JOURNAL OF MATERIALS SCIENCE 11 (1976) 1475–1486

Effect of molecular weight on the fracture surface energy of poly(methyl methacrylate) in cleavage

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By the radiolysis of poly(methylmethacrylate) (PMMA), the fracture surface energy (γ) was determined at room temperature as a function of viscosity average molecular weight ($\bar{M}_v$). Using a modified parallel cleavage technique, results showed that γ decreased more than two orders of magnitude with decreasing molecular weight. In the high molecular weight region ($\bar{M}_v \gtrsim 10^5$), γ ($\sim 1 \times 10^5$ erg cm^{-2}) was relatively insensitive to polymer chain length; whereas for $2.5 \times 10^4 \lesssim \bar{M}_v \lesssim 1 \times 10^5$, γ was strongly dependent on molecular weight. A linear regression analysis in the range $\bar{M}_v = 2$ to 2.25×10^3 indicated that a truly glassy "Griffith" material was approached for which $\gamma \simeq 750$ erg cm^{-2}. The results confirm the sigmoidal dependence of γ on molecular weight tested in notched tension. The apparent independence which variations in crack velocity have on γ with decreasing $\bar{M}_v$ is shown and explained in terms of the increasingly brittle character of PMMA. Problems associated with the measurement and interpretation of experimental data are considered, particularly with respect to the lower $\bar{M}_v$ regions.

1. Introduction

The observation that many materials yield higher values for surface work energy than theory would indicate has prompted many investigators to study the extent of plastic deformation that must occur about the crack tip [1–11]. These findings show that the fracture morphology is not featureless but rather covered with details indicative of viscous flow, e.g. interference colours [1, 12–14] and crazing [3, 15]. Many investigators have maintained that the Griffith fracture criterion for "brittle materials" [16] might be utilized to describe the observed phenomenon if the addition of a second term, the contribution to γ from viscous flow processes, were considered [8, 10, 17]. While there has been some question of the applicability of Griffith's criterion under such circumstances [18], results have shown that at least an empirical correlation does exist.

The present effort is not concerned with whether or not the rigorous application of the criterion is correct (although Sih has presented some stimulating discussion along these lines [18]), but rather under what circumstances the theoretical brittle values for which the classical theory was derived can be approached. On the premise that the deformation mechanisms which result in a high γ value are strongly dependent upon the molecular chain length of the glassy polymers [17], a series of parallel cleavage test bars of PMMA were prepared. Utilizing the fact that the radiolysis of PMMA results in random fracture of molecules with no incidence of cross-linking [19, 20], a molecular weight gradient was produced on each test bar. Since the modulus of elasticity is not dependent upon the chain length [17, 21], the cleavage technique first suggested by Berry [22] and later modified and used extensively by Broutman and McGarry [5, 23] was adapted for the present study.

While a number of investigators have evaluated the fracture surface energy of high molecular

weight glassy polymers [2, 5, 8, 11, 17, 22–32], few have studied the effect which molecular weight has on γ [17, 27–30]. Using cleavage bars of PMMA, Berry [27] indicated that there was a slight dependency of γ over the molecular range, 9×10^4 to 2×10^6. From the relationship $\gamma = A - (B/\bar{M}_v)$ in which A and B are arbitrary constants, he stated that γ should approach zero for $\bar{M}_v \sim 2.5 \times 10^4$. Work done with tensile bars on PMMA [17, 28] showed that γ has a sigmoidal dependence on molecular weight, the greatest sensitivity occurring over the range $\bar{M}_v \sim 2.5 \times 10^4$ to 1×10^5. This functional behaviour was first suggested by Robertson [29] for narrow molecular weight fractions of polystyrene in which γ dropped from $3.1 \pm 2.5 \times 10^4$ erg cm^{-2} ($\bar{M}_w = 1.1 \times 10^5$), a value lower than that found by other observers [3, 11, 30–32], to $1.7 \pm 0.1 \times 10^2$ erg cm^{-2} ($\bar{M}_w = 3.5 \times 10^3$), a value some four times greater than the critical surface tension of the polymer. In addition to polystyrene, low molecular weight PMMA has been shown to approach the ideal glassy material for which $\gamma = 450 \pm 250$ erg cm^{-2} at $\bar{M}_v = 2 \times 10^4$ in notched tension [17]. Within the limitations of the experimental procedure, the present results confirm that trend.

2. Experimental

2.1. Preparation of material

The material used in this study was a commercially available ummodified PMMA, Plexiglas G (Rohm and Haas Co, Phila., Pa.). Sheets varying from ¼ to 1 in. thick were machined into parallel cleavage bars (Fig. 1) by slotting the rectangular parallelepipeds down the midline with an 0.008 in. saw a total of $W/2$. Pinning holes 1/8 in. diameter were cut into the leading specimen edge (1/10 in. in × 1/8 in. down) to allow the double cantilever bar to be pulled in tension and a "swallow-tail" cut to initiate failure (type a). Type b samples were similar except that pinning holes were not drilled into the test bar proper but rather through two small high molecular weight blocks which were cemented in place using Teflon (Dupont de Nemours, Co, Wilmington, Dela.) as a spacer forward of the swallow-tail to prevent adhesion across the beams (Fig. 1, lower). All specimens were annealed at one of three equivalent time–temperature schemes: 5 h at 90° C, 10½ h at 80° C, or 24 h at 70° C.

