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Crazing and fracture of polystyrene

Part 2 *The effect of polymerization route and internal lubricant concentration*

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The effects of the concentration of internal lubricants on the deformation and fracture of commercial polystyrenes produced by bulk and suspension polymerization routes are described. The addition of internal lubricant in the range 0 to 6% was shown to cause a decrease in the extent of craze-yielding and in the incidence of secondary fracture features, and over-all the changes in behaviour were similar to those observed when the test temperature is increased.

1. Introduction

Beahan *et al.* [1] have developed a model for the craze-controlled fracture process in polystyrene by taking into consideration the micromorphology of crazes in which nucleation and propagation of cracks occurs. Their results indicate that the micromorphological characteristics of the craze could dictate the conditions for the nucleation and growth of a crack. The fracture model has been modified slightly [2] to take account of additional features observed in failure of crazes over a range of temperatures between 78 and 360 K.

In such a craze-controlled fracture process, where fracture is controlled by the breakdown of fibrillar craze material, it is reasonable to assume that the structure and formulation of the polymer will influence the micromorphological characteristics of the craze and hence the exact conditions for the nucleation and growth of the crack.

In the preceding paper [3] a systematic study was made of variations in craze and fracture surface morphology in a range of commercial polystyrenes having different molecular weight characteristics and additive contents. The results suggested that additive and impurity content had a significant effect on the fracture process. In addition, studies by other workers [4–7] have indicated that additives, in particular internal lubricant, can affect the deformation processes in polystyrene.

In this investigation an attempt has been made to clarify the effect which additives have on the deformation mechanisms in polystyrene and hence develop a more detailed understanding of the craze-controlled fracture process. A systematic study of the effect of polymerization route and internal lubricant concentration on crazing and fracture behaviour in polystyrene has, therefore, been carried out.

2. Experimental details

The polystyrenes used together with a description of their molecular weight characteristics, are shown in Table I and extend the number of poly-

TABLE I Polystyrenes used and their molecular weight characteristics

Polystyrene	$\bar{M}_w$ ($\times 10^3$)	$\bar{M}_n$ ($\times 10^3$)	$\bar{M}_w/\bar{M}_n$	T_g (°C)
PSH	192	100	1.92	99.0
PSJ	197	78	2.53	97.0
PSK	185	105	1.76	89.0
PSL	212	101	2.10	90.0
PSM	180	108	1.67	78.0
PSN	238	129	1.84	79.0
PSP	217	101	2.15	69.0

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TABLE II Methods used to polymerize the polystyrenes and their respective lubricant contents

Polystyrene	Polymerization route	Lubricant concentration (%)
PSH	Suspension	0
PSJ	Bulk	0
PSK	Suspension	2
PSL	Bulk	2
PSM	Suspension	4.5
PSN	Bulk	4.5
PSP	Suspension	6.0

styrenes studied in this investigation of fracture in polystyrenes [3] to fourteen. The methods by which these polystyrenes were polymerized and their respective internal lubricant contents are shown in Table II. Those manufactured by a suspension route contained a number of suspension stabilizers and catalysts, whereas those manufactured by a bulk route contained no such additives.

Light microscope observations were made on tensile-tested specimens compression-moulded from pellets. Tensile tests were carried out at 293 K on an Instron machine using a constant cross-head speed of 0.01 cm min^{-1}.

To study craze microstructure, thin sections of the polystyrenes were produced by sectioning uncrazed compression-moulded bulk material with an ultramicrotome at room temperature using glass knives and a cutting speed of 2.0 cm min^{-1}. The sections were collected on electron microscope grids in deionized water and were then deformed by straining the grids manually in a microstraining device.

This method was used in preference to solvent casting as in the latter case some of the additives could have been removed by the solvent.

3. Results

3.1. Mechanical properties

The tensile properties of all seven of the polystyrenes listed in Table I were measured and although there were no changes in modulus, the fracture stress and, therefore, the elongation to failure were found to vary with both lubricant concentration and polymerization route. This is illustrated by the plots of fracture stress versus lubricant concentration for both the bulk-polymerized polystyrenes and the suspension-polymerized polystyrenes shown in Figure 1.

