondly, the only departure from sphericity of the rubber particle was in the vicinity of crazes emanating from the rubber particles which indicated that shear yielding was not operative as a major deformation mechanism. This result suggests that matrix molecular weight and rubber content, as such, are not significantly important in controlling the contribution of shear and crazing processes to the overall deformation behaviour of ABS, and therefore supports the proposal that in order to promote shear yielding craze growth must be restricted, i.e. by large rubber particles. Shear yielding is not readily detectable in ultra-microtomed sections by electron microscopy and it is therefore necessary to rely on changes in rubber particle shape, in the absence of crazing, as an indicator of the operation of shear yielding. Van der Sande and Hall [34] have recently claimed that scanning transmission electron microscopy can result in the successful imaging of shear bands in sections prepared by ultramicrotomy. This is clearly an important development.

The fracture surfaces of all ABS specimens were found to contain characteristic regions corresponding to slow and fast crack growth and the extent of the slow crack-growth region increased with increasing rubber content. On closer examination in the SEM, the slow crack-growth region of specimens containing 10% rubber content, was found to include a large number of voids, similar in size to the rubber particles observed in thin sections, which indicated that for materials with low rubber content crack growth may be associated with breakdown of individual crazes. The slow crack-growth region of specimens containing 30% rubber contained a highly drawn morphology with little indication of individual rubber particles and thus the crack growth mechanism was most likely comparable to that described in detail for commercial ABS materials [35].

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