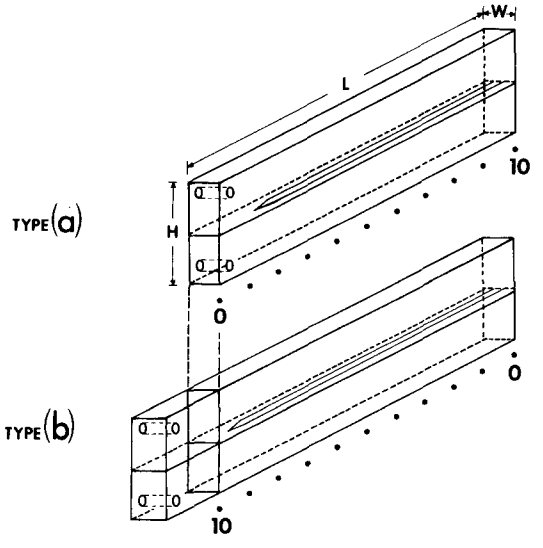


Figure 1 Illustration depicting the two types of parallel cleavage bars prepared.

2.2. Radiolysis of PMMA

Of the common glassy polymers, the radiation chemistry of PMMA is unique in that degradation proceeds without cross-linking [20]. This fact has been shown for doses up to 40 Mrad [33] in which the production of fractures per 100 eV of energy deposited, i.e. the $G(F)$, equals 1.7 [34]. With this knowledge the molecular weight ($\bar{M}_v$) may be deduced for a given radiation dose provided that the initial $\bar{M}_v$ of the polymer is known. In the present work the required dose was achieved by exposure of the samples to gamma-radiation from a ^{60}Co source at a dose rate of 2.0 Mrad h^{-1}. The controlled slow degassing [35] of test bars was necessary for periods up to 1 year in order to reduce the likelihood of cracking from internal pressure gradients. This was carried out by storage at low temperatures, which for high $\bar{M}_v$ PMMA has been shown to increase the surface work necessary to propagate a crack [4], and by the encapsulation of specimens to reduce the large stress gradients which result from too rapid surface diffusion. Despite this care a number of specimens shattered, e.g. cf. Table I, c, d and e. (A lower dose rate would alleviate this tendency). The limiting viscosities $[\eta]$ were determined in benzene at 25° C from the Mark–Houwink relation,

$$[\eta] = K\bar{M}_v^{\alpha}$$

in which $K = 5.5 \times 10^{-5}$ dl g^{-1} and $\alpha = 0.76$ [36].

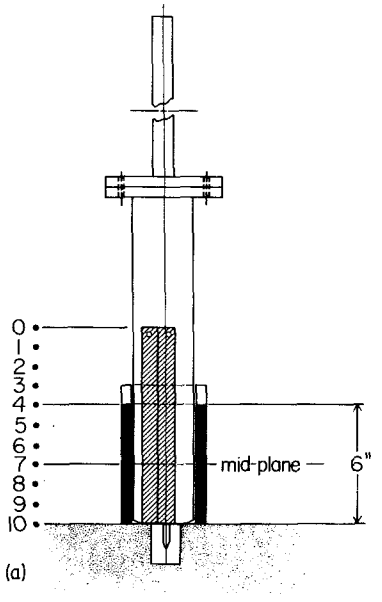
Since the radiation source geometry available was not compatible with the cleavage bar geo-

metry, a radiation dose gradient resulted across each specimen (Fig. 2). To handle this problem, 10 in. calibration strips of PMMA were irradiated, sectioned at 1 in. increments, and the limiting viscosities determined. At each of these increments, an $\bar{M}_v$ was determined, the minimum of which corresponded to the maximum dose. In the radiation source used (Fig. 2a) the ^{60}Co rods are 6 in. long and situated such that the mid-plane, and hence the maximum dose rate, occurs at the 7 in. mark. (Note the symmetrical disposition of the dose 3 in. about the source mid-plane, Fig. 2b.). The dose, D, was evaluated by substitution into the expression [35]

$$10^6/\bar{M}_v = 0.892\,(D + D_0),$$

$$\text{where } D_0 = 1.2 \times 10^6/\bar{M}_{v_0},$$

the initial dose (Mrad) which would be required to reduce the infinite molecular weight sample to the molecular weight of the as received material, $\bar{M}_{v_0}$. This expression assumes that the random fracture of PMMA results in the "most probable distribution" [19, 37], or $\bar{M}_v = 1.89\,\bar{M}_n$, ($\bar{M}_n$ = number average molecular weight). This has been shown, in fact, to be the case [19]. From the calculated dose at each increment, the data were normalized with respect to the midline of the source (Fig. 2b). By this procedure the radiation profile of each test bar was evaluated merely by noting the total exposure time in the source. The fiducial marks, ranging from $L = 0$ to 10, (Fig. 1)



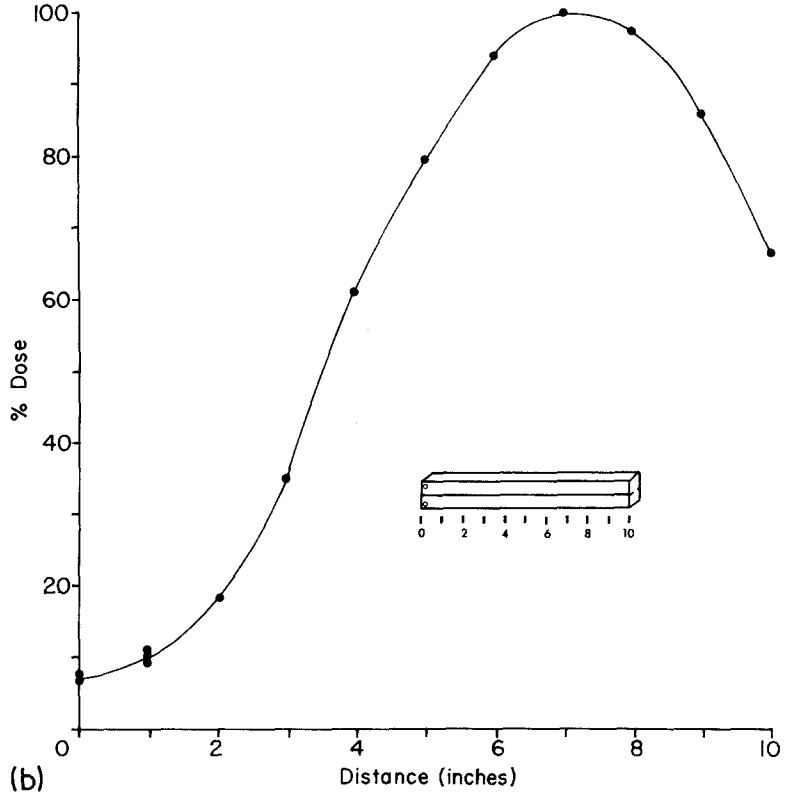


Figure 2 Geometric arrangement of test bar in radiation source (a) and resulting dose distribution (b).