The largest difference in fracture stress can be seen to be between the bulk and suspension polymerized polystyrenes PSJ and PSH which were free from lubricant. This is further illustrated by the examples of the stress-elongation curves of both of these polystyrenes shown in Figure 2. Apart from the fact that PSH, the suspension polymer, exhibited a higher fracture stress than PSJ, the bulk polymer, PSH craze-yielded just prior to fracture.

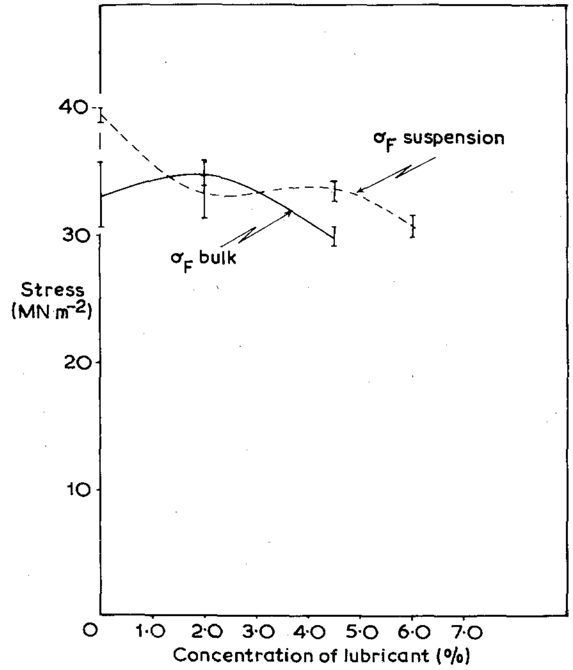

Figure 1 A plot of fracture stress versus lubricant concentration for bulk- and suspension-polymerized polystyrenes.

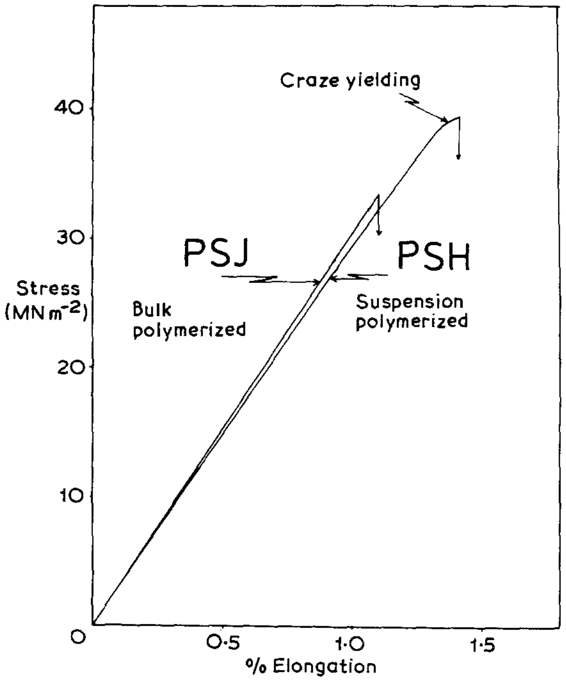

Figure 2 Typical stress-elongation curves for specimens of PSH and PSJ.

The differences in mechanical behaviour between PSK and PSL which contained 2% lubricant were not very large, whereas when the lubricant concentration was increased to 4.5% the suspension polymer, PSM, again exhibited a markedly higher fracture stress than the bulk polymer, PSN.

3.2. Fracture surface morphology

The fracture surface morphologies of PSH and PSJ differed mainly by the fact that PSH exhibited craze-yielding and, therefore, exhibited the associated fracture-surface morphology. That is, crack nucleation in a large preformed craze followed by propagation of the crack through an array of preformed crazes to give a completely mirror-like fracture surface [3, 6]. An example of the fracture surface of a specimen of PSH is shown in Figure 3. The initiation region of fracture was observed to be highly voided. PSJ also exhibited a highly voided initiation region, but in this case the mirror region was very small and was followed by a distinct hackle region [1]. An example of the fracture surface of a specimen of PSJ is shown in Fig. 4. Both PSH and PSJ exhibited large numbers of secondary fracture features in their respective initiation and intermediate regions of fracture.

