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Crazing and fracture of polystyrene

Part 1 *A systematic study of variations in craze and fracture surface morphology in a range of commercial polystyrenes*

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An attempt has been made to gain a more detailed understanding of crazing and craze controlled fracture processes in polystyrene, by studying the deformation behaviour of a range of commercially available poly- and monodisperse polystyrenes. The basis of the investigation was the characterization of the microstructures of crazes formed in thin film specimens, and studies of the remnants of crazes retained on the fracture surfaces of bulk specimens. Marked differences in the morphology of crazes and craze-controlled fracture surfaces were observed. Additives and impurities appeared to have more effect than a wide range of molecular weight distributions on the crazing and fracture process.

1. Introduction

It is well established that crazing is a precursor to brittle fracture in many glassy polymers [1–4]. The models that have been developed to explain the fracture process, in terms of the formation and initial growth of a crack within a previously formed craze, have been derived mainly from experimental observations on the fracture of polystyrene [5–9].

The majority of the observations on fracture in this polymer have been confined to investigations of the behaviour of a few general purpose grades. Very little attention has been paid to the effects of the structure and formulation of the polystyrene on the deformation and fracture processes.

In a craze-controlled fracture process, where fracture is controlled by the breakdown of fibrillar craze material, it is reasonable to expect that the structure and formulation of the polymer will influence the micromorphology of the craze and hence, the exact conditions for the nucleation and growth of a crack. This paper reports on an attempt to develop a more detailed understanding of the craze-controlled fracture process in polystyrene, by observing the crazing and fracture behaviour of a range of commercially available polystyrenes, differing in both formulation and molecular weight characteristics.

The basis of the investigation was the characterization of the microstructures of crazes formed in thin film specimens, and studies of the remnants of crazes retained on the fracture surfaces of bulk specimens.

2. Experimental details

The polystyrenes which were used in the investigation together with a description of their molecular weight characteristics are given in Table I. PSA, PSB and PSC were commercial grades with varying molecular weight distributions but similar weight average molecular weights. PSD, PSE, PSF and PSG were monodisperse polystyrenes of varying weight average molecular weights.

The commercial grades contained some impurities such as catalyst remnants, suspension stabilizers and varying amounts of internal lubricant. The monodisperse polystyrenes were specialist polymers such as those used in G.P.C. calibra-

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TABLE I Polystyrenes used, their suppliers and their molecular weight characteristics.

Polystyrene	Supplier	Supplier's code	$\bar{M}_W$	$\bar{M}_N$	$\bar{M}_W/\bar{M}_N$	T_g (° C)
PSA	RAPRA P.S.C.C.	PS1	209 000	94 000	2.2	92.3
PSB		PS2	267 000	148 000	1.8	103.0
PSC		PS3	199 000	117 000	1.7	98.0
PSD	Pressure Chemical Co. Pittsburgh	PS/2b	20 400	20 200	< 1.06	90.0
PSE		PS/4b	110 000	110 000	< 1.06	106.0
PSF		PS/1c	200 000	193 000	< 1.06	102.5
PSG		PS/2a	51 000	51 000	< 1.06	99.0

tion, and were, therefore, largely free from impurities and contained no internal lubricant.

Light and scanning electron microscope observations were made on tensile tested specimens, compression moulded from granules of PSA, PSB and PSC. Observations were also made on tensile tested specimens compression moulded from chopped extruded PSA, PSB and PSC. Tensile tests were carried out at 293 K and a constant cross-head speed of 0.01 cm min^{-1} was used.

The fracture surfaces of hand-broken, compression-moulded pieces of PSD, PSE, PSF and PSG were also examined by light microscopy. Prior to observation in the scanning electron microscope the fracture surfaces of all specimens were coated with a thin layer of gold–palladium alloy by vapour deposition.

To study craze microstructure, thin films were prepared by solvent evaporation of a 5% by weight solution of each polystyrene in xylene, prepared by refluxing. Electron microscope grids were placed on clean glass slides prior to coating with the solution so that after evaporation of the solvent the grids were embedded in a thin polystyrene film. The grids were then strained to produce crazes in the polystyrene films, which were then examined with a transmission electron microscope.

3. Results

3.1. Mechanical properties at 293 K

The stress at the onset of crazing, σ_c, the fracture stress, σ_f, the Young's modulus, the per cent elongation to failure, and the visual craze morphology prior to fracture for each of the three polystyrenes, PSA, PSB and PSC are shown in Table II.

All three of these polystyrenes had $\bar{M}_W$ greater than that for constant mechanical properties [10], so the increase in fracture stress from PSA to PSB was attributed to a narrowing of the molecular weight distribution [11]. PSB and PSC exhibited high craze densities prior to fracture and were quite different from PSA, which, under the same conditions exhibited a low density of coarse crazes prior to fracture. Unlike the specimens of PSA and PSB, the majority of specimens of PSC were observed to reach a yield point just prior to fracture. This is illustrated in Fig. 1 by the examples of typical stress–elongation curves for the three polystyrenes. The yielding which occurred in specimens of PSC was attributed to the high density of fine crazes which formed in the material during the deformation process, i.e. it was attributed to the phenomenon of 'craze yielding' [12, 13].

