Effect of molecular orientation on the fracture toughness of thermoplastics

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An account is given of fracture toughness experiments on injection moulded plaques of a propylene homopolymer and two different molecular weight grades of poly(methyl methacrylate). The study was concerned essentially with the behaviour of large, centrally notched, plaques since this represents a step towards component testing. However, in order to establish this point, small specimens machined from the plaques were also tested. Analysis of behaviour is by linear elastic fracture mechanics. The study showed that the fracture toughness parameter, K_{IC}, was not a material constant. Variations in fracture toughness are attributed to molecular orientation produced during the injection moulding process. As expected, the propylene homopolymer was tougher than the PMMA. However, a potentially ductile material can still fail in a brittle manner if a large enough specimen is tested. Overall, this study has emphasized that tests on complete mouldings can provide a valuable means of assessing potential practical performance, and also that data obtained on small specimens can be misleading with respect to the performance of large components.

INTRODUCTION

During the past decade there has been an increasing use of linear elastic fracture mechanics for analysis of mechanical failure in thermoplastics. The technique has been employed in a wide context to embrace such phenomena as environmental stress cracking and crazing[1–3], fatigue[4,5] and more recently, impact[6,7]. In addition, the behaviour under monotonic loading has also been examined with the aim of solving particular fracture problems, e.g. failure in UPVC pressure pipe[8]. Other aspects such as the temperature dependence of fracture toughness[9,10] has also been investigated.

The results of these various investigations exemplify the general applicability and usefulness of this kind of analysis but at the same time demonstrate that K_I or K_{IC}, the fracture toughness at onset of crack propagation or the value of this parameter in the event of a subsequent instability respectively, are not constants of the material under examination. This is not surprising since we are simply dealing with the quantification of mechanical behaviour from a different set of considerations from for example modulus, yield stress, tensile strength, etc. It follows naturally, therefore, that these parameters will be sensitive to changes in temperature, material and fabrication variables. In particular, the influence of molecular orientation on fracture toughness has received little consideration and this paper describes the results obtained with a fan-gated injection moulded plaque.

It is well known that the potential service performance of a thermoplastic material cannot be assessed from traditional single point characterization tests such as those described by National or International Standards. Tests of longer term duration like creep, creep rupture and dynamic fatigue have been found to be a necessary adjunct in the pursuance of data for design purposes. However, such tests are invariably based upon small test specimens which have been prepared either directly by injection or compression moulding or indirectly by machining from a larger sample. The main criticism of this approach is that the measurements made may not reflect the potential behaviour of actual moulded articles. As a consequence, our investigation has been concerned mainly with the fracture behaviour of complete plaques. This interest in the testing of complete mouldings has been further stimulated through our experience with glass fibre reinforced thermoplastics which naturally exhibit a marked degree of anisotropy in their mechanical performance[11] and whose behaviour is not adequately described by tests on individual small specimens selected and prepared from the whole. In addition, there have been instances of brittle fracture in service which have been difficult to reproduce in small scale laboratory tests.

The investigation into the effect of molecular orientation on fracture toughness has been made using a classically brittle thermoplastic, poly(methyl methacrylate) and a tough thermoplastic, polypropylene. The experiments are all short term but form part of a growing investigation designed to assess the potential of fracture mechanics both as an analytical tool for the study of fracture in thermoplastics as well as an aid to the prediction of long term performance and design.

EXPERIMENTAL

General

An injection moulded plaque, 4 mm thick, was used as the test piece. Its geometry and injection moulding details are given in *Figure 1.*

The materials used were: poly(methyl methacrylate) (PMMA): (i) weight-average molecular weight 124 000, referred to as sample A; (ii) weight-average molecular weight 77 000, referred to as sample B; a propylene homopolymer (PP) weight-average molecular weight 347 100.

