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The fracture of vinyl-urethane polymers

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The fracture properties of a series of polyurethane polymers have been studied by making measurements of fracture toughness and impact strength. In addition, the crack and the craze at the crack tip were examined by optical microscopy. It has been possible to interpret the results in terms of the Dugdale plastic zone model, and in this way gain physical understanding of the factors influencing the fracture behaviour.

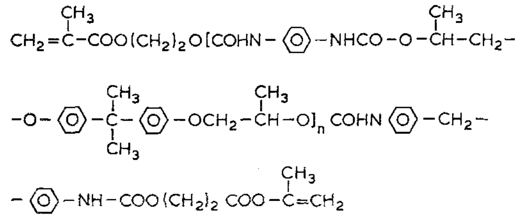
1. Introduction

In recent years the principal advances in our understanding of the fracture behaviour of polymers have come from the development of two distinct approaches. These are the quantitative measurements of fracture toughness first in terms of surface energy [1-3] and more recently with linear elastic fracture mechanics [4, 5], and the exploration of the craze at the crack tip in glassy polymers and its relationship to crack propagation [6, 7]. The research described in this paper attempts to bring together these two approaches by making both fracture toughness measurements and optical examination of the craze zones in a series of glass urethane polymers whose structure can be systematically varied. The fracture toughness measurements include both controlled cleavage and impact tests on sharply notched specimens. It will be shown that the fracture and craze size results, taken together, can be given a consistent explanation in terms of the structural changes in the polymers.

2. Experimental

2.1. Preparation of materials

The polymers examined were a series of unsaturated ended urethanes of general formula



The preparation of the final polymer was made in a number of stages [8]. First, a prepolymer was formed by reacting a bifunctional diol with an excess of a bifunctional isocyanate. The prepolymer chain length was controlled by the stoichiometry, which is defined by the –NCO : –OH end group ratio. This prepolymer was then end capped to form a prepolymer in which each chain was unsaturated at both ends. The prepolymer was prepared in styrene so that the whole system could be cured to give a thermosetting resin, in a similar manner to the preparation of a polyester resin. The final polymer can then be described by the NCO : OH ratio used to form the prepolymer and by the styrene concentration. NCO:OH ratios of 2:1, 3:2 and 4:3 were chosen, together with a range of styrene concentrations from 20 to 70%.

In addition, a polymer was examined which contained no styrene and possessed an NCO:OH ratio of 4:3. In this case the unsaturated-ended prepolymer was prepared in methylene chloride, which was then removed by evaporation. The white powder which remained was rapidly cross-linked in a compression moulding press to form small plaques suitable for testing. Although this material is of considerable interest in providing the extreme situation in terms of chemical composition, there is naturally some doubt as to whether its physical structure is directly comparable with those of the other polymers formed by casting.

Results are also presented for commercial polystyrene and polymethylmethacrylate.

2.2. Fracture toughness and modulus measurements

Measurements of fracture toughness were made using the double cantilever beam (DCB) and

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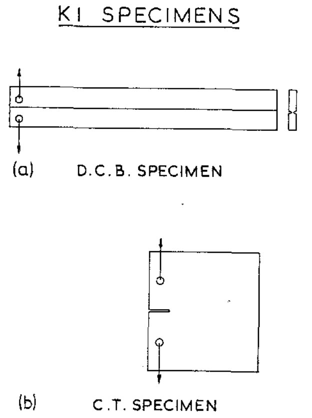

Figure 1 (a) Double cantilever beams (DCB) specimen, (b) compact tension (CT) specimen.

compact tension (CT) specimens shown in Figs. 1a and b respectively. The compact tension specimen does not need to be grooved, which has the great advantage that the craze zone can be obtained for a simple geometry. Providing that the initial notch (the saw cut) is sufficiently long, the crack travels in a straight line across the specimen. This makes the optical observation of the craze and the interpretation of the data in terms of existing schemes of linear elastic fracture mechanics a feasible proposition. Most of the tests were therefore performed on CT specimens. A few comparisons were made between grooved and ungrooved specimens of the same shape and material, in order to study the effect of grooving.