As the lubricant concentration was increased to 2%, the suspension polymer PSK was found not to exhibit craze yielding, but the initiation and intermediate regions of fracture were still found to contain large numbers of secondary fracture features. An example of the initiation region of fracture in a specimen of PSK is shown in Fig. 5. The mirror regions were generally large and exhibited well-

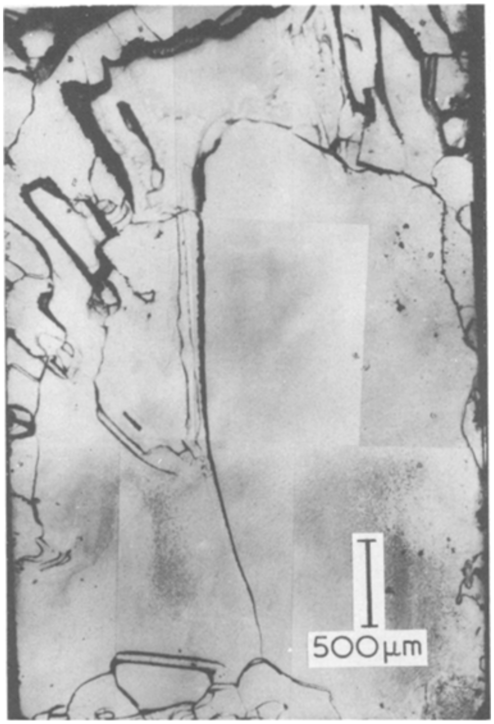

Figure 3 A composite light micrograph of the fracture surface of a specimen of PSH.

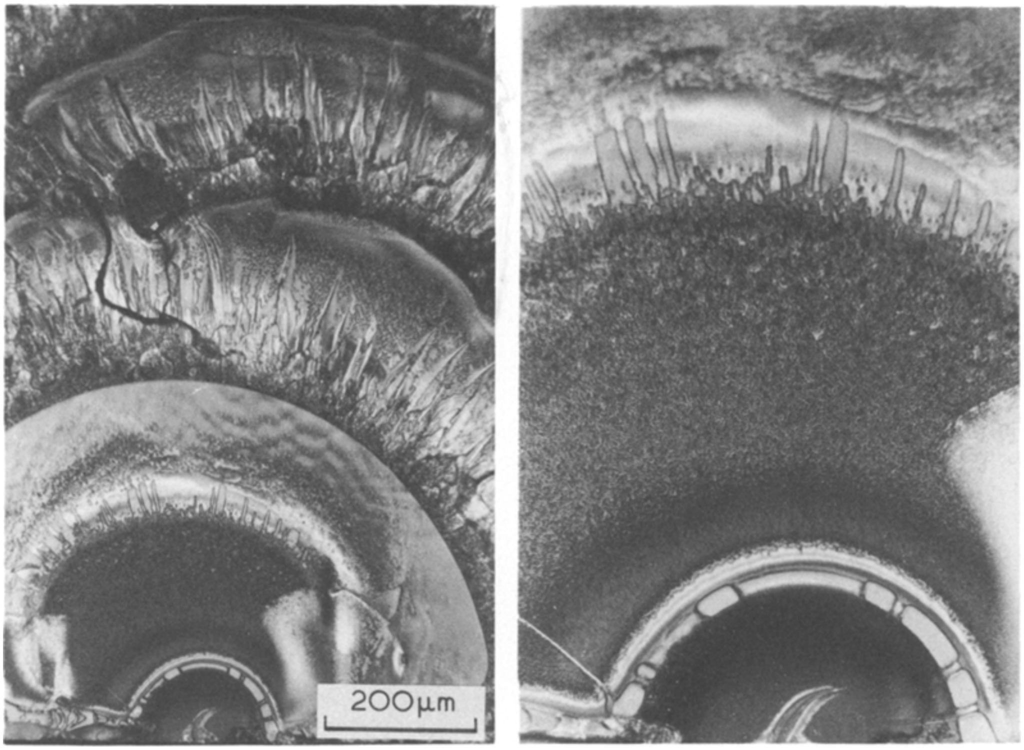

Figure 4 Light micrographs of the fracture surface of a specimen of PSJ. The low magnification micrograph shows the hackle bands.