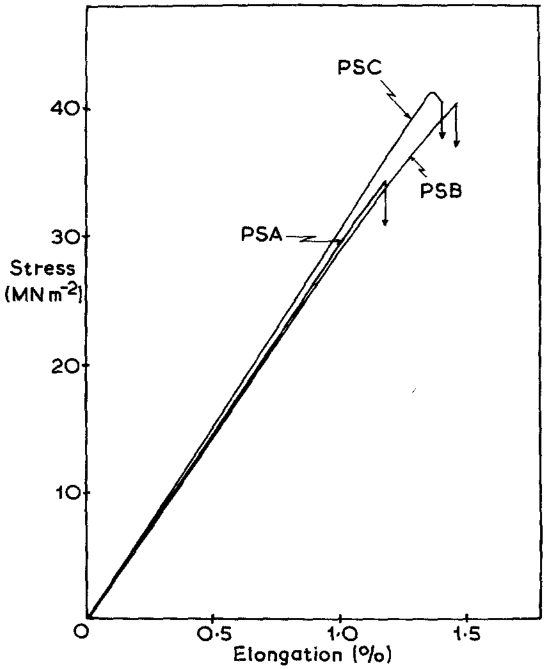

Figure 1 Typical stress–elongation curves for PSA, PSB and PSC tested at 293 K.

TABLE II Mechanical properties of PSA, PSB and PSC at 293 K

Polystyrene	$\bar{M}_W$	$\bar{M}_N$	$\bar{M}_W/\bar{M}_N$	σ_c ($MN\,m^{-2}$)	σ_f ($MN\,m^{-2}$)	Young's modulus ($\times 10^3\,MN\,m^{-2}$)	Elongation to failure (%)	Craze morphology prior to failure
PSA	209 000	94 000	2.2	21.8 ± 2.3	35.8 ± 1.5	3.1 ± 0.2	1.20 ± 0.6	Medium craze size and density
PSB	267 000	148 000	1.8	17.9 ± 1.7	40.0 ± 1.3	3.1 ± 0.2	1.40 ± 0.07	High density narrow crazes
PSC	199 000	117 000	1.7	17.7 ± 4.0	39.5 ± 0.8	3.1 ± 0.2	1.36 ± 0.04	High density narrow crazes

3.2. Fracture surface morphologies at 293 K

The differences in crazing behaviour prior to fracture between PSA, PSB and PSC were reflected in their relative fracture surface morphologies. Fig. 2 shows an optical micrograph of a typical PSA fracture surface. The morphology is very similar to that of a general purpose grade of polystyrene [9] with the exception of the regions indicated by X. On examination in the scanning electron microscope these regions were found to contain large numbers of secondary fracture features which are not normally found in the mackerel-patch region of fracture [9]. A scanning electron micrograph of typical region X is shown in Fig. 3. It was thought that these regions of secondary fracture features may have arisen because of localized craze widening which produced the type of craze morphology normally associated with secondary fracture feature formation, and that this may have occurred in areas where there was a depletion, or a high concentration, of additives caused by incorrect compounding during manufacture of the plastic or fabrication of the specimen.

Figure 2 A light micrograph of the fracture surface of a specimen of PSA fractured at 293 K.

The fracture surfaces of specimens of PSB were found to be almost completely made up of mirror regions. Fracture was observed to have been initiated at a large "particle" and had propagated within an array of crazes which formed before or at the same time as the craze in which

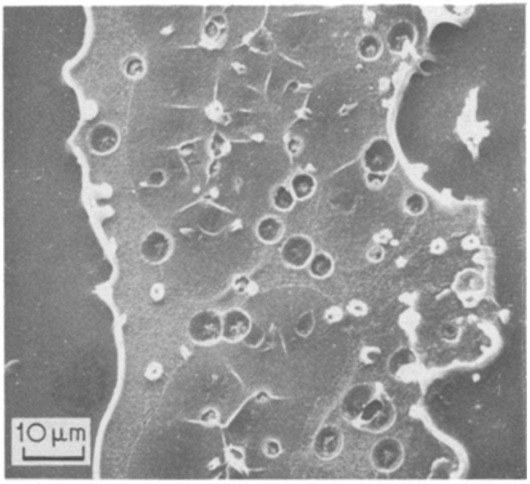

Figure 3 A scanning electron micrograph of an area of secondary fracture features in the "mackerel" region of fracture on the fracture surface of a specimen of PSA fractured at 293 K.

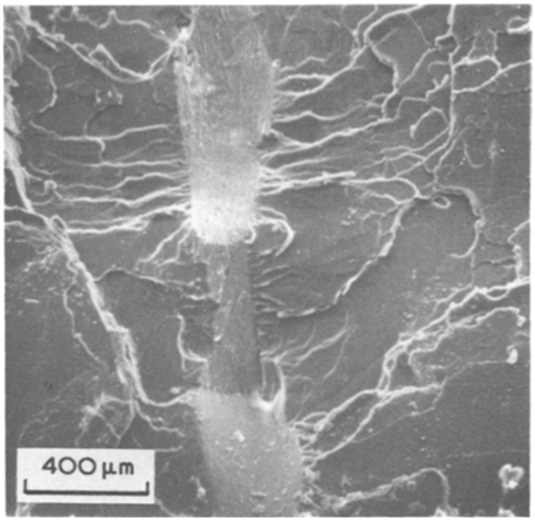

Figure 4 A scanning electron micrograph of the initiation of fracture on the fracture surface of a specimen of PSB fractured at 293 K.

fracture was initiated. A typical example of a fracture surface of PSB is shown in Fig. 4.

The fracture surfaces of specimens of PSC were also found to be almost entirely mirror-like. Fracture was always initiated in a large craze and propagated within an array of preformed crazes. Fig. 5 shows a light micrograph of the initiation region of fracture of a specimen of PSC. On closer examination in the scanning electron microscope, the initiation region of fracture was observed to be very highly voided and the intermediate region was observed to contain a very high density of secondary fracture features. These details are shown in Fig. 6.

The very low molecular weight polystyrene, PSD exhibited a very glass-like fracture surface morphology of the type shown in Fig. 7 and no evidence of craze-controlled fracture was found.

