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The fracture of acrylic polymers in water

R. G. HILL, J. F. BATES
Department of Restorative Dentistry, Welsh National School of Medicine, Heath Park, Cardiff, UK

T. T. LEWIS, N. REES*
*Department of Mechanical Engineering and Energy Studies, and *Department of Chemistry, University College, Cardiff, UK*

This paper describes the application of linear elastic fracture mechanics analysis to the fracture of acrylic polymers in water. Three denture base acrylics were studied in addition to Perspex. The effects of strain rate and temperature were investigated using double torsion specimens and three-point bend specimens. It was found for most materials that the fracture toughness was dramatically increased on testing in water compared with testing in air. Crack propagation at fast strain rates was unstable in water and the fracture toughness and flaw size were strain-rate dependent, increasing with decreasing test rate, whilst the un-notched fracture strength decreased with decreasing strain rate. At low strain rates, stable crack propagation was achieved and fracture toughness then decreased with decreasing strain rate. The results are discussed in terms of Williams' model for environmental fracture and the effect water has on the crazing process taking place at the crack tip.

1. Introduction

Berry [1–3], in his early work on the fracture of polymers, concluded that the fracture properties were dependent on the craze that formed at the crack tip. He suggested that the large flaw sizes and fracture surface energies (Y_p) found for polymers such as polymethyl methacrylate and polystyrene were the result of craze formation prior to and during fracture.

Later studies on fracture in polymers were confused by the publication of widely different values for fracture toughness (K_{Ic}) particularly for polymethyl methacrylate. Williams and Marshall [4] eventually showed that K_{Ic} for polymethyl methacrylate tested in air was dependent on crack velocity or strain rate at the crack tip. Further studies [5–7] showed that K_{Ic} increased due to an increasing modulus up to an adiabatic isothermal transition, whilst the strain energy release rate, G_{Ic}, equivalent to $2Y_p$, and flaw size, a^*, remained approximately constant over a narrow strain-rate range. Recently, Ward and coworkers [8, 9] have investigated crazes at crack tips in polymethyl methacrylate. They have shown that the craze can be modelled successfully using a Dugdale plastic zone and that the measured crack opening displacement, δ_c, was constant, whilst the craze stress, σ_0, and craze length, R, varied with temperature. Fig. 1 shows a typical Dugdale plastic zone.

Recent studies [10] have demonstrated that G_{Ic} and a^* are similarly constant for a range of two-phase denture base acrylics and that K_{Ic} also rises with increasing strain rate due to an increased modulus.

In recent years a great deal of interest has been shown in the following three areas:

1. the fracture properties of the acrylic bone cements and the related denture base acrylics;
2. the factors that control the stability of crack propagation in specimen geometries designed to give stable crack propagation;
3. the effect of the environment on crack propagation.

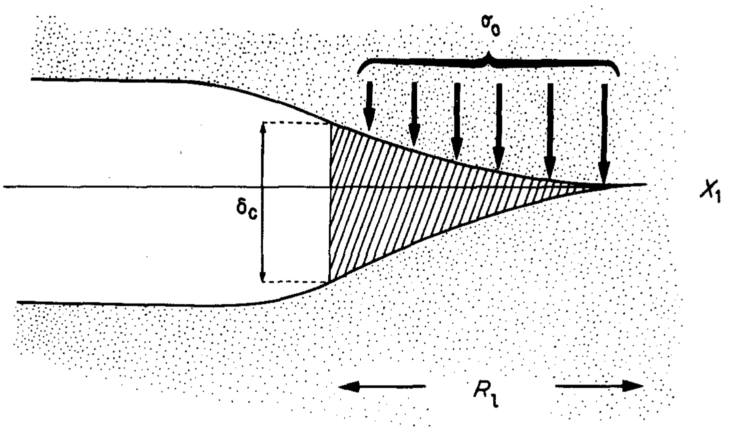

Figure 1 Dugdale plastic zone. The shaded area is the crazed polymer. σ_0 is the craze stress, δ_c the crack opening displacement and R_l the craze length.

Recently, Hakeem and Phillips [11, 12] have used polymethyl methacrylate in methanol as a model system to study crack stability.

This paper examines the effect of water on the fracture of acrylic polymers with the aim of understanding the fracture process in terms of the three areas mentioned.