indicate the inch marker under consideration, the 0 of which distinguishes the low dose portion of the bar from the high dose end (10). It then can be seen that, in general, the difference between type a and b specimens is that in the former γ decreases with crack length, whereas in the latter the opposite is true.

TABLE I Schedule of cleavage test bars prepared

Test no. (Sample no.)	Dose (Mrad)	Geometry (in.) width	height	length	Comments*
Type a					
1	0	1/4	1.2	10	a
2	0	1	2	10	a
3	0	1/4	1.2	12	a
4	0.6	1/2	2	10	a
5	2.6	1/2	2	10	a
6	4.4	1/4	1.2	12	a
7	4.7	1/4	1.2	10	a
8	4.7	1/4	1.2	10	a
9	10	1/2	2	12	a
10	11	1/4	1.2	12	a
11	13	1/4	1.2	12	a
12	16	1/4	1.2	10	a
13	16	1/2	2	10	b
14	20	1/2	2	12	a
15	20	1/4	1.2	12	a
16	24	1/4	1.2	12	a
17	27	1/4	1.2	10	b
18	27	1/2	2	10	b
19	31	1	1/2	12	a
20	31	1/2	2	12	b
21	31	1/4	1.2	12	a
22	39	1/2	2	12	a, f
23	44	1/4	1.2	10	a, e
24	44	1/2	2	10	b
25	44	1	1/2	12	a
26	44	1/2	2	8 1/2	a, f
27	52	1	2	10	b, e
28	55	1	1/2	12	a
29	55	1/2	2	9	a, f
30	55	1/4	1.2	12	b, e
31	61	1/2	2	10	b, d
32	61	1/2	2	10	a, d
33	82	1/2	2	10	b, d
34	130	1	2	10	a, c
35	155	1	2	10	a, c
Type b					
36	24	1/2	1	10 1/2	a, g
37	26	1/2	1	7 3/4	a, g
38	29	1/2	1	8 3/4	a, g
39	30	1/4	0.6	11 1/2	a, h

*a, machined with full slot; b, machined with partial slot; c, shattered during irradiation; d, post-irradiation cracking; e, slight post-irradiation cracking; f, first 10 Mrads cut-off; g, pinning blocks (1/2 in. × 1/2 in. × 1/2 in.); h, pinning blocks (1/4 in. × 0.3 in. × 1/4 in.).

2.3. Schedule of cleavage test bars prepared

The test bars prepared are summarized in Table I. A total of 35 samples were machined on which 39 tests were run. Experience indicated that no significant errors resulted from the remachining and testing of a previously fractured parallel cleavage bar providing the dose was high, i.e. the test forces were small and the failure was quite brittle. (Berry [27] claimed that both the elastic modulus in three-point bending and the ultimate tensile strength could be measured reliably on ruptured cleavage bars of PMMA in which $9.8 \times 10^4 \lesssim \bar{M}_v \lesssim 6 \times 10^6$.) The dose represents the maximum value for each bar while the geometry indicates the final dimensions prior to testing. A partial slot (comment b) defined a specimen in which a "swallow-tail" did not begin until the high molecular weight region ($\bar{M}_v \gtrsim 10^5$) had been traversed. This is in contrast to a test bar in which the first 10 Mrads were cut off to eliminate the high $\bar{M}_v$ region and the "swallow-tail" machined in (denoted as "a, f"). These modifications were made in an attempt to reduce the occurrence of unstable failure.

2.4. Testing procedure

While a number of cleavage techniques have been described [5, 11, 22, 25, 30, 31, 38], the parallel cleavage technique first set forth by Berry was selected [22]. In this technique grooves were utilized to conveniently restrict the crack to the central plane of the specimen. This procedure was used despite claims that such grooves could adversely influence the stress field, since even in the proposed alternative solution of Marshall *et al.* [25] side grooves were an experimental requirement and a calibration factor was necessary to correct the stress field intensity factor at fracture, K_c. An Instron testing machine was utilized at cross-head extension rates varying from 5×10^{-1} to 6×10^{-5} cm min^{-1}. Reduction of testing speeds by over three orders of magnitude can be easily accomplished on such machines with the addition of a variable speed timing motor. On the present apparatus controlled speeds can be attained ranging from 5×10^{1} to 1×10^{-5} cm min^{-1}.

3. Data analysis

Analysis of data was based on the procedure out lined by Broutman and McGarry [5]. From the generalized beam formula,

$$f = a\delta/l^n,$$

in which f, δ, and l are the applied force, the deflection of one beam, and the crack length from the pinning holes ($a = 3EI$ and $n = 3$ for a true cantilever beam), a plot of $\log_{10} f/\delta$ versus $\log_{10} l$ was made. At this point the intercept, a, a function of the elastic modulus (E) and the moment of intertia (I), and the slope of the line, n, were determined. In earlier work the intercept was constant for PMMA samples of equal geometry, while the slope equalled a value characteristic for PMMA (2.67) [5, 27]. In the log–log plots of the two test bars shown (Fig. 3a), the intercept is dependent on the sample geometry (¼ in. × ½ in. versus ½ in. × 2 in.) while n is constant (2.67). This is despite the fact that the molecular weight, i.e. the radiation dose, varies continuously over the entire cleavage bar. Thus both the beam exponent and the intercept are independent of molecular weight. While surprising at first, the foregoing conclusion substantiates previous observations on tensile bars [21] and in transverse bending [17] that E is independent of molecular weight; and if n represents the departure of PMMA from true cantilever beam theory, then the departure from elastic to viscoelastic behaviour may also be considered independent of $\bar{M}_v$. The invariance of these parameters provides the necessary simplifications which make a solution tractable.