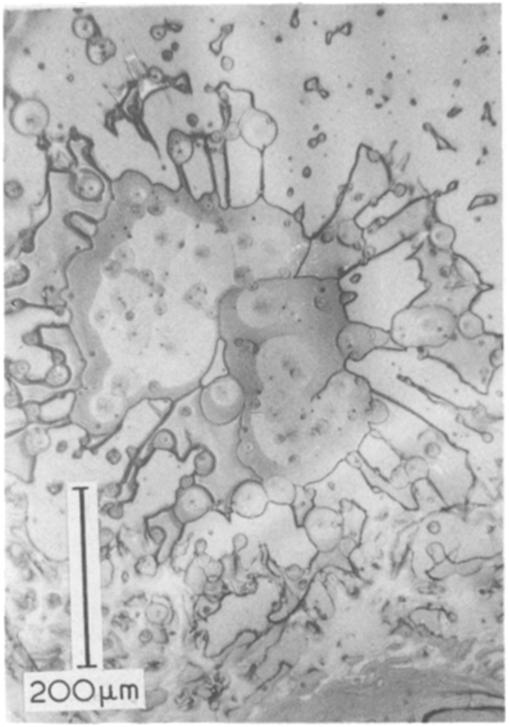

Figure 5 A light micrograph of the fracture surface of a specimen of PSK.

defined mackerel-patch and hackle regions. There was evidence of crack propagation through preformed crazes. The bulk polystyrene PSL contained 2% lubricant and exhibited a small initiation region of fracture with very few secondary fracture features and well-defined mackerel-patch and hackle regions. The fracture surface morphologies of suspension polystyrenes PSM and PSK which contained 4 and 2% lubricant respectively were very similar. The initiation region of fracture of a specimen of PSM is shown in Fig. 6. The bulk polystyrene PSN contained 4.5% lubricant and exhibited a very flat initiation region of fracture with no secondary fracture features, and well-defined mackerel patch and hackle regions. An example of the initiation region of fracture in a specimen of PSN is shown in Fig. 7. PSP, the suspension polystyrene containing 6% lubricant, exhibited an initiation region containing a number of secondary fracture features and well-defined mackerel-patch and hackle regions.

Thus, the suspension polystyrenes exhibited far larger numbers of secondary fracture features in their initiation and intermediate regions of fracture throughout the range of lubricant concen-

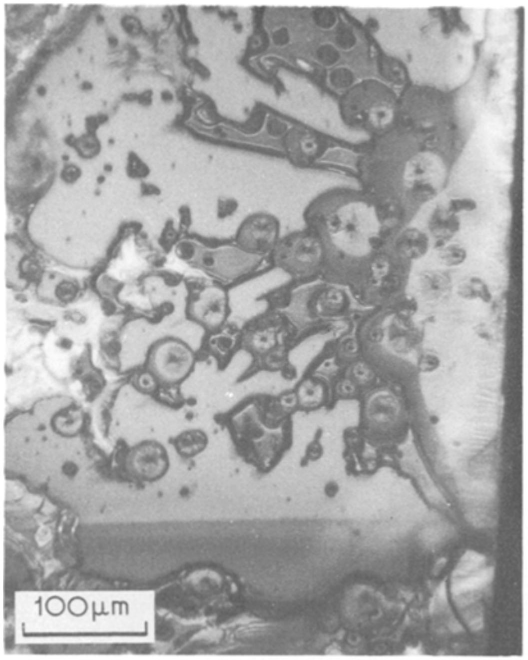

Figure 6 A light micrograph of the fracture of a specimen of PSM.