Most of the studies of the fracture toughness of denture base materials, or the related bone cements, have been carried out in air or in liquid environments using test pieces that give unstable crack growth. Stable crack growth is defined here as:

$$\frac{\mathrm{d}V}{V} \leqslant 0$$

where V is the crack velocity. This means that crack velocity must remain constant or decelerate as the crack progresses through the test specimen. During the slow crack-growth region of failure it is known that K_{Ic} is dependent on environmental conditions. Surprisingly few studies have looked at the fracture toughness of bone cements and denture base materials in water at 37° C, i.e. under clinically relevant test conditions, and all these with one exception, Beaumont and Young [13], have used unstable specimen geometries. It is particularly desirable to use a test specimen in which stable crack growth can be achieved, preferably one in which the crack velocity or strain rate is constant since crazing in liquid environments is known to be rate dependent. This enables modulus and unnotched fracture strength determinations for the calculation of flaw sizes to be carried out at identical, known strain rates.

Benbow [14] noted the dramatic increase in toughness of polymethyl methacrylate and its unstable fracture when tested in water. Gurney and Hunt [15] suggested that in the presence of a solvent the toughness ($\equiv G_{\mathrm{Ic}}$) would be increased by the bluntening of the crack tip by the craze wedge so formed. When the crack jumped out of the plasticized tip into virgin unplasticized material the toughness was lower and cracking was unstable because:

$$\frac{\mathrm{d}G_{\mathrm{Ic}}}{\mathrm{d}A} \leqslant 0$$

where A represents the crack area. Later Mai [16] similarly found toughness to increase on testing polymethyl methacrylate in water and also noted the rate dependence of toughness in liquid environments such as ethanol.

Andrews [17] and his co-workers examined the effect of higher alcohols on craze formation in polymethyl methacrylate and put forward a model based on the reduction of the yield stress or craze stress of the materials at the crack tip. This led Williams [18] to propose his general model for environmental fracture. Williams considered the effect of a reduction of the craze stress, σ_0, by the liquid environment on K_{Ic}. The craze stress, σ_0, fracture toughness, K_{Ic}, modulus, E, and crack opening displacement, δ_c, are related by an expression derived by Rice [19]:

$$\delta_c = \frac{K_{\mathrm{Ic}}^2}{\sigma_0 E}. \qquad (1)$$

Many liquids that crack or craze polymers are chemically inert to them but simply diffuse into the bulk polymer very slowly. The craze, however, because of its porous nature has a high surface to volume ratio so that penetration of the liquid only a small distance within the polymer results in the complete plasticization of the ligaments of the craze resulting in a reduction of their load-carrying

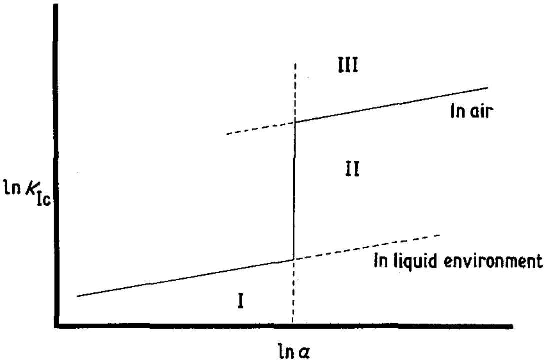

Figure 2 Williams' model for environmental crack growth. Note the reduced fracture toughness in the liquid environment, region I compared with in air region III. Region II is a transition region where fracture toughness is dependent on diffusion of the environment into the crack tip.

capacity; since the ligaments are small ($\simeq$ 20 nm) this process occurs very rapidly so that the material behaves almost instantaneously as one with a lower craze stress. Williams, when first proposing his general model for environmental fracture, assumed that the liquid environment is instantaneously available within the craze and the crack opening displacement (δ_c) is constant.

Williams' model is shown schematically in Fig. 2.

This paper looks at the effect of water on the fracture of homogeneous polymethyl methacrylate and on a range of commercially available denture base acrylics over a range of test rates. The fracture toughness test chosen for this study was the double torsion (DT) test developed by Williams and Evans [20]. This test piece is particularly suited for correlating K_{Ic} with crack velocity and for studying unstable fracture. It is a linear compliance test piece with the crack length measurement not being required for the calculation of K_{Ic} (which eliminates one source of error). It has a constant load to fracture feature and, for stable cracks, the crack velocity is constant along the length of the specimen.

Additional fracture toughness tests were carried out using the compact tension (CT) test to ensure valid plane strain fracture toughness results were being obtained from the DT specimens.

A three-point bend test was used to determine the effect of water on the modulus of elasticity and the unnotched fracture strength.

2. Materials

Three denture base materials were examined in addition to Perspex. The materials, together with their sources, are listed in Table I.

TABLE I List of materials tested and manufacturers

Perspex 3 mm sheet	ICI Plastics Division, Welwyn Garden City, Herts, UK.
Perspex 6 mm sheet	ICI Plastics Division, Welwyn Garden City, Herts, UK.
TS 1195	Cole Polymers Ltd, 686 Mitcham Road, Croydon, UK.
TS 1195 XL	Cole Polymers Ltd, 686 Mitcham Road, Croydon, UK.
Lucitone 199	Caulk Co, Delaware, USA.