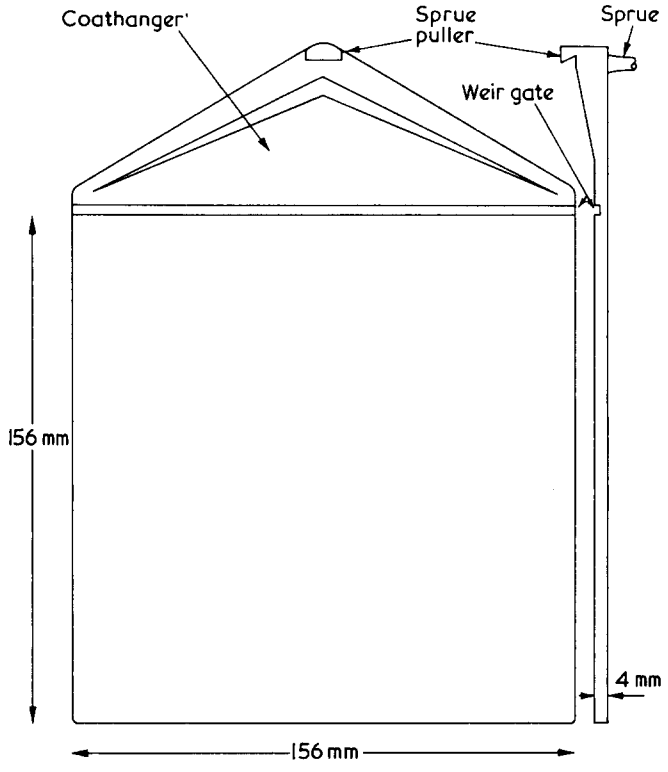

Figure 1 Geometry of plaque moulding

Measurements of fracture toughness (K_I) were made at 23°C, 50% r.h. at a rate of increase in $K \simeq 200$ MN/m$^{3/2}$/ min. Cracks were initiated at the root of machined notches by cleavage, using a razor blade which was forced into the tip of the notch by light tapping. It is recommended[12] that a fatigue crack be produced at the tip of notch by cycling between tension and zero. Such practice is not considered to be desirable for viscoelastic materials since it can lead to the build-up of unrecovered strain ahead of the crack.

Specimen geometries

Three basic geometries were used. These are detailed in *Figure 2*. (a) Plaque with a centre notch. Tested in tension; (b) compact tensile specimen (*CTS*); (c) single edge notch bar (*SEN*). Tested in flexure. (Both the miniature specimens were prepared so that the cracks propagated from the tip towards the centre of the plaque).

The equations for evaluation of the fracture toughness parameter, K, corresponding to these specimen geometries are as follows: For (a) (from ref 13)

$$K_I = \sigma_R(\pi a)^{1/2}\left(\frac{2b}{\pi a}\tan\frac{\pi a}{2b}\right)^{1/2}$$

For (b) and (c)

$$K_Q = \frac{PY}{BW^{1/2}}$$

where P is the applied force at onset of crack propagation; B is the thickness; $W = 2b$ = width; a is the initial crack length, but measured after fracture; Y is a factor dependent on (a/W) given in *Tables 2* and *3*[12]; σ_y is the yield stress; σ_R is the stress remote from crack; K_I is the stress intensity factor in the crack opening mode at onset of crack propagation (based on 'a'); K_{IC} is the critical value of K_I at onset of instability in crack propagation rate (based on 'a' + length of slow crack growth) and K_Q is the provisional value of K_{IC}. For PMMA, length of slow crack growth was negligible.

RESULTS AND DISCUSSION

Objectives

(1) To study the 'fracture toughness' behaviour of complete injection moulded plaques. (2) To investigate how 'fracture toughness' is influenced by molecular orientation within the plaque.

Experimental programme

Our investigation has been mainly concerned with the fracture behaviour of complete plaques. This approach has the merit not only of markedly reducing the amount of specimen preparation in any investigation but also is a step towards component testing and thus towards assessing potential service behaviour.