A second plot is necessary to arrive at a value for γ. By applying Griffith's criterion to the cleavage test the following is derived [22],

$$f\delta/w = 4\gamma l/n$$
$$= 1.50\,\gamma l \text{ (for PMMA)}$$

where w is the measured crack width. In principle, if f and δ are monitored as a function of l, (¼ in. increments in the present effort) and w is determined for each l, then γ can be calculated from the slope of the $f\delta/w$ versus l plot. As seen in Fig. 3, however, the solution does not always yield the straight line relationship shown in Fig. 3b but can lead to other variations (e.g. Fig. 3c). Such results illustrate that the γ is dependent on molecular weight. A schematic representation typical of type a bars and the radiation source geometry utilized are depicted in Fig. 4. In the high molecular weight region ($\bar{M}_v \gtrsim 10^5$, i.e. the maximum

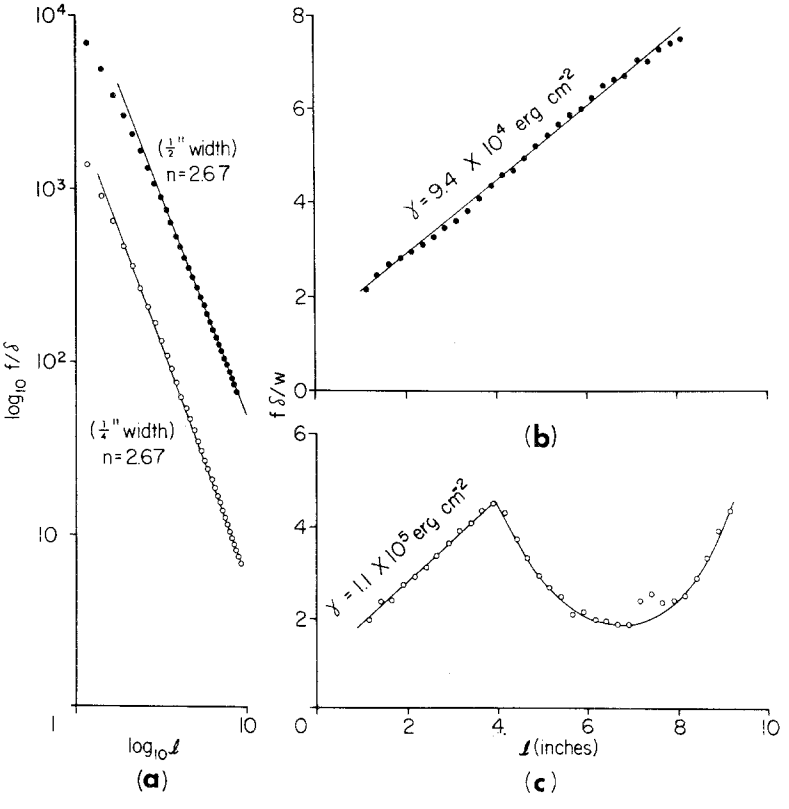


Figure 3 Typical plots used to determine n and γ in type a bars: •, test 5; ○. test 12.

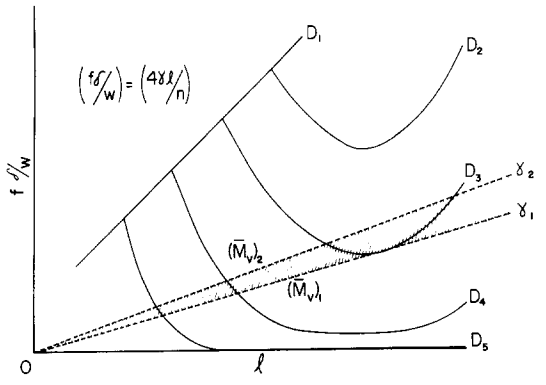


Figure 4 Schematic illustration of $f\delta/w$ versus l plots as a function of dose, D, for type a bars. Method of partition into $\bar{M}_v$ (i.e. γ) range is shown.

or mid-plane dose $\lesssim D_1$), the slope, and hence γ, is generally invariant. However with increasing mid-plane doses ($D_1 < D_2 < D_3$, etc.) a bell-shaped curve begins to predominate reflecting the large decreases in γ which occur with small changes in molecular weight. At D_4 the bell-shaped portion takes on a flat bottom indicative of an invariant γ being realized once more. Such behaviour corresponds to the lower plateau of the sigmoidal relation between γ and $\bar{M}_v$. Further increments of dose D_5 result in the extension of this lower plateau region. Note that the relative values for $f\delta/w$ in the lower plateau region (D_5) are orders of magnitude less, and as such γ is orders of magnitude less, than those in the upper plateau region.

Other forms of the $f\delta/w$ versus l are possible depending upon the radiation source configuration, test bar geometry, and material properties. In Fig. 5 data from a type b PMMA bar is shown. Once again the log f/δ versus log l remains unchanged for a PMMA cleavage bar of the same geometry, and the slope of $f\delta/w$ versus l is not a simple straight line. In this case, however, the slope (γ) continuously increases with l since the high dose or low molecular weight end of the bar occurs first with the slope increasing as higher molecular weight material is encountered. An advantage of testing the parallel cleavage bar from the high dose end is that the progressively higher γ values of the material act to prevent the unstable propagation of the crack analogous to the way that the geometric design of a tapered cleavage bar results in a more stable test [25]. This was an inherent problem in the type a specimens since the energy released with the formation of the crack was used to form new surfaces in material with still lower γ, ultimately creating an unstable state which lower crosshead extension speeds or geometric modifications (cf. Table I, b and f) only could delay.