PSG, however, exhibited craze-controlled fracture, and the fracture surfaces consisted of a distinct mirror region and a hackle region of fracture as illustrated by Fig. 8. However, no evidence of mackerel-patch morphologies was found.

PSE exhibited well-defined craze-controlled fracture. The most notable features observed on the fracture surfaces of this material were the long tails of craze material which had been drawn out from the edges of patch structure. An example of this is shown in Fig. 9. PSF also exhibited well-defined craze-controlled fracture. Long tails of craze material drawn out from the edges of patch structure were also observed in this material. The tails were, however, far more pronounced, a detail which is clearly apparent in Fig. 10.

Manual fracture tests, high speed tensile and bend tests were carried out on specimens of a general purpose grade of polystyrene to see if the long tails referred to above were a direct result of the test method used, that is, a high speed bend test. It was found that such tails could be produced in G.P. polystyrene by using a similar test method, but that the tails were less pronounced than those observed in PSF.

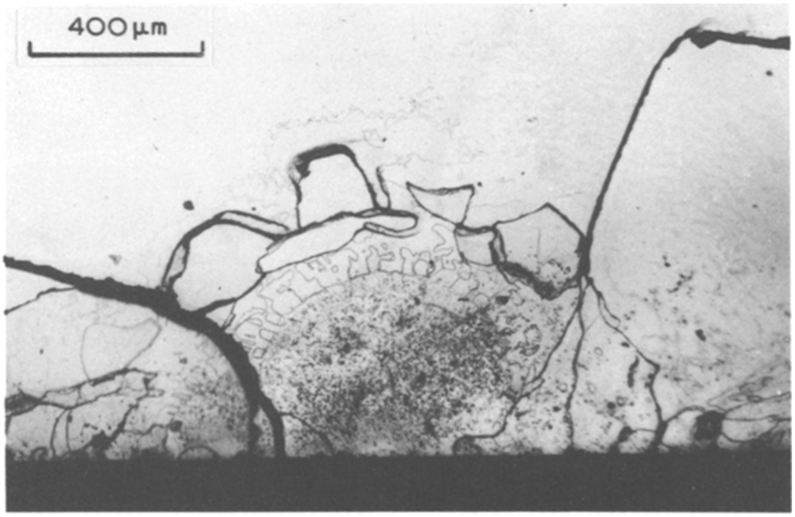

Figure 5 A light micrograph of the initiation and intermediate regions of fracture on the fracture surface of a specimen of PSC fractured at 293 K.

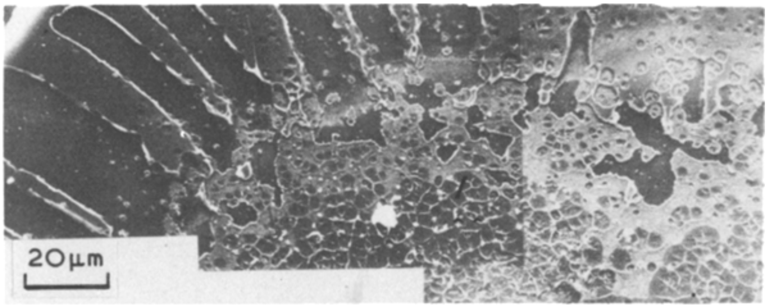

Figure 6 A scanning electron micrograph of the initiation and intermediate regions of fracture on the fracture surface of a specimen of PSC fractured at 293 K.

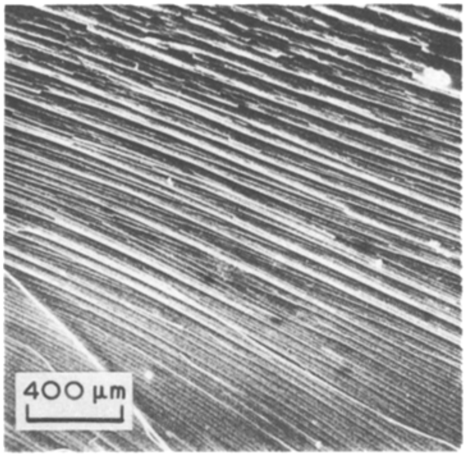

Figure 7 A scanning electron micrograph of the fracture surface of a specimen of PSD.

3.3. Effect of extrusion prior to compression moulding

As described in Section 3.2, the fracture surfaces of PSA exhibited some peculiarities which were thought to be due to poor compounding of of the plastic. PSB had also been found to contain some large particles which affected the fracture process. Samples of PSA, PSB and PSC were, therefore, extruded prior to compression moulding in order to improve the compounding and to break up and disperse impurities.

The mechanical properties of all three polystyrenes were markedly affected by extruding prior to moulding. In the case of PSA, the fracture stress and elongation to failure increased by about 15%. This is illustrated by Fig. 11 which shows stress–elongation curves for PSA moulded as-received and moulded after extrusion. The visual craze morphology prior to fracture was also affected. A dense zone of crazes was seen to nucleate at one edge of the specimen and as the load increased the zone grew across the specimen. Failure occurred within the zone just before it reached the opposite specimen edge.