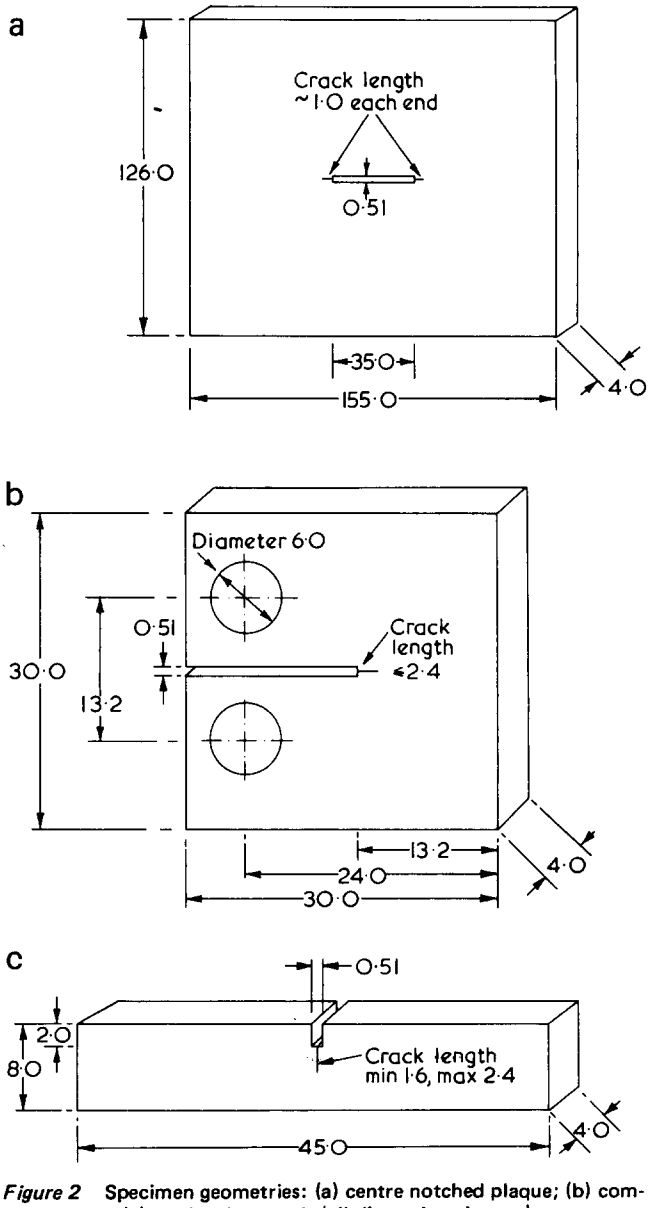

Figure 2 Specimen geometries: (a) centre notched plaque; (b) compact tensile; (c) single edge notch (all dimensions in mm)

Table 1 Values of K_{IC}, expressed in $MN/m^{3/2}$, for the centre notched plaque specimens

Angle of crack (degrees)	Low mol. wt PMMA, 'B'	High mol. wt PMMA, 'A'	Propylene homopolymer
0	0.99	1.39	3.32
22½	1.00	1.23	2.85
45	1.04	1.29	3.06
67½	1.09	1.46	3.34
90	1.46	1.89	4.77
112½	0.89	1.47	3.38
135	0.92	1.20	3.04
157½	0.96	0.95	2.74

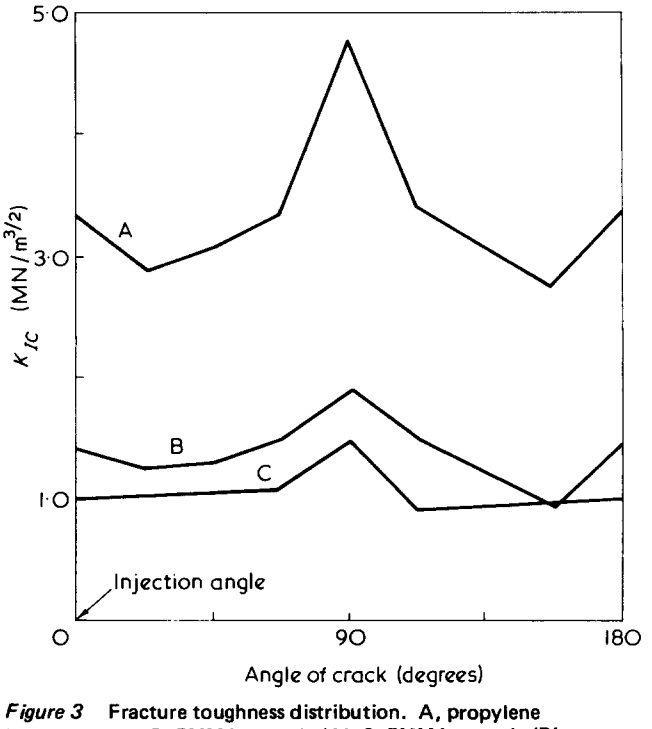

Figure 3 Fracture toughness distribution. A, propylene homopolymer; B, PMMA, sample 'A'; C, PMMA, sample 'B'

Poly(methyl methacrylate)

The plaque tests were done using the geometry of *Figure 2a* with the central notch machined at 0° and other orientations, at 22½° intervals, up to 157½°. In all cases, the stress (σ_R) was applied in a direction normal to the central notch. The results are detailed in *Table 1* for both grades of PMMA and show that the plaque is anisotropic in toughness. The form of the anisotropy is most easily seen from the distribution diagram shown in *Figure 3* which has been constructed assuming symmetry about the 0° direction. The anisotropy in fracture toughness of both grades essentially takes the form of an ellipse with its major axis in the 90° direction of the plaque. The degree of anisotropy in both grades is considered to be of practical importance, from a design viewpoint, if such a component were to be subjected to load in service.