The CT tests were performed as follows: Approximately equidistant marker lines were scratched onto the specimen at points along the crack path, and then the initial crack was formed by slowly pushing a razor blade into the base of the saw cut. The specimen was then mounted on an Instron tensile testing machine and pulled apart at constant crosshead speed. The crack travelled across the specimen at an approximately constant speed, which was determined by the cross-head speed, the specimen modulus and the value of K_1, the stress intensity factor required to give crack propagation. As the crack passed the scratch lines, the load P was note. Using the stress intensity factors calculated by Brown and Srawley [9] with the boundary collocation technique, a series of values of K_1 corresponding very nearly to a unique crack speed, could be calculated from tests on one specimen.

The Young's modulus, E, of the polymer can also be determined from the measurements on the CT specimens. Using the Irwin-Kies relationship [10] the strain energy release rate is given by

$$\frac{K_1^2}{E^*} = \frac{P^2}{2B}\frac{\mathrm{d}c}{\mathrm{d}a} \tag{1}$$

where c is the compliance of the specimen, B and a the width and length of the crack respectively, and E^* the reduced modulus, equal to Young's modulus E, in conditions of plane stress and to $E/(1 - \nu^2)$ in plane strain (ν is Poisson's ratio). Equation 1 can be integrated numerically to give the compliance for a given crack length. E^* was then obtained from the gradient of a plot of calculated compliance against experimental compliance.

2.3. Impact tests

The impact tests were performed on a Hounsfield Plastics Impact Tester, which is a Charpy machine of maximum pendulum energy 2.75J and striker velocity 2.54 m sec^{-1}. The specimen dimensions were 3.3 mm × 7.5 mm × 50 mm, and both unnotched and notched tests were undertaken. Notching was carried out by slowly pushing a razor blade in the centre of the 3.3 mm side until the crack, which travelled slowly in from the razor blade, reached a length of about 3.3 mm.

2.4. Optical measurements

The plastic zones and crazes were observed in the first instance by looking at the side of the specimen using a standard polarizing microscope and transmitted light. The crazes at the crack tips were then examined by the method used by Kambour [6] and first described by Bessonov and Kuvshinskii [11]. In this technique a surface of the specimen parallel to the crack plane is polished so that by looking through this surface the crack and craze can be examined in either transmitted or reflected light. Because the specimen dimensions required are controlled by the working distance of the microscope objective, it is best to set up the crack and then cut the specimen to the required size.

3. Results

3.1. Fracture toughness and modulus measurements

The fracture toughness results given in Table I, were measured using CT specimens and a cross-head speed of 0.005 cm min^{-1}. The value of fracture toughness quoted is not, in general, the crack take-off value, K_{1c}; it is the value of K,

TABLE I Values of stress intensity factor K_I (MN m$^{-3/2}$)

Styrene content	NCO:OH ratio		
	2:1	3:2	4:3
0%			2.8 ± 0.02
20%	0.97 ± 0.01	1.25 ± 0.01	1.51 ± 0.02
28.6%	0.90 ± 0.02	1.15 ± 0.02	1.42 ± 0.01
50%	1.23 ± 0.03		1.60 ± 0.03
70%			1.90 ± 0.02

required to propagate a crack at approximately 0.05 mm sec^{-1}.

In general, stable crack growth requires both a material for which K_I is an appreciably increasing function of crack speed and an advantageous specimen geometry [12]. The stability of crack growth, therefore, gives a qualitative indication of the variation of K_I with crack velocity in the slow growth region. In polymethylmethacrylate (PMMA), K_I varies by about a factor of 2 over the slow growth range [5] and for that reason the crack growth rate is tremendously stable in cleavage experiments, the crack showing no tendency either to oscillate in speed or to take-off.

In these polymers, slow crack growth is not as stable as in PMMA, indicating a much slower change in K_I with crack speed. The difference between a value of K_I for slow crack growth and its critical value at crack instability, K_Ic, is, therefore, not great. The stability of crack growth did increase with increasing styrene concentration, which means that K_I became more dependent on crack speed. In fact, it was not possible to sustain slow crack growth in the polymer with zero styrene content, and the value of K_I given in Table I for this material is, therefore, K_Ic. The variation of K_I with crack speed was measured in the polymer with highest styrene concentration (Fig. 2) and can be seen to be very small, even in this case, compared with that found in PMMA [5].