2.1. Analysis of the materials tested

An analysis of the materials follows. Perspex consists of a high $\bar{M}_w$ single-phase polymethyl methacrylate. TS 1195 is a suspension polymerized homopolymer polymethyl methacrylate with a pure methylmethacrylate monomer component. TS 1195 XL is the same as TS 1195, but the monomer contains 10% wt/wt of the cross-linking agent ethylene glycol dimethacrylate. Lucitone is a rubber-toughened polymethyl methacrylate. The structure is shown in Fig. 3. Using the technique of Hill [21], the liquid component was found to consist of 89% methyl methacrylate and 11% ethylene glycol dimethacrylate.

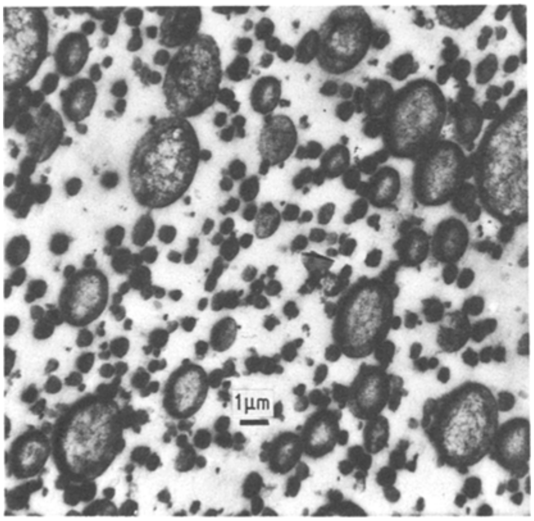

Figure 3 Structure of rubber-reinforced material Lucitone as seen under an electron microscope. The rubber particles appear black, note the occluded polymethyl methacrylate phase within the rubber particles.

2.2. Specimen preparation

Specimens for testing were produced using an identical method to that used to construct dentures. Specimen blanks were prepared by mixing the required amount of polymer powder with the appropriate monomer in the ratio of 2.5 : 1 by weight. This mixture was then left until the polymer/monomer mass reached a dough consistency whereupon it was pressed into plaster moulds slightly larger than the required specimen size; the moulds were contained within a dental flask. The two halves of the flask were squeezed together in a press, removed and placed in a sprung compress clamp that maintained a pressure on the polymer/monomer mass. The clamps and flasks were placed in a water bath at 70° C for 14 h and finally boiled for 1 h. During the cure cycle, benzoyl peroxide thermally decomposes to benzoyl radicals which initiate a free radical polymerization of the monomer; this long cure cycle and subsequent boil ensures a negligible residual monomer content.

The specimen blanks were removed from the plaster moulds and ground to the required specimen dimensions with an Engis polishing[†] machine, using initially 180 grit silicon carbide paper and finishing with 600 grit paper. Perspex specimens were cut from a suitably sized sheet and finished in an identical manner.

3. Test methods

3.1. Double torsion test

Double torsion specimens 65 mm × 40 mm × 3 mm (Fig. 4) were produced in the form of rectangular plates. A vee notch was made at one end of the specimen and a sharp groove was cut down the centre of the plate approximately 0.5 mm in depth using a microslice cutter[‡]. The specimens were precracked in the test jig by loading applied by an Instron[§] 1185 Model at a crosshead speed of $1\,\mathrm{mm\,min^{-1}}$ with rapid unloading once the crack had started to propagate.

During the test the specimen was supported on two parallel rollers of 3 mm diameter and 30 mm apart. The load was applied at a constant rate to the vee-notched end of the specimen via two 3 mm diameter ball bearings spaced 10 mm apart. The specimen was therefore subjected to four-point bend loading during which the crack initiated and propagated along the centre of the specimen within the groove.

3.1.1. Determination of the stress intensity factor

In a double torsion test the mode I stress intensity factor, K_I, is independent of crack length and is given by Kies and Clark [22]:

$$K_\mathrm{I} = PW_\mathrm{m}\left[\frac{3(1+\gamma)}{Wt^3t_\mathrm{n}}\right]^{1/2} \qquad (2)$$

where W_m is the moment arm, W the specimen width, t the specimen thickness, t_n the specimen thickness in the plane of the crack, and γ Poisson's ratio. Values for K_Ic were obtained for both continuous fracture and stick–slip fracture by substituting the load at fracture (P_c) and specimen dimensions into Equation 2. Load/deflection plots for continuous fracture and stick slip fracture are shown in Figs. 5 and 6, respectively.