To ensure that component (plaque) testing in no way overlooks important local variations in mechanical performance, the degree of resolution of test was increased by resorting to use of small specimens. Two levels of testing were done: (i) with compact tensile tests using a specimen of geometry shown in *Figure 2(b)* and (ii) *SEN* bend specimens of geometry shown in *Figure 2(c)*. The disposition of these specimens within the plaque is shown in *Figure 4*. These tests increased the number of tests per sample to 18 and 78, respectively, with one half being tested in the 0° and the other half in the 90° direction using two plaques. The individual results for the *CTS* tests are given in *Table 2* and for simplicity the *SEN* bend data are presented as histograms in *Figure 5*.

We conclude from the data as a whole that the increase in frequency of testing within any one plaque has not materially added to our appreciation of the fracture toughness of the plaque. Admittedly the histograms, describing samples A and B, are interesting in that they nicely define the respective distributions for the 0° and 90° directions. They also indicate that increase in molecular weight seems only to improve fracture toughness at 90° to the molecular orientation, leaving, the 0° largely unaffected. What additional information has been gained, however, is not considered to be commensurate with the considerably increased amount of testing and specimen preparation required to generate the data.

The results show that the fracture toughness parameter, K, is not constant for PMMA even at a constant rate of

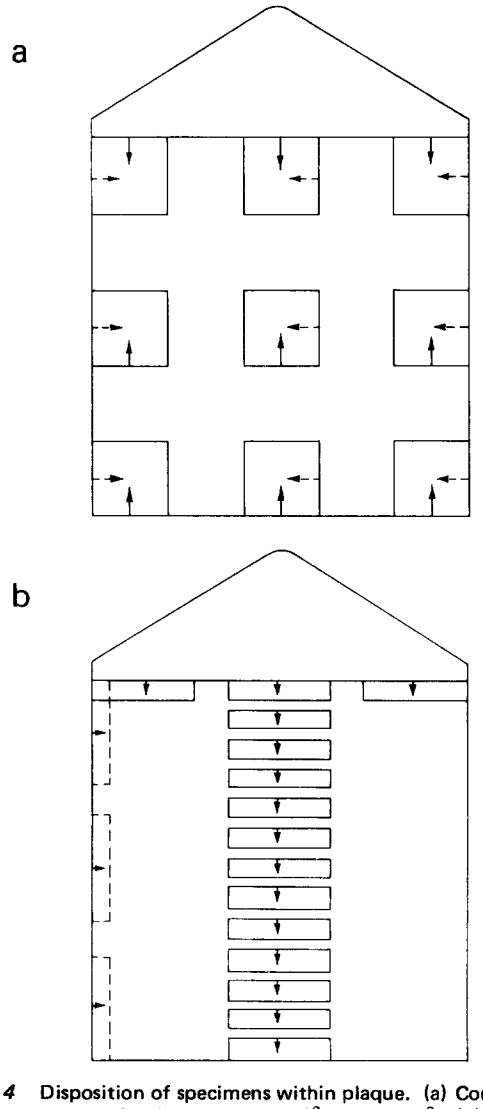

Figure 4 Disposition of specimens within plaque. (a) Compact tensile specimens. Crack direction: →, 0°; – – →, 90°. (b) Single edge notch bend specimens. Only one specimen is shown in each column or row except as indicated to show spacing. Test direction: (——), 0°; (– – – –), 90°. Crack direction and position, →

Table 2 Values of K_{IC}, expressed in $MN/m^{3/2}$, for the compact tensile specimens

Direction of crack	Low mol. wt PMMA, 'B'			High mol. wt PMMA, 'A'			Propylene homopolymer*		
	1.42	1.12	1.11	1.84	1.25	–	–	3.31	3.06
0°	1.41	1.16	1.25	1.85	1.64	1.94	3.17	3.44	3.37
	1.72	1.51	–	1.48	1.33	–	3.43	3.16	3.49
	1.54	1.35	1.66	1.99	–	1.79	D	4.26	D
90°	1.29	1.34	–	1.60	2.08	2.00	D	D	4.96
	1.82	1.60	1.49	1.77	2.01	2.06	4.25	4.92	3.79

D = Ductile failure; *values for propylene homopolymer should be treated as provisional values, i.e. K_Q