To analyse the present results, a molecular weight range was selected (e.g. $\bar{M}_{v1}$ to $\bar{M}_{v2}$, Fig. 4) and all measurements on cleavage bars which fell into this band were collated. Using two techniques, one in which each datum point was considered alone and γ determined by passing a line through origin (method I: Fig. 6 and Table II), and the

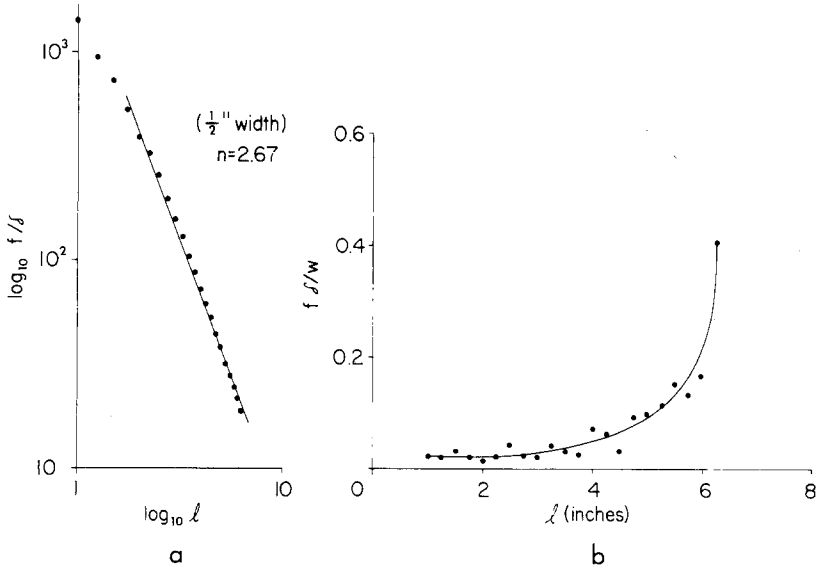
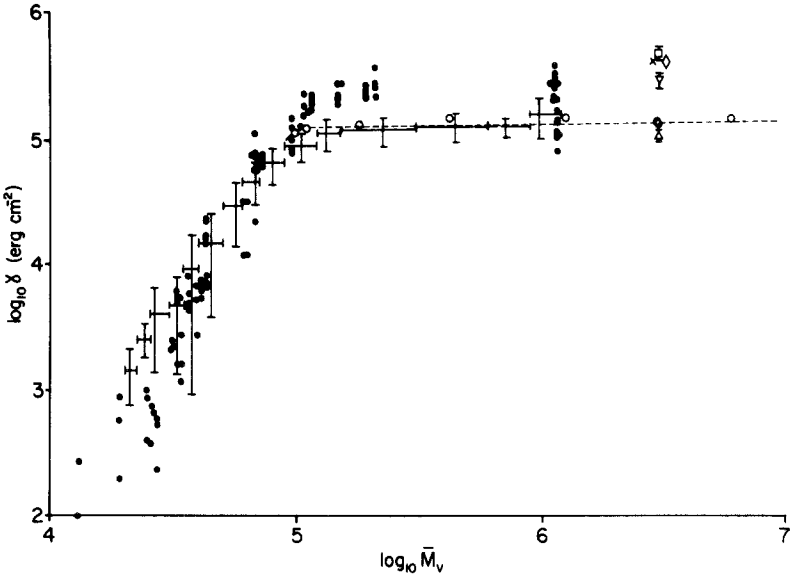


Figure 5 Typical plots used to determine n and γ in type b bars: test 38.



Symbol	Investigators	Poly(methyl methacrylate) Designation	Test Method
□	Benbow & Roesler	Perspex	Wedge Splitting
×	Irwin & Kies	Plexiglas II	Central Notch
◊	Svennson	Perspex	Wedge Splitting
▽	Berry	Plexiglas II	Tensile Test
○	Berry	Plexiglas II	Cleavage Test
△	Broutman & Mc Garry	Plexiglas II	Cleavage Test
●	Kusy & Turner	Plexiglas G	Tensile Test
⊢⊣	Present Work	Plexiglas G	Cleavage Test

Figure 6 Influence of $\bar{M}_v$ on γ in cleavage (method I) versus other investigators [2, 5, 8, 11, 17, 27, 28, 31].

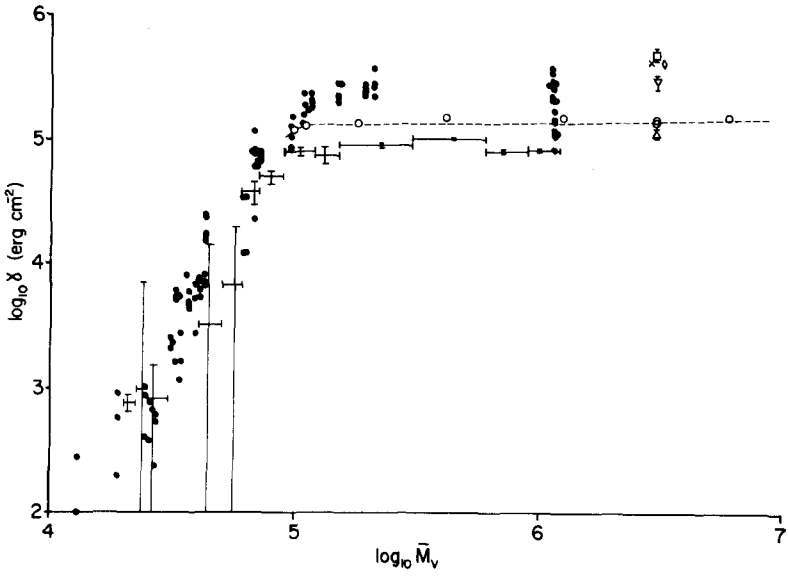
TABLE II Tabulation of fracture surface energy measurements for $\bar{M}_v$ range indicated (method I)