The results for grooved specimens, using both The DCB and CT geometries, were in general slightly higher than those for the ungrooved CT specimens, and they showed cosiderably greater scatter. For this reason, only the results for the ungrooved CT specimens will be considered in detail.

TABLE II Values of Young's modulus (10^9 N m^{-2})

Styrene content	NCO:OH ratio		
	2:1	3:2	4:3
20%	3.14	3.10	3.22
28.6%	3.29		3.12
50%			3.30
70%			3.15

The modulus results are given in Table II and show that there is no significant variation in modulus with changing chemical composition. These results were obtained from the plots of experimental compliance against calculated compliance, of which Fig. 3 shows a typical example.

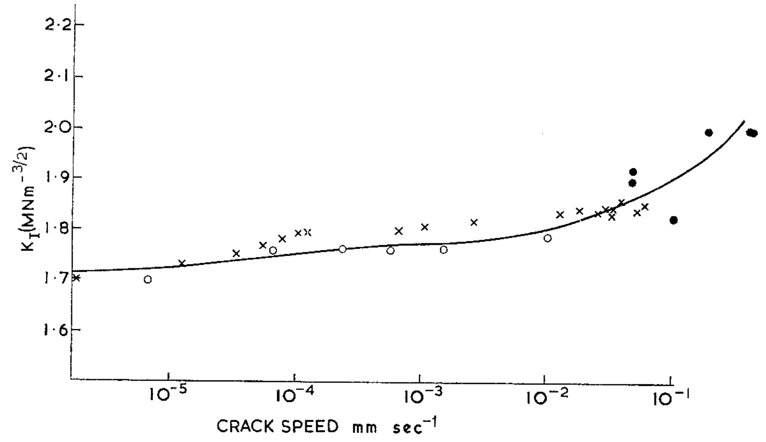

Figure 2 Variation of stress intensity factor K_I with crack speed for polymer with NCO:OH ratio of 4:3 and 70% styrene concentration.

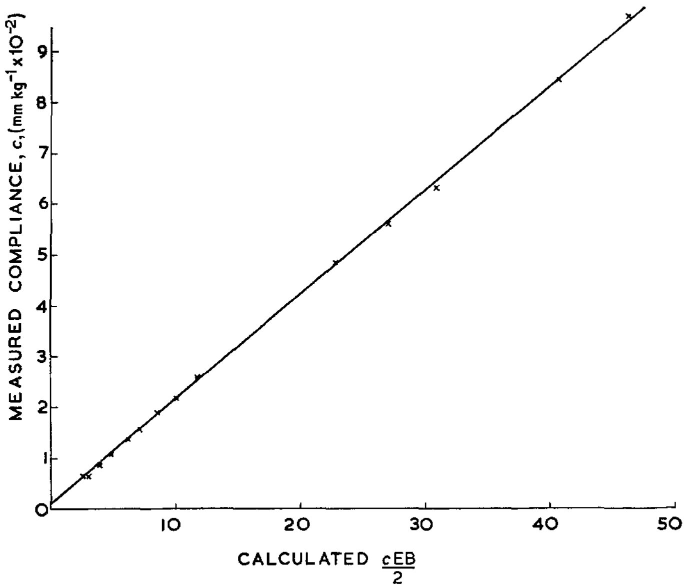

Figure 3 Comparison of the measured and calculated compliancies for a CT specimen.

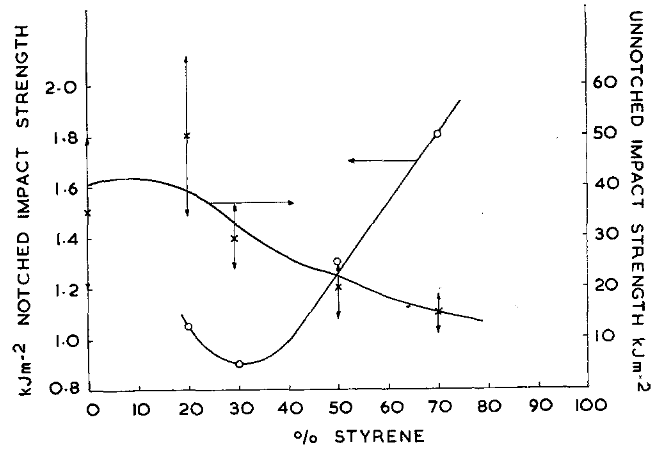

Figure 4 Notched and unnotched impact strengths for polymer with NCO:OH ratio of 4:3.