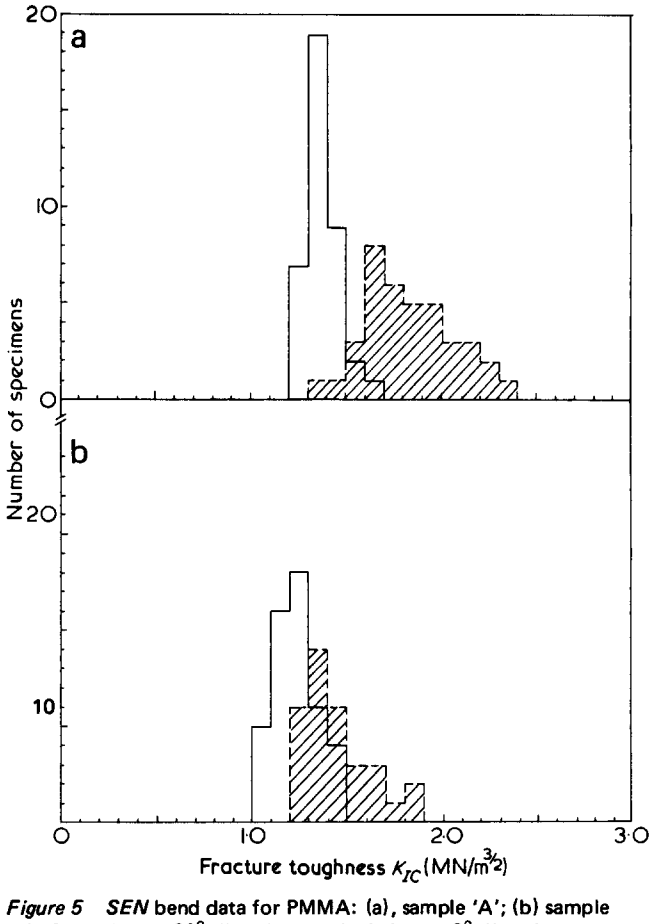

Figure 5 *SEN* bend data for PMMA: (a), sample 'A'; (b) sample 'B'. Shaded area, 90° direction; unshaded area, 0° direction

change of K. This variation in the magnitude of K can be attributed to molecular orientation within the plaque induced during the injection moulding process. This hypothesis is supported by the fact that the pattern of variation is similar for both grades of PMMA and also for the polypropylene sample discussed in the next section. The basic pattern emerging from the *SEN* bend and *CTS* tests is one of uniaxial orientation in the 0° direction.

Polypropylene

A smaller but similar exercise was done with a propylene homopolymer, with testing limited to the complete plaque and *CTS*.

Tests on plaque specimens were made at 0° and other orientations at 22½° intervals up to and including 157½°. The results are detailed in *Table 1*. These tests support the previous work on PMMA and show that the plaque is anisotropic. This is most conveniently seen from *Figure 3* which also includes the corresponding data for PMMA. Again the magnitude of anisotropy is of practical importance. Another striking feature is the similarity in pattern of anisotropy exhibited by both polymers. Clearly, the strongest direction within this particular plaque mould lies in the 90° direction but the weakest is not quite in the 0° direction but rather at a small angle to it. This would suggest that there is some slight perturbation of the flow in the 0° direction. This finding is consistent with that observed by Stephenson *et al.*[11]. These tests on the complete plaque resulted in quasi-brittle fracture at all angles, i.e. an instability in the fracture process was observed with a change in crack growth rate from slow to catastrophic. For the *CTS* tests, however, behaviour was different since in a number of instances, in the 90° plaque direction only, failure was by propagation of a slow ductile crack through plastically deformed material. The individual results for the *CTS* are recorded in *Table 2*.

This anomaly in behaviour between the plaque and *CTS* can be explained from a consideration of plastic zone size. In the *CTS* experiments, the highest value of fracture toughness recorded was $K_I = 4.1$ and $K_{IC}/K_Q = 4.96\ MN/m^{3/2}$ (see footnote, *Table 2*). Otherwise, failure was ductile with some initial slow crack growth through plastically deformed material followed by general yielding ahead of the crack tip across the remainder of the specimen. *Figure 6* is a photograph of such a specimen.