Stress–elongation curves of specimens of PSB moulded as-received and moulded after extrusion (Fig. 12) indicate that the fracture stress increased by about 10%, the elongation to failure increased by about 25%, and that yielding was more pronounced. A dense zone of fine crazes was seen to nucleate on one specimen edge and grow across the specimen under the applied

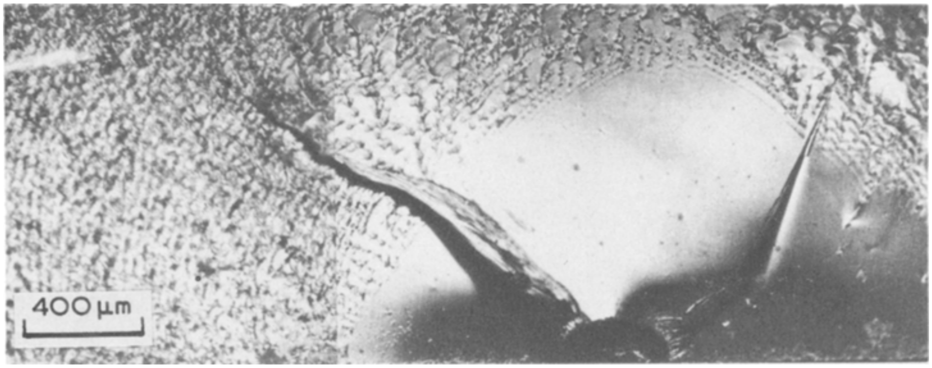

Figure 8 A light micrograph of the fracture surface of a specimen of PSG.

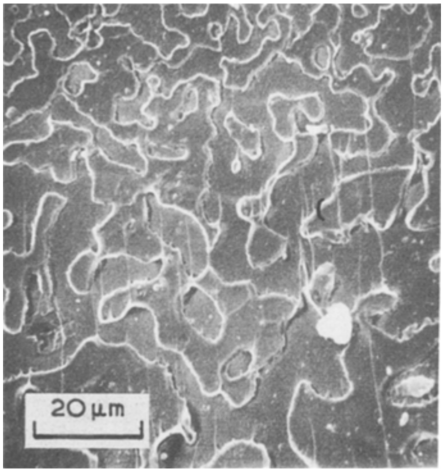

Figure 9 A scanning electron micrograph of "patch" sturucture on the fracture surface of a specimen of PSE showing the presence of long tails.

load. In this case, however, the zone reached the opposite specimen edge at which point yielding occurred. The zone then expanded in a direction parallel to the tensile axis until fracture occurred within the zone. This is the phenomenon known as craze-yielding.

PSC on the other hand exhibited a slight drop in fracture stress and elongation to failure, and no yield was observed.

The fracture surface of a specimen of PSA extruded prior to moulding (Fig. 13) showed that fracture had initiated in a large preformed craze and had propagated through several other preformed crazes. The fracture surface was, however, not completely mirror-like and a hackle region was evident. No regions of secondary fracture features of the type indicated by X in Fig. 2 were observed in the Mackerel-patch region of fracture, but large numbers of secondary fracture features were seen in the intermediate region of fracture.

PSB extruded prior to moulding exhibited the fracture surface morphology associated with craze-yielding (Fig. 14), i.e. initiation of fracture occurred in a large craze and the crack then propagated through an array of preformed crazes to produce a completely mirror-like fracture surface. No evidence of "particles" was observed, although the initiation region of fracture was large and highly voided.

The fracture surface morphology of PSC was relatively unaffected by extruding prior to moulding. The hackle region was, however, more in evidence and crack propagation had proceeded through only a few preformed crazes.

3.4. Craze morphology

Thin films of the different grades of polystyrene were prepared for examination in the electron microscope in the way described in Section 2. On comparing the morphologies of crazes formed in PSA, PSB and PSC, it was observed that there was no trace of impurity particles in the films of PSB, indicating that the impurities had been lost during the solvent casting process. Another feature that was immediately apparent was the large number of secondary fracture features which had formed in crazes in PSC. This result indicated that with respect to secondary fracture features there was a good correlation between the morphology of crazes formed in thin films and the morphology of crazes formed in the bulk specimens. Fig. 15 shows a composite electron micrograph of a craze formed in PSA and Fig. 16 one formed in PSC.

PSD, the very low molecular weight, monodisperse polystyrene, did not exhibit well-defined crazing. Cracks were observed, but some material

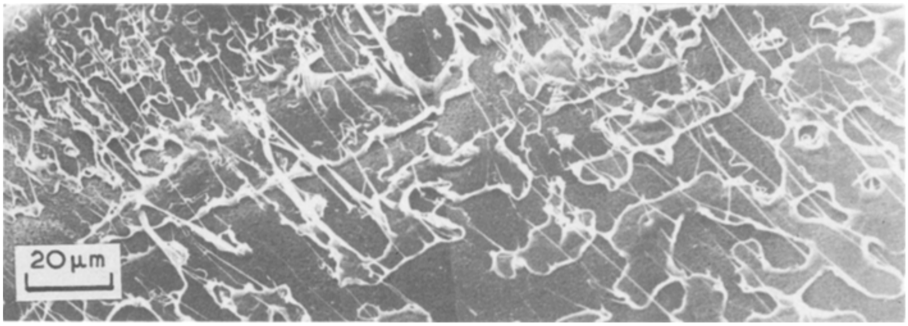

Figure 10 A scanning electron micrograph showing the presence of very long tails drawn out from "patch" structure on the fracture surface of a specimen of PSF.