3.2. Impact tests

The results of both notched and unnotched impact tests on the polymer with NCO:OH ratio of 4 : 3 are shown in Fig. 4. It can be seen that the notched impact strength values show a minimum as a function of styrene concentration, the trend being similar to that shown by the K_1 values in Table I. The unnotched impact strength values, on the other hand, decrease steadily with increasing styrene concentration.

3.3. Optical measurements

Examination of cracked specimens under the optical microscope revealed that plastic zones were formed where the cracks met the sides of the specimen, in the polymers of low styrene concentration ($< 50\%$). Fig. 5 shows an example where scratch marks on the specimen make the plastic flow clearly visible. The plastic zones were very clear in polarized light indicating that they consist of material which is to some

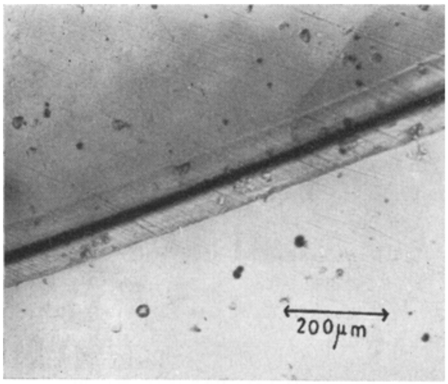

Figure 5 Photograph of plastic zone at edge of crack.

extent oriented. A sketch of the actual shape of the zones is shown in Fig. 6. Although the dimensions of the zones, given in Table III, were not very dependent on crack speed at low crack speeds, no zones were observed at high crack speeds.

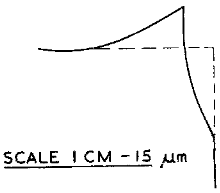

Figure 6 Section normal to crack plane and side of specimen showing distortion of surface caused by plastic. zone. Scale 1 cm. = 40μm.

TABLE III Plastic zone sizes (μm)

Styrene content	NCO:OH ratio		
	2:1	3:2	4:3
0%			130 to 180
20%	22	60 to 75	120 to 130
28.6%	0-30	30 to 50	30 to 60

In the polymers of high styrene concentration which showed no plastic zones, surface crazes were observed near the crack tip, in a pattern which followed the contours of the minor stress vector. An example of these crazes is shown in Fig. 7. The pattern is very similar to that described for polystyrene by Bevis and Hull [13], and is consistent with previous studies of craze formation by Sternstein and his collaborators [14].

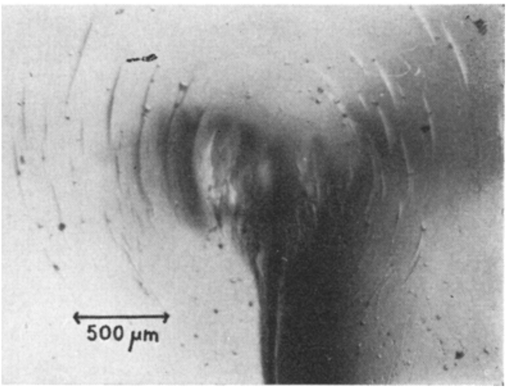

Figure 7 An example of surface crazes.

Primary crazes were observed in front of the crack tip in all cases, two examples being shown in Fig. 8a and b. In these photomicrographs the crack was travelling in the direction of the arrow, and the primary craze is the speckled region in front of the crack tip. The evidence for this is twofold. First, in transmitted light, the fracture surface and crack tip were clearly visible whereas