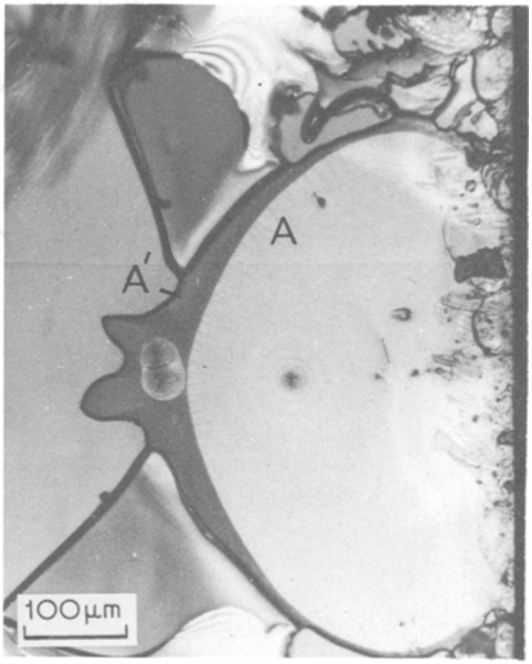

Figure 7 A light micrograph of the fracture surface of a specimen of PSN.

trations. The main difference occurred between 0 and 2% lubricant when there was a change from craze-yielding to brittle craze-controlled fracture.

3.3. Craze morphology

The morphologies of crazes formed in PSH and PSJ were compared in order to establish the effect of polymerization conditions, and the morphologies of crazes formed in PSH and PSP were compared in order to identify the effect of lubricant concentration.

A comparison of the craze microstructures was made by carrying out the measurements, outlined in Fig. 8, on transmission electron micrographs of crazes formed in the three polystyrenes. The results of these measurements are shown in Table III. Comparing the results for PSH and PSJ it can be seen that the craze width a is slightly higher in the case of PSJ and that the angle α and the fibre diameters at both a and the craze tip in both materials are similar.

TABLE III Results of measurements on electron micrographs of crazes formed in ultramicrotomed sections of PSH, PSJ and PSP

	α	a (µm)	Fibre diameter at a (Å)	Fibre diameter at craze tip (Å)
PSH	1° → 2°	0.20 ± 0.03	210 ± 20	220 ± 40
PSJ	1° → 2°	0.24 ± 0.04	210 ± 60	250 ± 60
PSP	1° → 2°	0.15 ± 0.02	150 ± 25	150 ± 50

Comparing the results for PSH and PSP it can be seen that the craze width a and the fibre diameters at both a and the craze tip are reduced by the presence of a large concentration of lubricant. Thus, the polymerization route used to manufacture the polystyrene appears to have only a slight effect on craze microstructure, whereas the presence of lubricant has a more marked effect.

4. Discussion

The effect of polymerization conditions on craze-controlled fracture was most noticeable when comparing the behaviour of PSH and PSJ, the two polystyrenes which were free of internal lubricant. PSH, the suspension polymerized polystyrene, exhibited craze yielding and the associated fracture surface morphology. The initiation and intermediate regions of fracture were seen to contain large numbers of secondary fracture features. PSJ the bulk polymerized polystyrene did not exhibit craze-yielding and failed at a lower stress than PSH. The fracture surface consisted of a small mirror region containing a large initiation region of fracture. The initiation and intermediate regions of fracture were highly voided, that is, they con-

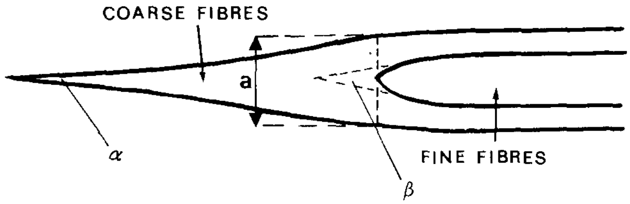

Figure 8 Schematic diagram of a craze indicating the parameters measured.

tained large numbers of secondary fracture features. The morphology of the fracture surface through the craze in which fracture was nucleated in PSJ was very similar to that in PSH.