In this specimen we see that the length of the plastic zone ahead of the ductile crack tip is 6 mm. A calculation of the size of the plastic zone (d_y) associated with the specimen for which K_{IC} was the highest recorded is:

$$d_y = 2r_p = \frac{K_{IC}^2}{\pi\sigma_y^2} \qquad \text{(ref 14)}$$

$d_y = 5.2$ mm $\qquad K_{IC} = 4.96\ MN/m^{3/2}$

σ_y† $= 38.9\ MN/m^2$ for PP

Thus for ductile failure, we would expect $d_y > 5.2$ mm which is seen to be the case. It would seem therefore that the lower propensity to brittle fracture in the *CTS* arises as follows.

The amount of energy required to propagate a crack through the plastic zone formed in PP is such that for a small

† Additional tests were performed to examine the relationship between σ_y and orientation within the plaque. Specimens were cut from the middle of the plaques in the 0° direction and other orientations, at 22½° intervals, up to 157½°. It can be seen from *Table 3* that orientation has little effect on σ_y and consequently the value of σ_y we have used above, is the overall mean value for the plaques. The straining rate used in these determinations of σ_y was of the same order as that used in the fracture toughness tests.

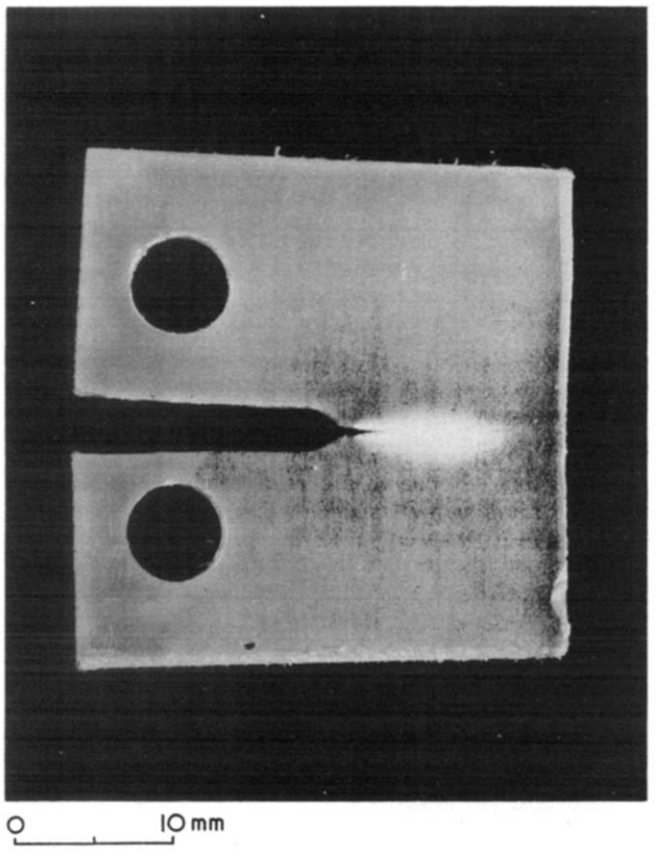

Figure 6 Propylene homopolymer: plastic zone, *CTS*

Table 3 Values of σ_y, expressed in MN/m^2, as a function of angle of test, for propylene homopolymer. Values of σ_y are the means of 3 specimens

Angle of test (degrees)	σ_y
0	39.7
22½	38.7
45	38.3
67½	39.6
90	39.8
112½	38.9
135	37.7
157½	38.6

CTS the associated strain in the specimen is high. The corresponding stress in the vicinity of the crack tip tends towards the yield stress and a ductile situation persists. As a consequence, the rate of crack propagation cannot increase sufficiently to precipitate an instability which is seen in the much larger specimen as brittle fracture.

Figure 7 shows the plaque specimen fractured in the 90° direction, $K_{IC} = 4.77$ MN/m$^{3/2}$. The length of the plastic zone, as seen in *Figure 7a*, is now small compared with the uncracked width (about 7%). Energy can thus be stored in the specimen at low strains with a correspondingly low rise in stress at the crack tip as it propagates. Under these conditions crack propagation rate can increase leading to instability in the failure process which terminates in brittle fracture. It can be seen both from the fracture surface (*Figure 7a*) and the material adjacent to this surface (*Figure 7b*) that a truly catastrophic situation developed with many additional cracks being initiated and propagated from the main crack path. This exemplifies the sense of testing, whenever possible, a complete moulded article, in this case a plaque, in preference to a small specimen machined from it. If, for instance, the data from the *CTS* were for design purposes, the design could be based on misleading information.