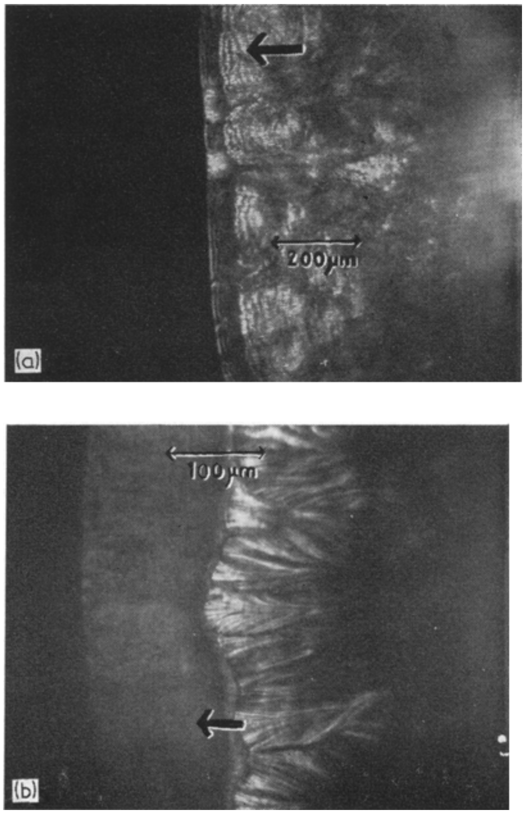

Figure 8 Photographs of primary crazes.

the speckled region was entirely lost. Secondly, in reflected light, adjustment of the focus showed that the speckled region is a thin plane coplanar with the crack. In addition, a few interference bands can be seen in Fig. 8a, similar to those observed by previous workers in PMMA and polystyrene [6, 11]. The lengths of these crazes for polymers with an NCO:OH ratio of 4:3 are given in Table IV.

TABLE IV Fracture parameter for polymers with NCH:OH ratio of 4:3

Styrene content	X (μm)	K_{IC} (MN m$^{-3/2}$)	σ_c (10^8 N m^{-2})	δ (μm)
0%	120	2.8	1.6	15
20%	37	1.5	1.5	4.5
28.6%	32	1.4	1.5	4.0
50%	76	1.6	1.1	6.9
70%	140	1.9	1.0	11.2
Polystyrene	550*	2.3†	0.6	26.6
PMMA	25*	0.9†	1.1	2.3

*Kambour [6].
†Marshall *et al* [5, 16].

4. Discussion

4.1. Fracture toughness measurements

Subsidiary measurements on these polymers [15] have shown that increasing either the prepolymer chain length or the styrene concentration leads to a decrease in cross-link density and yield stress. On the grounds that the fracture toughness might be expected to follow the ductility, it is, therefore, not surprising that the results shown in Table I show the trend of increasing toughness with increasing prepolymer chain length.

On the other hand, the effect of styrene concentration on fracture toughness, does not show a similar trend. Instead, the fracture toughness shows a minimum value at about 30% styrene concentration. We will propose that this is connected with the more complex effect of styrene on the crazing properties.

Fig. 2 shows the small change of K_1 with crack speed for the polymer with an NCO:OH ratio of 4:3 and 70% styrene concentration. As discussed in Section 3.1 this change is the largest shown by these polymers but much less than that found for either PMMA or polystyrene [5, 16]. There is, therefore, good reason to believe that the values of K_1 given in Table I are close to the take-off value K_{1c}.

4.2. Impact tests

The notched impact tests for the 4:3 ratio polymer show the same trend with styrene concentration as the fracture toughness results of Table I and Fig. 4. A similar correlation was observed in polyethylene terephthalate for different molecular weight amorphous specimens, and it was concluded that "the notched impact strength involves the work required to initiate a fast crack from the notch" [17]. Recent work has quantified these observations by showing that, if the notch is made using a razor blade, forming a very sharp crack, the impact strength can be quantitatively related to the fracture toughness using linear elastic fracture mechanics [18, 19].

Fig. 4 shows that the unnotched impact strength falls monotonically with increasing styrene concentration. We propose that the unnotched impact strength is a measure of the difficulty in forming the initial craze and crack on the surface of the specimen. Once the crack is formed there is always sufficient energy for crack propagation; the fracture toughness is, therefore, not important, and the unnotched impact strength will be determined by the craze stress at the relevant strain rate. The importance of surface crazing in determining the strengths of unnotched polymer specimens has been emphasized in previous work on the low temperature fracture of polystyrene [20] and amorphous polyethylene terephthalate [17].

