Influence of temperature on the fracture rib spacing of poly(methyl methacrylate)

The earliest studies on the influence of temperature on fracture were concerned mainly with measurements of tensile strength. These results were complex and did not prove amenable to interpretation. More recent studies have been concerned with measurements of the temperature dependence of fracture surface energy γ which is more laborious but conceptually simpler. For further simplicity, such measurements were made at low temperature in an attempt to eliminate contributions from plastic deformation, since γ might might be expected to be more temperature-dependent than a simple surface energy term of the type considered by Griffith in his theory of brittle fracture [1]. The greatest success along these lines has been achieved by Gilman [2] in cleavage experiments at $-196°$ C. Measured values of γ for both lithium fluoride and magnesium oxide were in good agreement with theoretical values calculated from simple ionic lattice theory, i.e. neglecting any contribution to the work of cleavage by plastic deformation. However, such simple behaviour was achieved only for materials in which γ at room temperature was close (within a factor of about three) to the theoretical value for brittle fracture [2]. In the case of poly(methyl methacrylate), PMMA, Berry [3] found that the fracture energy measured at room temperature is very high, of the order 10^5 erg cm^{-2}. Moreover, lowering the temperature to $-196°$ C resulted in an *increase* in γ by one order of magnitude. These findings, reinforced by observations of fracture surface morphology, provide evidence for a large plastic contribution to fracture surface energy which is not reduced even by wide variations of the temperature of fracture.

The present note reports novel findings concerning the influence of temperature on the rib spacings which are seen on the fracture surfaces of PMMA and confirms the temperature dependence of the fracture surface energy of PMMA. The motivation for this work was to find whether or not these spacings are dependent on temperature and hence, by inference, on processes involving plastic deformation. The only information about the temperature dependance of rib spacing in PMMA is the statement by Andrews that "the periodic rib markings only appear at temperatures above 23° C" [4]. In the case of polystyrene, another glassy polymer which exhibits bands or ribs, Doyle, Maranci, Orowan, and Stork reported that "the width of the bands was of the order 50 μm at the temperature of liquid helium and 500 to 1000 μm at room temperature" [5]. This last observation was based on only a limited number of experiments [6].

Sheets of PMMA ("Plexiglas G", thickness 0.25 cm, Rohm and Haas Co., Philadelphia) of $\bar{M}_v = 1.2 \times 10^6$ were cut into bars and separated into two groups. In the first group, notches 0.2 mm thick were cut in the middle of each bar with a saw (notch size $c_o = 0$ to 1.0 mm). These bars were fractured by bending by hand after thermal equilibration in an oven, in solid carbon dioxide ($-78°$ C), or in liquid nitrogen ($-196°$ C). In the second group, slots 0.2 mm thick were cut in the middle of each bar, a crack initiated by driving in a wedge, and the original slot machined off ($c_o = 0.77$ to 5.78 mm). After equilibrating in an environment chamber these 15 cm × 2.5 cm × 0.25 cm bars were fractured in tension using an Instron testing machine at a crosshead separation of 0.1 cm min^{-1}. Values of γ were calculated using the Griffith equation

$$\sigma = [2E\gamma/\pi c_o(1-\nu^2)]^{1/2},$$

in which the Poisson's ratio ν was assumed to remain constant over the temperature range studied, while the modulus of elasticity E was assumed to vary according to the values obtained by Berry from force–elongation curves of unnotched bars and from three point bending tests [3]. All ribs were measured using a travelling microscope. The morphology of ribs and definition of their spacing have been described previously in work which detailed their dependence on molecular weight [7].