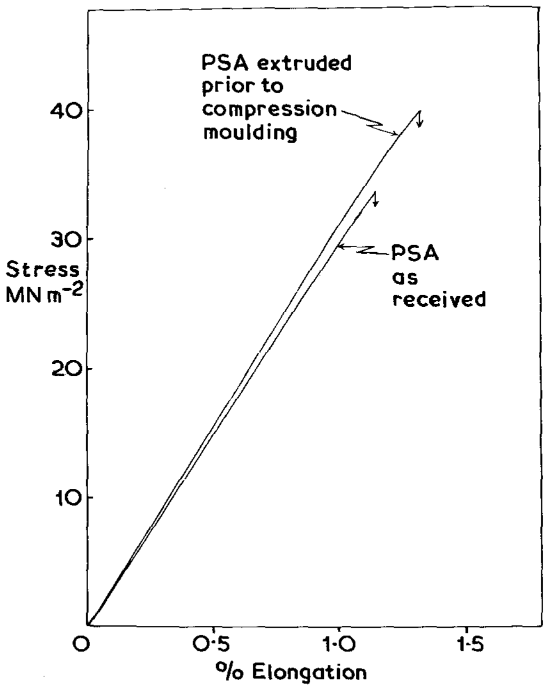

Figure 11 Typical stress–elongation curves for specimens of PSA moulded as-received and extruded prior to compression moulding, tested at 293 K.

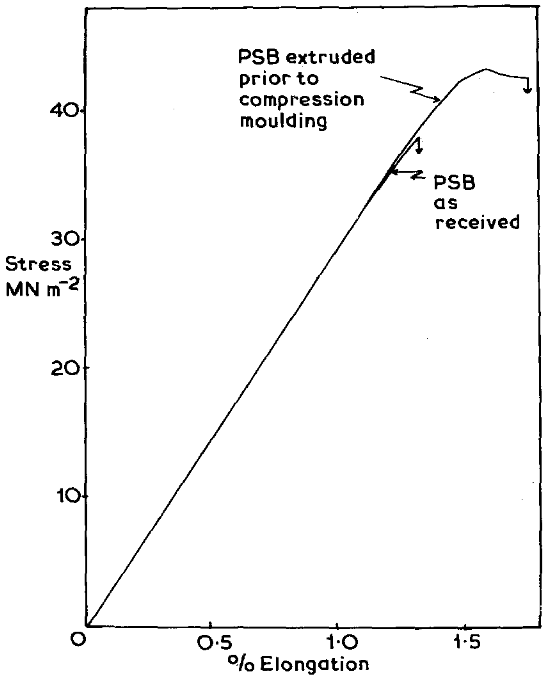

Figure 12 Typical stress–elongation curves for specimens of PSB moulded as-received and extruded prior to compression moulding, tested at 293 K.

different from the surrounding matrix material was found at the tips of these cracks, although no fibrillar structure could be resolved in this material. One example of a transmission electron micrograph of a deformed film of PSD is shown in Fig. 17.

Crazes with well-defined fibrillar structures were, however, observed in PSG, an example of which is shown in Fig. 18. The fibres had diameters in the range 24 to 60 nm. Failure of the fibres occurred at craze widths in the range 0.3 to 0.4 μm and no well-defined breakdown of major to minor fibres was observed.

PSE and PSF both exhibited well-developed crazes similar to those observed in PSA. Thus in order to try to develop a better understanding of the differences in craze morphology throughout the range of polystyrenes, measurements as outlined in Fig. 19 were made on transmission electron micrographs of crazes formed in thin films of all of the polystyrenes, the results of which are shown in Table III. These measurements indicated that the angle α between the craze–matrix interfaces at the craze tip is constant, throughout the range of polystyrenes, at 2°. The angle β at the start of the region of breakdown of major to minor fibres was low for PSE, which had $\bar{M}_W$ below the level for constant properties [10], whereas the other polystyrenes, with $\bar{M}_W$ above the level for constant mechanical properties had

TABLE III Results of measurements on electron micrographs of crazes

	$\bar{M}_W$	$\bar{M}_N$	$\bar{M}_W/\bar{M}_N$	α	β	a (μm)	Fibre diameter at tip (nm)	Fibre diameter at a(nm)
PSA	209 000	94 000	2.2	2°	9° ± 4°	1.90 ± 0.4	30 ± 5	20 ± 5
PSB	267 000	148 000	1.8	2°	8° ± 1°	2.15 ± 0.4	30 ± 10	20 ± 5
PSC	199 000	117 000	1.7	2°	9° ± 2°	2.24 ± 0.34	30 ± 5	20 ± 5
PSD	20 400	20 200	< 1.06	2°	–	–	–	–
PSG	51 000	51 000	< 1.06	2°	–	–	24 → 60	–
PSE	110 000	110 000	< 1.06	2°	6° ± 1°	1.01 ± 0.32	20 ± 5	20 ± 5
PSF	200 000	193 000	< 1.06	2°	9° ± 1°	1.31 ± 0.17	30 ± 5	20 ± 5

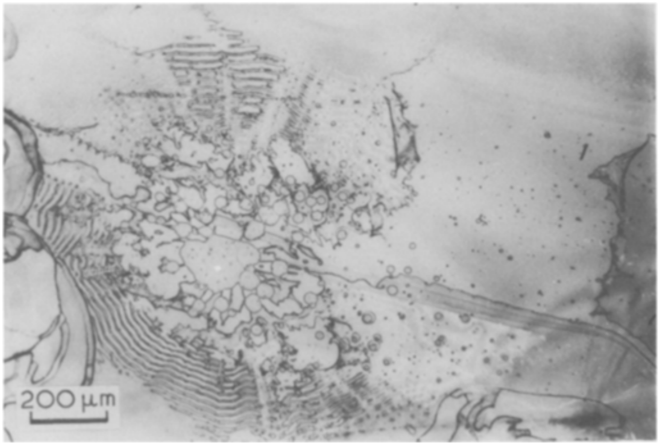

Figure 13 A light micrograph of the fracture surface of a specimen of PSA extruded prior to compression moulding.

similar values of β. The value of the craze width a at which breakdown of major to minor fibres first occurred was low for the monodisperse polystyrenes compared to the broader distribution polystyrenes. There appeared to be little variation in the diameters of fibres at the craze tip with changing molecular weight characteristics.