Fracture surfaces

Visual examination of the fracture surfaces of the plaques, simply by 'naked eye', showed differences in appearances which were generally consistent with changes in magnitude of fracture toughness (K_{IC}). The measured value of K_{IC} is associated with the state of orientation normal to the crack front. In all cases, an increase in the magnitude of K_{IC} was accompanied by an increase in the roughness of the fracture surface. This roughness is associated with plastically deformed material left on the fracture surface and reflects work done during the fracture process. The application of a stress at a notch leads to the development of plastic deformation at the notch tip. The amount of growth of plastic deformation will be one of the factors involved in whether brittle fracture or ductile fracture ensues. Even in quasi-brittle materials such as PMMA, increase in craze strength, as a result of increase in molecular weight or molecular orientation, can affect the amount of work done during crack propagation and thus the appearance of the surface. This will be particularly noticeable in the unstable, fast crack growth part of the fracture process. For any one material there was seen to be virtually a 1:1 relationship between K_{IC} and roughness. *Figure 8* shows the fracture surfaces representing

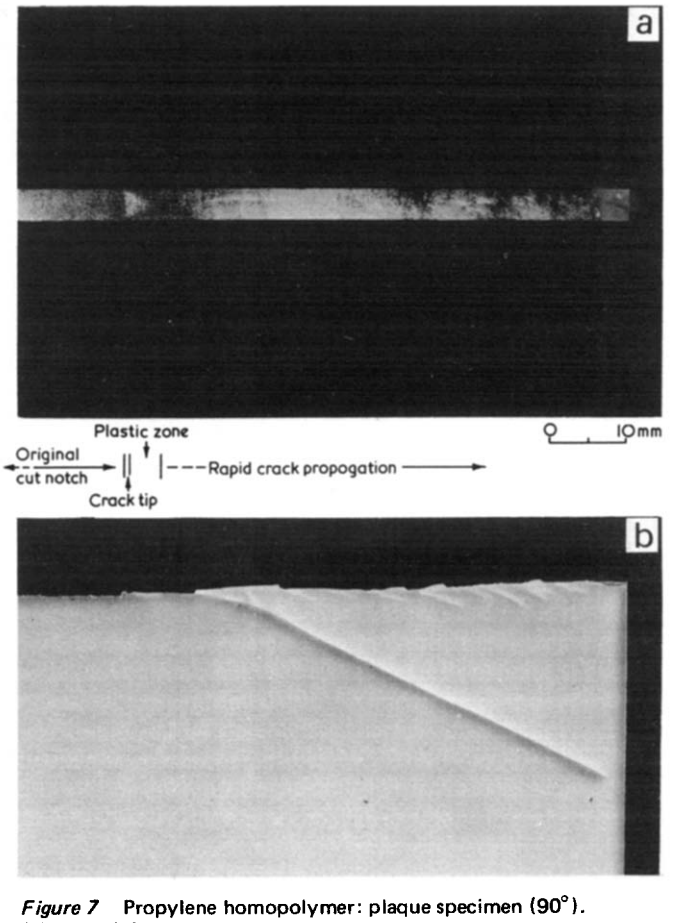

Figure 7 Propylene homopolymer: plaque specimen (90°). (a) Edge; (b) face

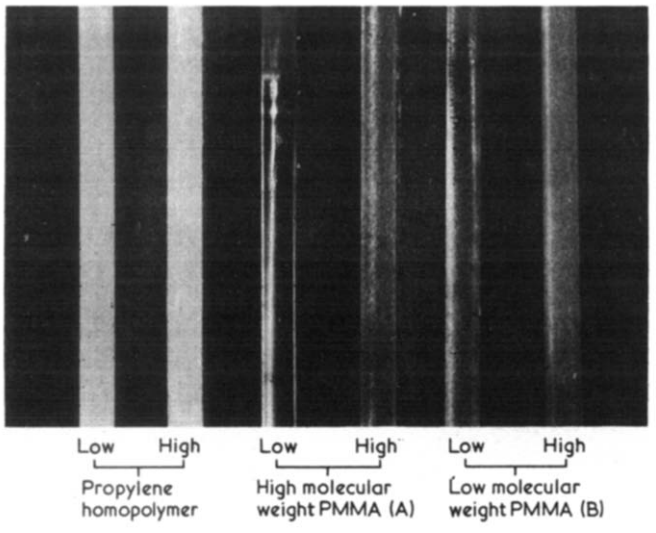

Figure 8 Fracture surfaces: highest and lowest values of K_{IC}

the highest and lowest values of K_{IC} for the three materials. The fracture surfaces for the higher molecular weight PMMA (sample A), shows the biggest variation in surface texture. For a change in K_{IC} from 0.95 to 1.89 MN/m$^{3/2}$ the respective changes in texture of the surfaces are from smooth polished to rough opaque. This is consistent with the findings of Broutman and McGarry[15] who concluded that the flaw surface of a crack propagating parallel to the direction of orientation, became smoother as the degree of orientation increased.