Values of fracture surface energy at various temperatures are in agreement with previous findings (Table I). The general implication of such results has been previously discussed by Berry and reliable evidence has been obtained that variation of the temperature results in a change in the fracture surface energy by a factor of ten. It is assumed that this provides a measure of the change in the

TABLE I Influence of temperature on fracture energy γ

Test temperature (°C)	Present work $\gamma \times 10^{-5}$ ($erg\,cm^{-2}$)*	Previous work $\gamma \times 10^{-5}$ ($erg\,cm^{-2}$)	Reference
+77	0.75 ± 0.15(5)	0.65	[9]
		1.8 (50° C)	[3]
		6.3	[8]
+25	3.4 ± 1.3(7)	1.2	[9]
		2.0	[3]
		4.2	[8]
−78	4.9 ± 1.2(5)	4.4	[3]
−196	8.8 ± 1.5(5)	10.5	[3]

*Mean ± SD of number of specimens in ( ).

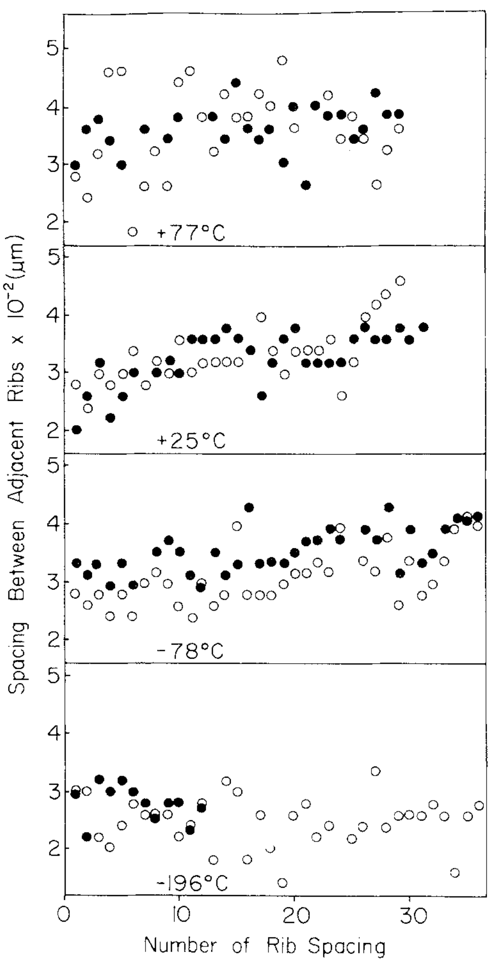

Figure 1 Influence of temperature on rib spacing in bending. The spacing between adjacent ribs are numbered from the end of the mist region. + 77° C; no slots, 2 specimens. +25° C; slot depths 0.5 mm ○ and 1.0 mm ●. −78° C; slot depths 0.5 mm ○ and 1.0 mm ●. −196° C; slot depth 1.0 mm, 2 specimens.

contribution of plastic deformation to the fracture energy via crazing. Furthermore, this factor of ten provides a measure against which to judge whether any other fracture phenomenon, specifically rib spacing, is related to plastic deformation.

In the first group of bars tested (Fig. 1, in bending), ribs were observed from −196° C, the lower limit of the temperatures studied, to +77° C, the upper limit above which no ribs were detected. The results show insensitivity to temperature, the spacing decreasing by a factor of less than two on decreasing the temperature from +77 to −196° C. These findings were independent of notch size. However in some cases, if the slot was too shallow, then the rib surface was too rough to allow definition of ribs; while if the slot was too deep, then the ribs were not formed at all. Therefore the specimens tested at +77° C were not slotted, whereas the specimens tested at −196° C were slotted to a depth of 1 mm.

Although the above experiments were easily performed, they involved a mode of fracture (bending) in which loading conditions were poorly defined. Therefore it was important that further results be obtained under better controlled conditions of tensile loading (Fig. 2). Depending on notching conditions, those experiments showed that the rib spacing may increase by a factor of about four with increasing distance from the origin of fracture. Although this factor varies with specimen geometry and strain rate, rib spacing was determined from the invariant intercept on the "spacing-axis" calculated from a linear regression analysis of all the data at each temperature for each notched bar. For each test temperature the five intercepts which corresponded to different notch sizes were averaged and the standard deviation computed at +25, −78, and −196° C, respectively (Table II). No ribs were observed for the bars tested at +77° C, because the notches were too large.