Figure 14 A light micrograph of the fracture surface of a specimen of PSB extruded prior to compression moulding.

4. Discussion

4.1. Polydisperse grades

It was immediately apparent that there were quite marked differences between the three polydisperse polystyrenes PSA, PSB and PSC, in particular in their respective fracture stress values and the morphologies of their fracture surfaces. At room temperature PSA exhibited a similar fracture stress and fracture surface morphology, except for the regions of secondary fracture features which occurred in the Mackerel-patch region of fracture, to that of a general purpose grade of polystyrene. The results for PSB were inconclusive because of the presence of large "particles" which initiated fracture and, therefore, controlled the value of the fracture stress and the appearance of the fracture surface. PSC exhibited craze yielding and the associated fracture surface morphology, which has previously been reported to occur in a heat-resistant grade of polystyrene [7, 12], that is, a grade of polystyrene of high average molecular weight, free from internal lubricant and containing a minimum of residual styrene monomer or low molecular weight products.

On extruding these polystyrenes prior to compression moulding, their properties were found to change quite markedly. PSA exhibited an increase in fracture stress and a slightly altered fracture surface morphology. PSB exhibited craze-yielding and the associated fracture surface morphology, which also involved an increase in fracture stress. PSC, however, showed a decrease in fracture stress and did not exhibit craze-yielding

Fig. 20 illustrates schematically the process of craze-yielding. The high density of fine crazes

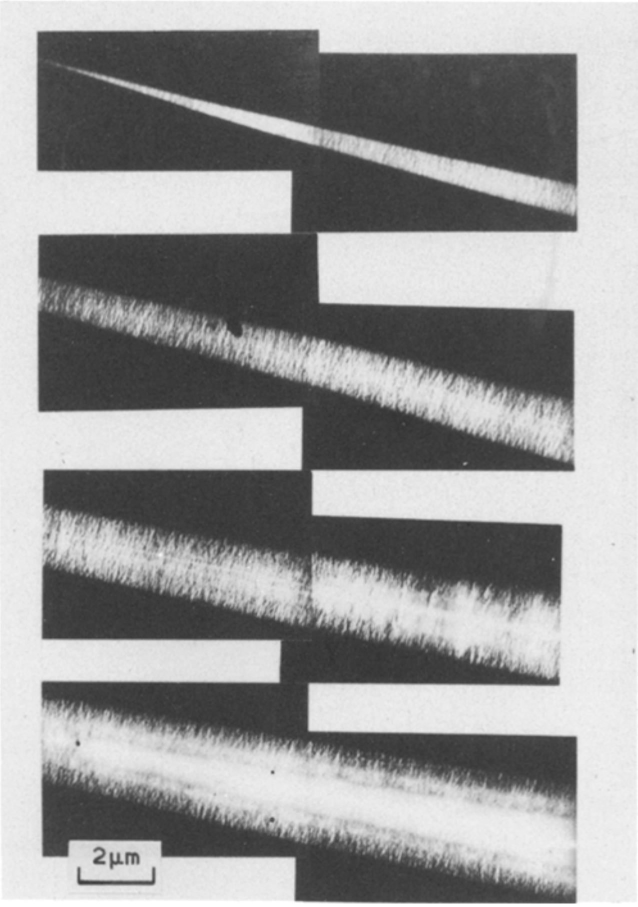

Figure 15 A composite transmission electron micrograph of a craze formed in a solvent cast thin film of PSA.

formed prior to failure also gives rise to a fracture surface which is completely mirror-like. In this case a propagating crack reaches the tip of the craze in which it was nucleated, and then jumps to and propagates through a "pre-existing" craze, rather than a craze generated by the stress field at the tip of the craze in which nucleation occurred. At room temperature PSC exhibited this phenomenon, but failure occurred just at the yield point, i.e. when the zone had just reached the opposite specimen edge. Specimens of PSA, extruded prior to moulding were observed to nucleate a zone of dense crazes but failure occurred just before the zone reached the opposite specimen edge, i.e. just before yield would have occurred. Thus by extruding prior to moulding the behaviour of PSA became similar to the behaviour of PSC moulded as-received. This similarity was also apparent when comparing the fracture surfaces of these two materials. This suggested that some of the internal lubricant in PSA was lost during the extrusion process making it behave like a heat-resistant grade. The migration of internal lubricant to the die walls during extrusion and to the plaque surface during the subsequent compression moulding could account for this.

The fall off in the properties of PSC when extruded prior to moulding could only be attributed to degradation of the polymer or to take up of impurities which occurred during the extrusion process.

The increase in the properties of PSB extruded prior to moulding could be due to the particles being broken up and evenly dispersed by the extrusion process, thus providing more sites for craze nucleation and therefore, giving rise to craze-yielding. It should be noted that no evidence of particles was found on the fracture surfaces of PSB extruded prior to moulding.

No major differences in the morphologies of crazes formed in solvent-cast thin films of PSA, PSB and PSC were observed, except for the large numbers of secondary fracture features observed in crazes formed in PSC. From the results of this