General discussion

From previous measurements of K_{IC} for injection moulded PMMA, we consider that the differences between values of K_{IC} quoted in *Table 2* are meaningful. For example, we would expect a coefficient of variation, (standard deviation/mean) of only 5%. This would suggest therefore, that the apparent inconsistencies in the pattern of K_{IC}, within the moulding, are real and can be attributed to local variations in fracture toughness caused by actual variation in molecular orientation and disorientation arising during the injection moulding process. In the case of the propylene homopolymer, the processability of this semicrystalline polymer, is sufficiently different again from that of amorphous PMMA, for the pattern of K_{IC} within the plaque, also to be different.

Increase in fracture toughness reflects an increase in the amount of work done to produce fracture. This energy will be absorbed within the specimen undergoing fracture in different ways for different materials. For instance the increase in fracture toughness of amorphous polymers as molecular weight increases could be attributed to greater molecular entanglement and interaction whereas in a semicrystalline polymer, increase in fracture toughness can stem from the actual rupture of C–C bonds.

We have seen that the value of K_{IC} is sensitive to molecular weight and molecular orientation and so it is probably meaningless and maybe even misleading to compare values obtained by different workers using different samples. In addition, for PMMA there is a possible added complication in the form of absorbed water[16], which may affect K_{IC}. The overall variation in K_{IC} observed for the injection moulding grades of PMMA is from 0.89 to 1.89 MN/m$^{3/2}$. This compared with a value for bulk cast PMMA (weight-average molecular weight $>2\times10^6$) of 1.6 MN/m$^{3/2}$ (refs 9, 16 and 17). Thus it seems that molecular orientation has a larger effect on K_{IC} than molecular weight of commercial grades though as Kusey and Turner have shown[18], fracture toughness falls appreciably for very low molecular weight PMMA. Curtis in his study of the effect of orientation on the fracture surface energy (γ) of bulk cast PMMA parallel to the orientation, showed that γ could be reduced to 1/5 of that of the essentially isotropic material[19]. Similarly Sims in his studies of oriented polypropylene film[20], showed that orientation has a very pronounced effect on γ measured again parallel to the direction of orientation. In this case for film the degree of orientation that could be produced was high and γ was seen to decrease by 2 orders of magnitude from the isotropic to the drawn state (birefringence 38×10^{-3}). In our experiments, however, with injection mouldings which will not be so highly oriented, we have not observed such marked changes, K_{IC} varying from 2.74–4.77 MN/m$^{3/2}$, a small change in comparison. However, such a change is clearly of importance when it comes to the problem of design using fracture toughness as a design parameter. The experiments have also demonstrated the overall advantages to be gained by testing whole components rather than sections taken from them. This point was particularly well demonstrated by the large differences in behaviour observed with polypropylene. For this material, failure could range from ductile to brittle with small specimens from the plaque whereas in all instances for the complete plaque, fracture was brittle. The importance of this finding with respect to using such data for design purposes needs no further emphasis.

CONCLUSIONS

These fracture experiments on PMMA and PP have clearly demonstrated the advantages to be gained by testing whole components rather than small test pieces prepared from them. The results also show that K_{IC} is not a constant and is not uniform throughout a particular sample. The variation in its magnitude is attributed to molecular orientation produced during the injection moulding process. In addition, increase in molecular weight of PMMA, as expected, produces a corresponding increase in fracture toughness. However, orientation is seen to have the larger influence on the magnitude of K_{IC}.

Tests on polypropylene, a semicrystalline material, as expected showed it to be tougher than non-crystalline PMMA. Its toughness, however, was dependent on specimen size. A potentially ductile material can still fracture in a brittle fashion if a large enough specimen is tested. By visual inspection, a 1:1 relationship between the magnitude of K and the degree of fracture surface roughness was observed, with roughness increasing as K increased.

From this initial investigation, it is generally concluded that fracture toughness measurements, on large plaques, can provide a valuable means of appreciating potential practical performance, as well as identifying the general pattern of molecular orientation induced within the sample during an injection moulding process.

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