$\bar{M}_v$ Range ($\times 10^{-4}$)	$\bar{\gamma} \pm$ %S.D. ( )* (erg cm^{-2})	
90–120	$1.6 \times 10^5 \pm 35$	(43)
60–90	$1.3 \times 10^5 \pm 17$	(32)
30–60	$1.3 \times 10^5 \pm 25$	(201)
15–30	$1.2 \times 10^5 \pm 23$	(104)
12–15	$1.1 \times 10^5 \pm 26$	(23)
9–12	$8.8 \times 10^4 \pm 26$	(50)
7–9	$6.4 \times 10^4 \pm 33$	(47)
6–7	$4.7 \times 10^4 \pm 36$	(25)
5–6	$3.0 \times 10^4 \pm 54$	(14)
4–5	$1.5 \times 10^4 \pm 74$	(9)
3.5–4	$9.2 \times 10^3 \pm 90$	(5)
3–3.5	$4.7 \times 10^3 \pm 72$	(7)
2.5–3	$4.0 \times 10^3 \pm 65$	(24)
2.25–2.5	$2.5 \times 10^3 \pm 29$	(5)
2–2.25	$1.4 \times 10^3 \pm 46$	(21)

*Data reported as the mean ($\bar{\gamma}$) ± percent standard deviation of the mean (%SD) of the number of datum points specified ( ).

other in which a linear regression analysis was computed on all data over the range of $\bar{M}_v$ considered (method II: Fig. 7 and Table III), plots of log γ versus log $\bar{M}_v$ were generated. These results represent the range of γ possible.

Errors are inherent in either method of analysis. While in theory the $f\delta/w$ versus l data should pass through the origin (as assumed in method I), there are end effects [5] which Marshall *et al.* [25] have quantitized. As a result a positive intercept is observed (cf. Fig. 3) which represents some offset (usually assumed to be systematic) of the $f\delta/w$ versus l slope. While this leads to higher values of γ, the slotting has been stated to reduce K_c by more than 30% [25]. Similarly, errors result in method II when a number of different test bar geometries are considered in which the slopes are the same but the intercepts vary. This is further complicated by the fact that a range of $\bar{M}_v$ is evaluated, each representing a unique γ (slope). The result is an



Symbol	Investigators	Poly(methyl methacrylate) Designation	Test Method
□	Benbow & Roesler	Perspex	Wedge Splitting
×	Irwin & Kies	Plexiglas II	Central Notch
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●	Kusy & Turner	Plexiglas G	Tensile Test
⊢⊣	Present Work	Plexiglas G	Cleavage Test

Figure 7 Influence of $\bar{M}_v$ on γ in cleavage (method II) versus other investigators [2, 5, 8, 11, 17, 27, 28, 31].

TABLE III Tabulation of fracture surface energy measurements for $\bar{M}_v$ range indicated (method II)

$\bar{M}_v$ range ($\times 10^{-4}$)	$\bar{\gamma}$ ± %S.D. ( )* (erg cm^{-2})	
90–120	8.1×10^4 1	(43)
60–90	8.0×10^4 ± 4	(32)
30–60	9.8×10^4 ± 3	(201)
15–30	8.8×10^4 ± 5	(104)
12–15	7.2×10^4 ± 16	(23)
9–12	7.7×10^4 ± 7	(50)
7–9	4.9×10^4 ± 14	(47)
6–7	3.7×10^4 ± 22	(25)
5–6	6.7×10^3 ± 200	(14)
4–5	3.2×10^3 ± 340	(9)
3.5–4	†	(5)
3–3.5	†	(7)
2.5–3	8.2×10^2 ± 130	(24)
2.25–2.5	9.7×10^2 ± 610	(5)
2–2.25	7.6×10^2 ± 15	(21)

*Data reported are the slope ($\bar{\gamma}$) ± percent standard deviation of the slope (%S.D.) of the number of datum points collated ( ).

†Insufficient data and a bimodal distribution prevent the meaningful analysis in this transition zone.

apparent lack of precision since the association of a collation of such data will not yield a high correlation coefficient despite the fact that a definite relationship exists [39]. In summary then, both methods of interpretation suffer intrinsic problems which, until more satisfactory data are obtained, place heavy reliance on the accuracy of the mean.

4. Results and discussion

4.1. PMMA surface work measurements

From Figs. 6 to 8 and Tables II to IV, the influence of molecular weight on γ can be clearly seen. For $\bar{M}_v \gtrsim 10^5$, γ is relatively insensitive to variations in $\bar{M}_v$ (Figs 6 and 7), the mean γ in the range $\bar{M}_v = 9 \times 10^4$ to 1.2×10^6 equalling 1.0×10^5 erg cm^{-2} (Tables II and III). This is in agreement with the values reported by other investigators using the cleavage bar techniques in which γ varied from 1.14×10^5 to 1.56×10^5 erg cm^{-2} for $\bar{M}_v$ ranging from 0.98×10^5 to 60×10^5 [27], and for a group of five specimens in which $\gamma = 1.2 \pm 0.1 \times 10^5$ erg cm^{-2} [5]. Other values reported

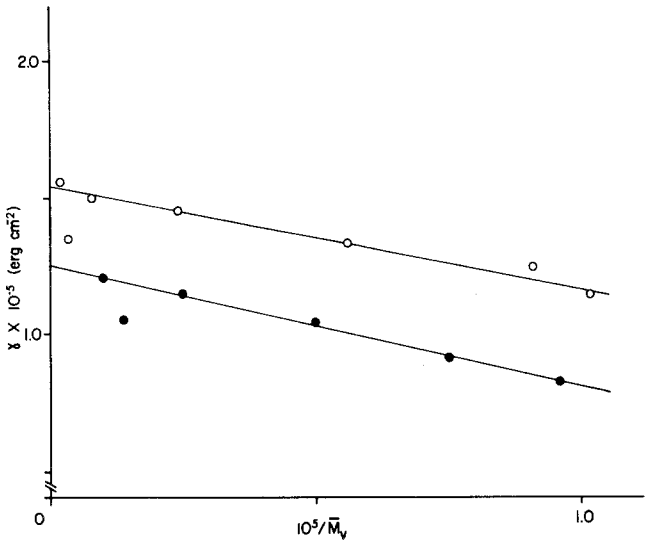

Figure 8 Dependence of γ on $\bar{M}_v^{-1}$ in cleavage when $\bar{M}_v \gtrsim 10^5$: ○, Berry [27]; ●, present work.