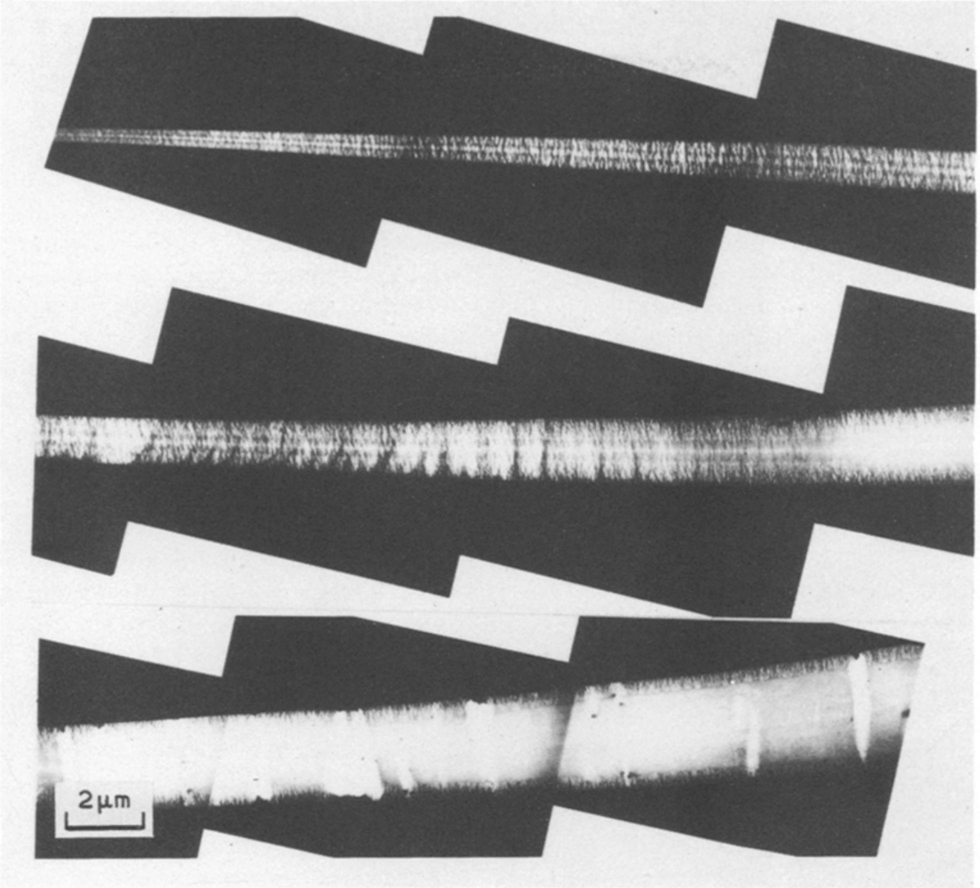

Figure 16 A composite transmission electron micrograph of a craze formed in a solvent cast thin film of PSC.

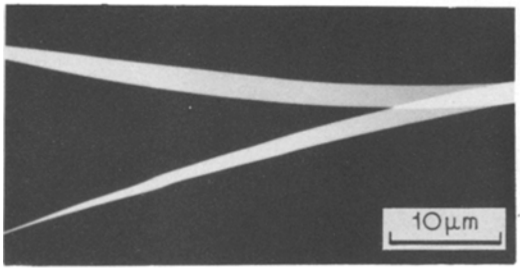

Figure 17 A transmission electron micrograph of a "craze" formed in a solvent cast thin film of PSD.

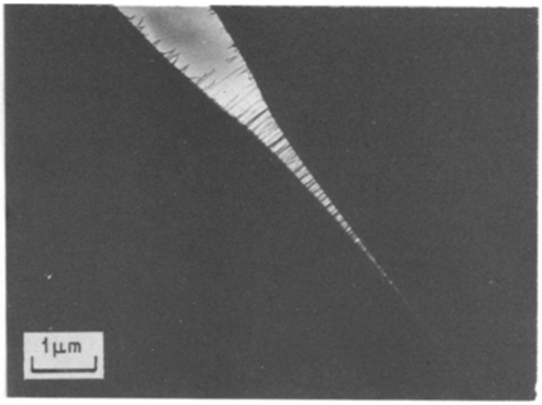

Figure 18 A transmission electron micrograph of a craze formed in a solvent cast film of PSG.

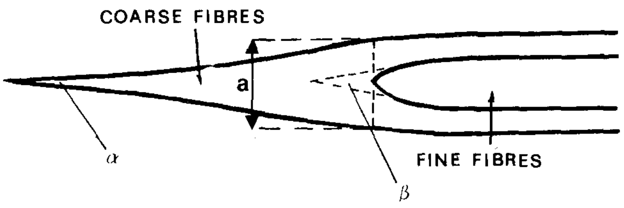

Figure 19 A schematic representation of a craze indicating the parameters measured.

investigation it is evident that secondary fracture feature formation is more pronounced in polystyrenes which are free from lubricant.

The differences in behaviour between PSA, PSB and PSC were mainly due to variations in craze density formed prior to fracture which were in turn due to varying amounts of additives and impurities. A dependence of the properties of these three polystyrenes on molecular weight characteristics could, therefore, not be conclusively stated.

4.2. Monodisperse grades

PSD, $\bar{M}_W = 20\,400$, did not exhibit craze-controlled fracture in the bulk or well-defined crazing in thin film specimens. PSG, $\bar{M}_W = 51\,000$, however, exhibited both well-defined crazes in thin film specimens and craze-controlled fracture in the bulk. Thus the onset of craze-controlled fracture in polystyrene must occur between $\bar{M}_W = 20\,400$ and $\bar{M}_W = 51\,000$.

This result agrees well with the theory of Gent and Thomas [14] who predicted that the onset of craze-controlled fracture would occur at a characteristic molecular weight M_c at which an entanglement network first becomes apparent in the polymer, which, in the case of polystyrene, lies between $\bar{M}_W = 30\,000$ and $\bar{M}_W = 35\,000$.

