The correlation of fracture data for *PMMA*

During the past twenty years, many workers have sought to apply the Griffith-Irwin criterion to the fracture of plastics. Many of these attempts have used the glassy plastic polymethylmethacrylate (PMMA) because it has excellent optical properties and hence cracks can be easily observed. It is also reasonably brittle, and would suggest that linear elastic theory can give meaningful parameters. A summary of the published results for the "Griffith" surface work γ_p and the crack toughness K_{IC} is given in Table I. At first sight, the results appear to be inconsistent, since the quoted values vary by considerable factors. These discrepancies in the toughness value cannot all be attributed to differences in material grades and it has been argued that as a consequence, fracture mechanics has no relevance to plastics since, if the theory does not correlate results on PMMA, then it is doubtful if it can work with other, more ductile, polymers.

However, it is noticeable that in the majority of previous studies, the effects of slow crack speeds have been disregarded. In a previous paper [14], the present authors have shown that crack speed can have a considerable effect on toughness because of the sensitivity of modulus (E) and yield stress (σ_y) of PMMA to changes in straining rate. As a crack accelerates, there is a corresponding increase in the straining rate at the crack tip, and this results in an increase in E and σ_y - thereby producing an increase in K_{IC} . Since plotting results on a K_{IC} /crack speed basis had correlated results from many different types of specimen geometry [14], it was felt that a similar treatment could be applied to the results of other workers and help clarify the apparent confusion in the literature.

A number of difficulties have to be overcome when attempting a comparison of results on a $K_{\rm IC}$ versus crack speed basis, the biggest being that quoted results have usually been given in terms of the surface work, $\gamma_{\rm p}$. There are problems involved in assessing the appropriate modulus necessary for the conversion of $\gamma_{\rm p} \rightarrow K_{\rm IC}$ (or vice-versa) via the relationship $K_{\rm IC}^2 = 2E\gamma_{\rm p}$. In some cases the difficulty resolves itself, since the texts show that many people who discuss results in terms of $\gamma_{\rm p}$ measured $K_{\rm IC}$ in their tests and they obtained $\gamma_{\rm p}$ from the Griffith equation:

$$\gamma_{\rm p} = \pi \sigma_{\rm c}^2 a/2E$$

i.e. E values had been assumed to obtain $\gamma_{\rm p}$ and hence for present purposes the $K_{\rm IC}$ value was easily found by reversing the result using the quoted modulus. Where $\gamma_{\rm p}$ was measured directly using experimental calibration techniques, a modulus is needed for the conversion; this modulus being the value appropriate to the velocity of the crack.

Williams [20] gives an analysis for the computation of the straining rate at the tip of a propagating crack via the expression:

$$\dot{\epsilon} = \pi \epsilon_{\rm y}^3 [E(t)/K_{\rm IC}]^2$$
. \dot{a}

where ϵ is the effective strain rate, ϵ_y is the yield strain and E(t) the time dependent modulus.

Using this expression, modulus values have been evaluated at the quoted crack speeds from creep data for PMMA. If no speed was quoted, a value was assumed on the basis that the results (which were all on cleavage specimens) would be close to the value of 10^{-3} mm/sec obtained by Berry [4].

Having taken these factors into account, a comparison of results is shown in tabular form in Table I and graphically on a K_{IC} /crack speed curve in Fig. 1. (The points on Fig. 1 are numbered as in the References.)



Figure 1 Comparison of published data on K_{IO}/d curve.

1. Instability

[3, 16 and 12]. These workers ignored slow growth and results would be correspondingly low by a factor of $(a_0/a_t)^{\frac{1}{2}}$ where a_0 and a_t are the initial and final crack lengths.

[8 and 13]. Doubtful notching techniques were used: a saw slit was used in [8] and [13] hammered in a

Notes continued opposite

© 1973 Chapman and Hall Ltd.

"sharp crack" with a screwdriver. Both give blunt cracks and hence high K_{IC} values.

2. Slow growth

[1, 2 and 17] used compressive forces to control cracks in cleavage tests, giving an unknown effect on the stress distribution, and there was no experimental calibration.

[19]. Results were quoted for crack initiation in rising load tests. They did not measure initiation stresses and hence the results are too high by a factor $\sigma_{instability}/\sigma_{initiation}$.