TABLE IV Dependence of γ on cross-head extension rate when $\bar{M}_v \gtrsim 10^5$

Cross-head extension rate (cm min^{-1})	Test no.	γ($\times 10^{-5}$) (erg cm^{-2})	$\bar{\gamma} \pm$ %S.D. (erg cm^{-2})
0.5	1	0.85	$0.97 \times 10^5 \pm 10$
	2	1.1	
	3	0.86	
	4	0.93	
	5	0.93	
	7	1.0	
	12	1.1	
0.05	3	0.79	$0.91 \times 10^5 \pm 12$
	6	0.82	
	9	0.94	
	10	0.85	
	11	0.88	
	14	1.0	
	15	1.1	
0.005	14	1.0	———

on notched tensile bars [17, 28] yield larger results which, while not directly comparable, nevertheless, show a similar functional dependence. The apparent variability between the two testing techniques is not surprising since the notched tensile bars were tested at much higher crack velocities ($\dot{a}$) than the cleavage bars. Green and Pratt [24] have summarized this crack speed dependence from $\dot{a} = 10^{-8}$ to 10^5 in. sec^{-1} ([24], Fig. 11) while Marshall *et al.* [25] have shown that γ is independent of test method, whether single edge notch, parallel cleavage, or tapered cleavage bars, for a given $\dot{a}$ ([25] Fig. 16). Furthermore, the threshold value of γ at the lowest crack velocities yields $1.1 \pm 0.1 \times 10^5$ erg cm^{-2} (the 9% standard deviation representing the scatter which resulted from slope-taking techniques on parallel cleavage bars) which is in good agreement with the present data. As expected ([24] Fig. 11), the effect on γ of varying the cross-head extension rate over two orders of magnitude ($\dot{a} < 0.1$ in. sec^{-1}) was insignificant (Table IV).

While the molecular weight dependence of γ in PMMA for $\bar{M}_v \gtrsim 10^5$ is insignificant in comparison with the overview, there does appear to be a slight negative dependency with decreasing $\bar{M}_v$ (Fig. 8). Berry [27] first suggested this trend when he ascribed to the functional relation [40, 41],

$$P = A - (B/\bar{M}_n) \qquad (1)$$

in which P is a property (e.g. tensile strength) and A and B are constants. Specifying P, A, and $\bar{M}_n$ as γ, γ^∞, and $\bar{M}_v$ respectively, Berry's data yielded

$$\gamma(\text{erg cm}^{-2}) = \gamma^\infty - \left(\frac{3.9 \times 10^9}{\bar{M}_v}\right)$$

in which

$$\lim_{\bar{M}_v \to \infty} \gamma = \gamma^\infty = 1.55 \times 10^5 \text{ erg cm}^{-2}$$

and

$$\lim_{\gamma \to 0} \bar{M}_v = \bar{M}_v^\circ = 25\,000.$$

If the combined mean of methods I and II is plotted for each $\bar{M}_v$ range, then a similar relationship results for which

$$\gamma(\text{erg cm}^{-2}) = 1.25 \times 10^5 - \left(\frac{4.45 \times 10^9}{\bar{M}_v}\right)$$

in which $\gamma^{\infty} = 1.25 \times 10^5$ erg cm^{-2} and $\bar{M}_v^{\circ} = 35\,600$.

The values of A represent the only computation of the threshold value of γ for $\bar{M}_v \to \infty$ at $T = 295$ K and $\dot{a} < 0.1$ in. sec^{-1}. In contrast the values for B should be regarded as only applicable for $\bar{M}_v \gtrsim 1 \times 10^5$, as it has been shown that the dependence of γ on $\bar{M}_v^{-1}$ is not linear for lower $\bar{M}_v$ ([28] Fig. 2 for PMMA; [29] for polystyrene). The fact that $\bar{M}_v \sim 2.5 \times 10^4$ as lim $\gamma \to 0$ is regarded as fortuitous with respect to Vincent's brittle strength measurements over $\bar{M}_n = 2 \times 10^4$ to 1×10^6 at 77 K [42] and fracture surface energy measurements in notched tension over a similar $\bar{M}_v$ range at 295 K [17, 28]. Berry [27] clearly recognized "the uncertain validity of that extrapolation", but the significance at high molecular weights appears to be genuine. It remains to be seen whether a similar dependence exists for the lower plateau of the sigmoid, i.e. for $\bar{M}_v \lesssim 2.5 \times 10^4$.