The two most likely explanations for the occurrence of craze yielding in the suspension polymer are that: (a) the additives used in the suspension polymerization process provided sites for craze nucleation as is the case when small glass spheres are introduced into amorphous polymers [8] or (b) the resultant molecular weight distribution, as given in Table I, causes the development of cracks within crazes to be more difficult allowing profuse craze nucleation and growth to occur before crack nucleation and propagation. The suspension additives or the molecular weight distribution in the suspension polystyrene caused a toughening effect when the material was free from the lubricant used in this investigation.

The presence of internal lubricant also had an effect on the stress-strain properties of polystyrene. In the suspension polystyrenes there was a substantial drop in fracture stress when 2% of lubricant was added and then a more gradual decrease as the lubricant concentration was increased further. The effect of lubricant on the behaviour of the suspension polymer was also to cause a reduction in the craze-yielding effect, which can be interpreted as reducing the difficulty of crack nucleation and, therefore, the craze density prior to fracture. As the concentration of lubricant was increased there was a marked reduction in the numbers of secondary fracture features formed on the fracture surfaces of polystyrenes manufactured by a bulk process. In the polystyrenes manufactured by a suspension process, the formation of secondary fracture features decreased gradually with increasing lubricant concentration. The presence of internal lubricant in both bulk and suspension polymers resulted in the formation of fewer secondary fracture features, which indicates that crazes containing lubricant have less resistance to crack nucleation and propagation.

Earl *et al.* [7] observed the cleavage fracture of two different polystyrenes, one a general purpose grade manufactured by a suspension route and the other a similar grade manufactured by a bulk route. They observed that a larger number of secondary fractures were formed in the suspension polystyrene and suggested that this was due to the impurity particles, such as soaps and suspension agents added during manufacture by the suspension method.

The results of this investigation, however, indicate that it is the concentration of lubricant which has a greater effect on the formation of secondary fracture features since comparable numbers of secondary fracture features were observed in both bulk and suspension polystyrene which were free from lubricant.

No great differences in craze morphology were detected in crazes formed in PSH and PSJ, which indicated that polymerization conditions alone have little effect on craze morphology. When 6% of internal lubricant was present in a suspension-polymerized polystyrene, a small reduction in the craze width a at which breakdown of the fibres within the craze occurs was observed. The change in craze morphology and craze-controlled fracture in the suspension polystyrene with increasing lubricant concentration bears close similarities with changes observed in a general purpose grade of polystyrene with increasing temperature of test [2]. The similarities range from the fine differences in fracture surface morphology, such as the density of secondary fracture features, to the craze-yielding behaviour observed in the lubricant-free suspension polymer at room temperature and the general-purpose polystyrene at low temperatures. The exception lies in the observed contrast effects associated with the change from viscous flow to viscous rupture [1, 2, 9] in the the initiation region of fracture. A marked change in contrast was observed in the initiation region of fracture, see for example Fig. 7. The relative extents of regions A and A′ were not observed to change in a systematic way with increasing lubricant concentration, unlike the observed increase in the areal extent of region A relative to A′ with decreasing temperature of test in a single general purpose grade of polystyrene [2]. With this exception the effect of increasing lubricant concentration on craze and fracture morphologies in suspension polystyrene can be likened to the effect of increasing the test temperature in the case of general-purpose polystyrenes. The presence of lubricants or possibly a low molecular weight fraction is, therefore, likely to cause a decrease in temperature at which craze-yielding will be observed.

Craze-yielding is an important phenomenon in the deformation of rubber-toughened plastics of the HIPS and ABS types. On the basis that the presence of lubricants can cause such marked differences in the crazing behaviour of polystyrenes it is reasonable to expect that the presence of lubricants in HIPS and ABS materials will also cause substantial changes in the distribution of crazes in these materials and, therefore, effect their deformation and fracture behaviour. An investigation of these effects is in progress [10], together with a study of the effect of lubricants on the deformation and fracture of injection-moulded test specimens, where the concentration of lubricants tends to vary through the thickness of the specimen.

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