PSE, $\bar{M}_W = 110\,000$, and PSF, $\bar{M}_W = 200\,00$, both exhibited well-defined crazes in thin film specimens and craze-controlled fracture in the bulk. A point in need of further clarification is the existence of long tails emanating from the patch structure on fracture surfaces of PSE and PSF. Similar tails were also observed by Haward and Brough [15] on the fracture surfaces of high molecular weight polystyrene. Both in this investigation and that performed by Haward and Brough the polystyrene specimens which exhibited these features were fractured manually, and it is this method of fracturing which gives rise to the long tails. In a tensile test at low strain-rate, short tails are formed on the edges of Mackerel bands on the fracture surface of polystyrene. This has clearly been demonstrated by Beahan *et al.* [9]. The mechanism of formation of these short tails has also been described by the same authors.

The same process occurred in PSE and PSF, but because of the rapid separation of the fracture surfaces a build up of heat resulted within the craze which allowed very large extensions of the tails before they fractured. This is shown schematically in Fig. 21. The molecular weight characteristics of the polystyrene affect the length of these tails. PSF the higher molecular weight polystyrene exhibited much longer tails than those formed in the lower molecular weight polystyrene PSE, the tails formed in PSF being able to accommodate much larger strains before they failed.

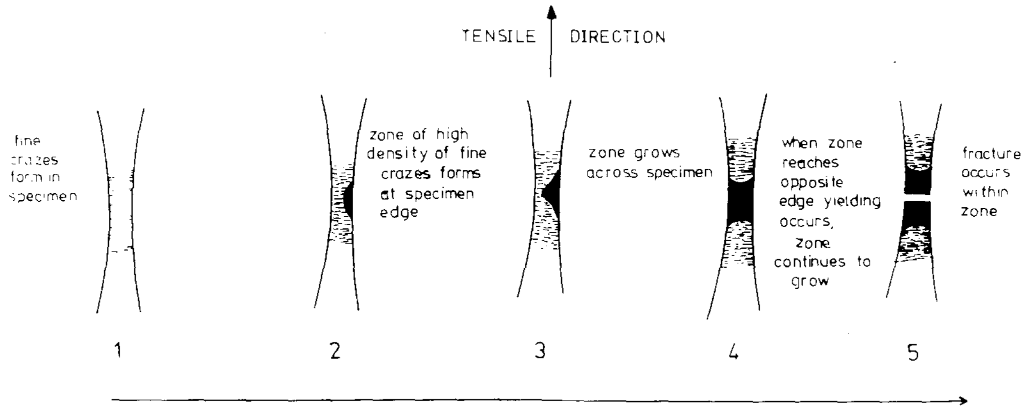

Figure 20 A schematic representation of the process of "craze-yielding".

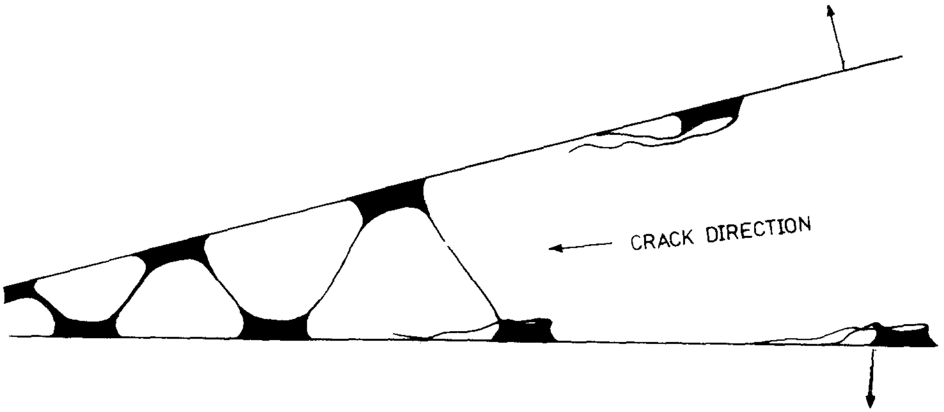

Figure 21 A schematic diagram illustrating the formation of long tails on the fracture surfaces of some polystyrenes.

5. Conclusions

At very low molecular weight well-defined crazes do not occur in polystyrene and therefore, fracture, is not craze-controlled. The polystyrene has very little strength and fractures in a brittle manner to give a glass-like fracture surface. At higher molecular weights well-defined crazes are observed, although the craze fibres cannot accommodate very large strains. Fracture is, however, craze-controlled, but the polystyrene still has little strength. This transition at low molecular weights from a brittle glass-like fracture to craze-controlled fracture occurs between $\bar{M}_W = 20400$ and $\bar{M}_W = 51000$ and may be associated with the occurrence of an entanglement network in the polymer. At higher molecular weights well-defined crazes are observed whose fibres can accommodate large strains.

In commercial polydisperse systems it was difficult to distinguish between effects caused by molecular weight characteristics and effects caused by additives and impurities, although the additives and impurities which are present in the plastics probably have a more siginficant effect on the fracture process than variations in molecular weight.

The microstructure and geometry of crazes is affected little by variations in molecular weight characteristics or additive and impurity content and, with one exception, the results of this investigation support the model of craze morphology and craze-controlled fracture in polystyrene proposed by Beahan *et al.* [9]. The exception is connected with fracture after craze yielding [12, 13] which is believed to be associated with the absence or low concentrations of lubricant.

The results presented above are clearly not conclusive in relation to the identification of the effects of additives on the deformation and fracture of polystyrene. This was mainly as a result of the limited amount of information available to the authors about the additives which were present in the polydisperse grades. Consequently, it was felt that a more detailed study of the effects of additive and impurity content on crazing and fracture in polystyrene would lead to better understanding of fracture in polystyrene. An investigation was therefore made of the effect of polymerization route, i.e. polystyrenes produced by the bulk and suspension processes, and the effect of lubricant concentration on the crazing and fracture behaviour of both plastics. The results will be presented in a subsequent paper.

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