With decreasing $\bar{M}_v$ the relatively invariant γ persists until a critical molecular weight is encountered. The immediate effect on the $f\delta/w$ versus l plot is a distinct break in the "straight line" relationship at $\bar{M}_v = 1.06 \pm 0.03 \times 10^5$ (5 values) (cf. Fig. 3c). This corresponds to the $\bar{M}_v$ at which a significant number of the molecules present can no longer contribute to the work of plastic deformation [17]. Simultaneously, the interference colours, positive indicators that viscous flow mechanisms are operative, change from red and greens to the lower wavelength regions (pale violets), later disappearing entirely [43]. As the number of molecules which can participate in plastic deformation continues to decline, the value of γ drops precipitously to the lower plateau ($\bar{M}_v \sim 2.5 \times 10^4$)(cf. Figs. 6 and 7, Tables II and III). In this central portion of the sigmoid-like curve, the γ values corroborate those previous results found on notched tensile bars [17, 28]. The close agreement differs with the results found when $\bar{M}_v \gtrsim 10^5$ and may be attributed to the decreasing sensitivity of γ to crack propagation rate as the failure becomes truly brittle in nature. This is particularly apparent when cracks propagated at even slow velocities ($\dot{a} < 0.1$ in. sec^{-1}) show a marked decrease in surface roughness. In any event the results obtained by two independent techniques show that γ decreases some two orders of magnitude over the range $2.5 \times 10^4 < \bar{M}_v < 1 \times 10^5$.

For $\bar{M}_v < 2.5 \times 10^4$, γ appears to be reaching a plateau once more. When the present results (Fig. 6) are compared with the theoretical calculation of $\gamma = 450$ erg cm^{-2} [2] or with the previous tensile bar data in which $\gamma = 450 \pm 250$ erg cm^{-2} [17], variations ranging from a factor of 2 to 6 are seen. In contrast, Fig 7 shows agreement when, for example, a linear regression analysis of data in the range $\bar{M}_v = 20\,000$ to $22\,500$ is shown to yield a value of $\gamma \sim 400$ erg cm^{-2} (computed from first 12 points of Fig. 5) or $\gamma \sim 760$ erg cm^{-2} (based on the collation of 21 datum points, Table III). For all $\bar{M}_v$ tested, the crack propagated by continuous tearing.

4.2. Future considerations

Distinct advantages result from the cleavage bar technique described. These include: (1) an increased accuracy and efficiency since one bar provides the data of >30 tensile bars [5, 22, 25]; (2) no requirement to measure the modulus of elasticity of the material [5]; (3) the capability of evaluating a range of molecular weights on one specimen; (4) a consistent surface finish at all $\bar{M}_v$, thereby increasing the reliability of the measurement at the lowest $\bar{M}_v$ (c.f. [27]).

There are other considerations, in addition to the statistical interpretation of the data, which may influence γ. A material factor which becomes more critical as γ of lower $\bar{M}_v$ are studied is the interrelationship of T_g to $\bar{M}_n$ and γ. A number of investigators [37, 44–47] have illustrated that an expression exists of the general form of equation 1, or specifically,

$$T_g(\mathrm{K}) = 378 - \left(\frac{\sim 1 \times 10^5}{\bar{M}_n}\right),$$

for $\bar{M}_n > 3 \times 10^3$ [47]. In the present work in which $\bar{M}_n > 10^4$, T_g is reduced a maximum of 10 to 368 K (95° C). This should not significantly affect the values of γ which result. With further reduction in $\bar{M}_n$, however, T_g more rapidly approaches room temperature. If the relative magnitudes of γ for high $\bar{M}_v$ Perspex as a function of temperature can be applied [30], then γ will at least double as the ratio of the test temperature (T_t) to T_g approaches unity. To obtain accurate measurements, normalization to constant T_t/T_g may be necessary.

A number of geometric factors are also worthy of consideration. The first is concerned with the fact that γ is measured on each bar at ¼ in. incre-

ments. In specimens having one molecular weight or covering either the plateaux or the intermediate slope, such measurements will yield a representative mean. But when the inflection point at $\bar{M}_v \sim 1 \times 10^5$ or, more importantly, at $\bar{M}_v \sim 2.5 \times 10^4$ is approached, the respective mean is weighted in favour of the higher γ. Furthermore, with decreasing $\bar{M}_v$, there is an increasing tendency for the width of the crack to vary as the crack fluctuates above and below the slotted plane. This wandering creates a greater crack area per unit of projected area which, because of the increments of l measured, can lead to inaccuracies in γ up to as much as a factor of two. In addition, the deviation from a symmetrical cantilever arrangement introduces some error. Future modifications centre around the slotting of a greater proportion of the bar, using the thinnest saw compatible with the machining requirements, taking measurements at shorter increments, and utilizing a more favourable radiation source geometry.

5. Conclusions

From the γ measurements of PMMA in parallel cleavage at room temperature, the following conclusions can be made.

(1) The radiolysis of PMMA provides a convenient method by which quality specimens can be prepared over a wide range of $\bar{M}_v$.

(2) The present functional behaviour of $\log_{10} \gamma$ versus $\log_{10} \bar{M}_v$ is in good agreement with previous single notch tension tests.

(3) While γ is comparatively insensitive to $\bar{M}_v \gtrsim 10^5$, the present results confirm earlier indications that a slight negative dependency exists of the form, $\gamma = A - (B/\bar{M}_v)$, in which $A = \gamma^\infty = 1.25 \times 10^5$ erg cm^{-2}.

(4) In contrast to results found for $\bar{M}_v > 10^5$, γ is not sensitive to crack propagation rates over the range $2.5 \times 10^4 < \bar{M}_v < 1 \times 10^5$.

(5) When $\bar{M}_v < 2.5 \times 10^4$, γ approaches the truly brittle "Griffith" material for which γ theoretical = 450 erg cm^{-2}. Current experimental evidence places the value at ca 750 erg cm^{-2} ($\bar{M}_v = 2$ to 2.25×10^4).

(6) A better estimation of γ for low $\bar{M}_v$ will be achieved by the control of certain material and geometrical factors.

Acknowledgements

The authors wish to thank Dr William Thompson and Mr Gilbert Libby for the development of the computer programs and the National Bureau of Standards for the use of the ^{60}Co facility. This investigation was supported by NIH research grant number DE-02668 from the National Institute of Dental Research and NIH grant number RR-05333 from the Division of Research Facilities and Resources.

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Received 9 December 1975 and accepted 9 February 1976.