[6]. One author gives γ_{p} , K_{IC} value in a more recent paper shown on Fig. 1 as [7].

All numbers refer to reference numbers.

It can be seen from Fig. 1 that although there would appear to be wide disparity between the results in the literature when they are quoted as constants, they show a high degree of consistency when plotted on a K_{IC} versus \dot{a} basis. The only value which ought to emerge as a constant is the K_{IC} value at the point of transi-

tion from slow growth to rapid unstable fracture. Data from edge notched tension specimens at many strain rates has confirmed that this value is independent of straining rate [14].

Those results which remain inconsistent with this type of correlation procedure are mostly explicable by doubtful experimentation and/or analysis of the results as indicated in the footnotes below Fig. 1 – and these values are shown as uncircled points since their relevance is disputable. The major errors in experimentation have arisen because various critical parameters were either ignored or not measured. The most common mistake is the evaluation of K_{IC} at instability by using the length of the initial notch, when in fact the crack length after the slow growth regime can be considerably greater.

The "slow growth" results given in [1, 2 and 17] are more difficult to judge, since they used a cleavage system which employed compressive stresses to control the direction of crack pro-

TABLE I Fracture toughness values quoted for PMMA in air

Author(s)	Test	ä	γp	K _{(I) c} (calc)
	method	(mm/sec)	imes 10 ²	
			(Joules/m ²)	$(MN/m^{3/2})$
Benbow and Roesler (1956) [1]	PC(c)	~10-2	4.9	[1.69]‡
Benbow (1961) [2]	CNC(c)	10^{-2}	4.2	[1.56]
Berry (1961) [3]	SEN	Instability	3.0	[1.12]
Berry (1963) [4]	PC	10-3	1.4	(0.76)†
van den Boogaart (1966) [5]	PC	$\sim 10^{-3}$	1.65	(0.83)
Broutman and McGarry (1965) [6]	PC	1.25	1.25	(0.99)
Broutman and Kobayashi* [7]	TC	1.25	2.0	(1.26)
Davidge and Tappin (1968) [8]	В	Instability	(3.65)	1.94
Olear and Erdogan (1968) [16]	CN	Instability	(1.39)	1.19
Key, Katz and Parker (1968) [12]	SEN	Instability	(1.15-2.7)	1.09—1.66
Kies (1953) [13]	SEN	Instability	6.15	[1.19]
Svennson (1961) [17]	CNC(c)	~10-2	4.5	[1.16]
Vincent and Gotham (1966) [18]	SEN	$6.8 imes10^{-2}$ —		
	PC, I	$4.3 imes10^{1}$	1.5-3.4	[0.93—1.6]
Williams, Radon, and	SEN, DEN,			
Turner (1968) (1) [19]	В	\sim 2.5 $ imes$ 10 ^{-3**}	(2.23.5)	1.13-1.43
Williams, Radon, and	SEN, DEN,			
Turner (1968) (2) [19]	В	Instability	(2.11-3.0)	1.48-1.75
Irwin and Kies (1954) [11]	CN	Instability	4.4	[1.6]
Fujishiro (1971) [9]	PC	$\sim 10^{-2}$	0.923	(0.63)
Higuchi (1965) [10]	DEN	Instability	3.6	[1.7]

 \dagger () = Converted value—using "derived" *E* (via Williams [1972]).

[] = Converted value—using quoted E.

*Private communication.

**"Apparent" speed.

CNC	= centre notch cleavage	CN	centre notched
PC	= parallel cleavage	I	= impact
TC	= tapered cleavage	В	= bending
SEN	= single edge notch	DEN	= double edge notch
(c)	= with compression		

pagation and the effects produced by the interactions of the compressive and crack tip stress fields are difficult to assess and the results remain as the only anomalies.

The remainder of the results are in close agreement with the measured $K_{\rm IC}$ /crack speed curve [14] and the values are sufficiently consistent to confirm that crack speed/viscoelastic effects are responsible for the observed differences in the literature and re-affirm the validity of linear fracture mechanics applied to this plastic.