The fall in unnotched impact strength with increasing styrene concentration therefore directly reflects the fall in craze stress (see Table IV). The calculation of these craze stress values is discussed in the next section.

If yield occurs rather than fracture, this can be taken to imply that the yield stress is lower than the craze stress at the effective strain rate involved.

4.3. Optical measurements

It has recently been shown [21] that the dimensions of the craze in front of the crack tip in PMMA fit very clearly to the predictions of the Dugdale model [22] for a plane stress plastic zone. In this model it is assumed that the stress across the craze is constant along its length, this length being determined by the necessity of cancelling the stress singularity at the crack tip. The stress criterion for craze formation is not important because if the craze length were not sufficient, the stresses at the crack tip would rise to meet the stress criterion for more crazing.

On the Dugdale model the crack opening

displacement δ and the craze length X are related to the stress intensity factor K_1 and the craze stress σ_c by the equations

$$\delta = \frac{K_1^2}{E^* \sigma_c} \tag{2}$$

and

$$X = \frac{\pi}{8} \frac{K_1^2}{\sigma_c^2} \tag{3}$$

It is, therefore, possible to calculate any two of the four quantities δ, X, K_1 and σ_c, providing that the other two are known. In this work, K_1 and X have measured for the polymers with NCO:OH ratio of 4:3. We have calculated the corresponding values of δ and σ_c; the collected results are shown in Table IV.

The most interesting feature of these results is the progressive decrease of the craze stress σ_c with increasing styrene concentration, from 1.6 to 1.0×10^8 N m^{-2}. The tensile yield stress of these polymers was measured in a separate study [15]. It is not very styrene dependent, and has a value of about 1.1×10^8 N m^{-2} at a strain-rate of 1 sec^{-1}. These results taken together are consistent with the view that the polymers with 0, 20 and 30% styrene concentration have a craze stress greater than their yield stress. The craze relieves the stress singularity at the crack tip to form a stress field whose maximum component is the craze stress. If the yield stress is below the craze stress, plastic zones will form on the surface where there is no transverse constraint. The size of this plastic zone will depend on the difference between the craze stress and the yield stress. On this view the results of Tables III and IV are entirely consistent and we see a gradual fall in the size of the plastic zone as the crazing stress falls. Because the polymers of high styrene concentration have a craze stress lower than the yield stress, no plastic zones are formed, surface crazes occurring instead.

Summarizing, the optical measurements showed that all the polymers failed by crazing, but those with low styrene concentration also showed surface plastic zones because the craze stress was higher than the yield stress.

5. Conclusions

1. A number of correlations have been obtained between the results of mechanical and optical measurements on the same series of glassy polymers. The first correlation is between notched impact strength and fracture toughness. This correlation has subsequently been shown to hold generally [18, 19], with the proviso that the fracture toughness test is performed at high speed in a ductile material. The second correlation is between the unnotched impact strength and the craze stress σ_c.

Table IV also shows calculated values for craze stress and crack opening displacement for PMMA and polystyrene, using values of K_1 obtained from the literature. Because there is some doubt about the value of K_1 for polystyrene, the value given here is an upper limit. This means that the calculated value of the craze stress σ_c is also an upper limit. Even so, the calculated craze stress for polystyrene is much less than that calculated from PMMA. This implies that although polystyrene has the higher fracture toughness, PMMA should be better in unnotched impact, where the craze stress the controlling parameter. This conclusion is borne out in service where PMMA is much tougher than polystyrene for most applications.

2. The mechanical and optical properties discussed in this paper can be described qualitatively, and sometimes quantitatively, in terms of two parameters, the craze stress and the crack opening displacement. The results suggest that these two parameters may be controlled by different structural features. The craze stress appears to be primarily related to the styrene concentration, decreasing monotonically with increasing styrene concentration. The crack opening displacement, on the other hand, changes in a more complicated manner, first decreasing and then increasing with increasing styrene concentration. It is interesting to speculate that the crack opening displacement may define an ultimate failure criterion. The initial fall with increasing styrene concentration can be attributed to a reduction in the strength of the vinylurethane network in which styrene is a weak link. The subsequent rise at high styrene concentration could be due to the high extensibility of polystyrene which can then exist as a separate phase. The whole situation will be complicated by the adhesion or separation between the styrene and urethane phases.

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