The above experiments show that the fracture energy γ *increases* by a factor of ten while initial rib spacing *decreases* by a factor of less than two when the temperature is lowered from +77 to −196° C. Despite this difference in sensitivity, it is not concluded that the two phenomena are unrelated. There are two reasons for this reservation. First, the one order of magnitude change in γ

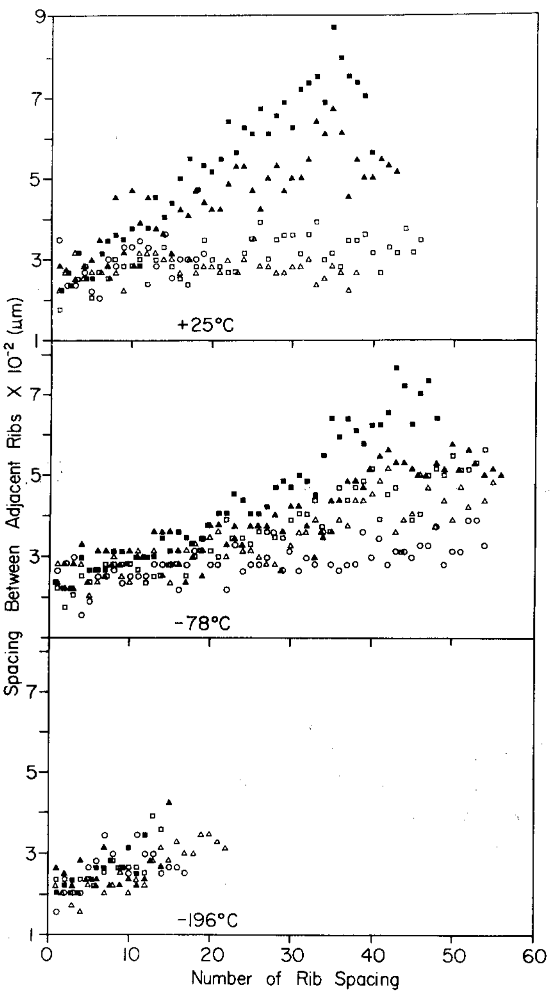

Figure 2 Influence of temperature on rib spacing in tension. The spacing between adjacent ribs are numbered from the end of the mist region. For Key, see Table II.

effected by variation of temperature is small relative to the experimental high values ($\gamma = 10^5$ to 10^6 erg cm^{-2}) as compared to the theoretical low values ($\gamma \sim 5 \times 10^2$ erg cm^{-2}). Second, an indication that the two phenomena may be related is provided by previous observations that both γ and rib spacing decrease with decreasing molecular weight at room temperature [7, 10]. Therefore, judgement is suspended pending investigation of the temperature-dependence of these two phenomena in specimens of lower molecular weight.

TABLE II Influence of notch size and temperature on initial rib spacing in poly(methyl methacrylate)

Test temperature (°C)	Notch size c_0 (mm)	Initial rib spacing (µm)	
+77	5.64	No Ribs Observed	
	3.37		
	2.61		
	2.29		
	2.07		
+25	5.40 ○	259	262 ± 26
	3.00 △	276	
	2.59 □	248	
	1.62 ▲	296	
	0.77 ■	229	
−78	5.78 ○	238	217 ± 24
	2.78 △	228	
	2.66 □	199	
	2.29 ▲	235	
	1.98 ■	184	
−196	4.90 ○	219	199 ± 24
	3.34 △	165	
	2.61 □	192	
	2.45 ▲	226	
	2.13 ■	192	

Acknowledgement
This investigation was supported by USPHS Research Grant No. DE 02668 from the National Institute of Dental Research and, in part, by General Research Support Grant No. RR 05333 from the General Research Support Branch of the National Institutes of Health.

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Received 7 January and accepted 18 February 1977

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