References

- 1. J. J. BENBOW and F. C. ROESLER, *Proc. Phys. Soc.* **70B** (1956) 201.
- 2. J. J. BENBOW, ibid 78 (1961) 970.
- 3. J. P. BERRY, J. Polymer Sci. 50 (1961) 107.
- 4. Idem, J. Appl. Phys. 34 (1963) 62.
- 5. A. VAN DEN BOOGAART: Proceedings of the Physical Basis of Yield and Fracture Conference Oxford, 1966, p. 167.
- 6. L. J. BROUTMAN and F. J. MCGARRY, J. Appl. Polymer Sci. 9 (1965) 589.
- 7. L. J. BROUTMAN and T. KOBAYASHI, US Army Materials and Mechanics Research Centre Report, AMMRC CR 71-14.
- 8. R. W. DAVIDGE and G. TAPPIN, J. Mater. Sci. 3 (1968) 165.

Crystallization behaviour of an amorphous FePC alloy

Rastogi and Duwez [1] have recently reported the rate of crystallization of an amorphous $Fe_{75}P_{15}C_{10}$ alloy (where subscripts indicate the atomic percentages of the respective elements) using thermal analysis, resistivity and X-ray techniques. In the present investigation, the morphology of the crystallites during the early stages of crystallization of this amorphous alloy has been studied using transmission electron microscopy. A detailed description of alloy specimen preparation and experimental techniques is given elsewhere [1, 2].

Preliminary ageing results indicated that the amorphous-to-crystalline transformation below 300° C was not detectable by transmission electron microscopy. On the basis of this observation, annealing experiments were performed at temperatures between 300 and 420°C, in steps of 20°C, with the annealing time at a constant 24 h. A new specimen was used for each of the annealing temperatures. Thin foils were

- 9. I. FUJISHIRO, H. M. and S. KATO, Chem. Abs. 74 (1971) 32234.
- M. HIGUCHI, Proc. 1st Int. Conf. on Fracture, Sendai Japan 1965, p. 211.
- 11. G. R. IRWIN and J. A. KIES, Welding J. Res. Supp. 33 (1954) 1938.
- 12. P. L. KEY, Y. KATZ, and E. R. PARKER, UCRL, 17911, N68-29464 (1968).
- 13. J. A. KIES, NRL Mem. Rept. No. 237 (1953).
- 14. G. P. MARSHALL, L. E. CULVER, and J. G. WILLIAMS, *Plastics and Polymers*, (February, 1969) 75.
- 15. Idem, Int. J. Fract. Mechs. to be published (1972).
- 16. P. D. OLEAR and F. ERDOGAN, J. Appl. Polymer Sci. 12 (1968) 2563.
- 17. N. L. SVENNSON, Proc. Phys. Soc. 77 (1961) 876.
- 18. P. I. VINCENT and K. V. GOTHAM, Nature 210 (1966) 1254.
- 19. J. G. WILLIAMS, J. C. RADON and C. E. TURNER, Polymer Eng. and Sci. (1968) 130.
- 20. J. G. WILLIAMS, Int. J. Fract. Mechs. to be published (1972).

Received 30 May and accepted 23 June 1972

> G. P. MARSHALL J. G. WILLIAMS Department of Mechanical Engineering Imperial College of Science and Technology London, UK

prepared from the annealed specimens using a solution of 10% perchloric acid in ethyl alcohol, maintained at 0° C, and were subsequently examined with a Siemens Elmiskop I electron microscope operating at 100 kV.

Specimens annealed at 300°C indicated the formation of 75Å crystallites of average size by random nucleation in the amorphous matrix. The corresponding electron diffraction pattern consisted of a few broad haloes and was very similar to that of the amorphous alloy. Annealing at 320°C resulted in the formation of spherulite-type microcrystals, as shown in Fig. 1a, and the matrix appeared to be amorphous. The corresponding electron diffraction pattern shown in Fig. 1b suggests that diffraction spots are due to crystallites, while the broad diffraction ring is associated with the amorphous matrix. At 340°C, these crystallites grow in the preferred direction, like dendrites, and this tendency seems to be more pronounced at 360°C (Fig. 1c). The appearance of broad haloes illustrated in Fig. 1d, indicates the presence of an amorphous matrix at 360°C. The analysis of the electron diffraction