3.2. Compact tension test

The test and geometry used is based on BS 5447 [23] and has been described previously [10].

3.3. Three-point bend test

The Young's modulus, E, and unnotched fracture strength, σ_f, of each material were determined using a three-point bend test performed with an Instron mechanical testing machine model no. 1185. The relationship between the applied load,

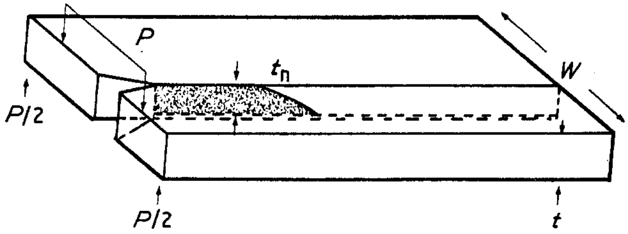

Figure 4 Double torsion specimen. The shaded area denotes the crack.

[†] Engis Ltd, Maidstone, Kent, UK.
[‡] Microslice 2, Metals Research Ltd, Cambridge, UK.
[§] Instron Ltd, High Wycombe, Bucks, UK.

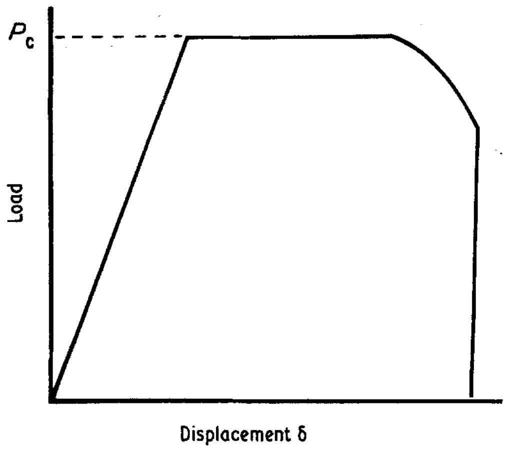

Figure 5 A typical load–displacement curve from a double torsion specimen undergoing continuous crack propagation.

P, and the displacement at the centre of the specimen, δ, for specimens of rectangular cross-sectional area is given by:

$$P = \frac{4EWt^3\delta}{L^3}$$

where t is the thickness of the specimen, W the width of the specimen, and L the distance between the supports.

The test was carried out in accordance with ASTMS D790-71 [24]. A span of 50 mm was used with a specimen size of 65 mm × 10 mm ± 0.03 × 3 mm ± 0.03.

Young's modulus was determined from the initial slope of the plot of P against δ.

The unnotched fracture strength, σ_f, is given by:

$$\sigma_f = \frac{3P_cL}{2Wt^2}$$

where P_c is the load causing fracture.

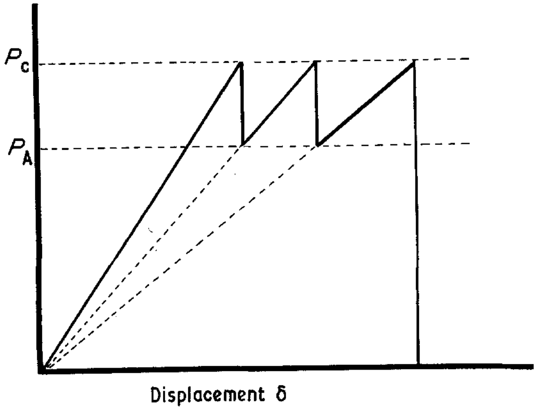

Figure 6 A typical load–displacement curve from a double torsion specimen undergoing stick–slip crack propagation.

3.4. Specimen testing conditions

Specimens were tested after storage in water for 1 month, an adequate time span to reach the equilibrium saturation conditions. The tests were carried out in air at room temperature (19 ± 2° C), in water at room temperature (19 ± 2° C) and in water at 37 ± 2° C. The water temperature of the baths in which the tests were carried out was maintained by a Grants Thermocycler†. Tests were carried out using crosshead displacement rates from 0.05 to 50 mm min^{-1}. The test conditions for each test are given in the appropriate table of results.

3.5. Calculation of the flaw size

A linear elastic fracture mechanics approach was used to calculate the inherent flaw size. This value estimates the size of microstructural features or defects which limit the strength of the material in the absence of an external crack. Actual flaws larger than this size will reduce the strength of the material.

The method used for the calculation of the flaw size is based on the Irwin relation which is applicable to the geometry and loading of a bend-type single edge notch specimen used by Brown and Strawley [25]

$$K_{Ic} = Y\frac{6M}{tW^2}\,a^{1/2}$$

where M is the bending moment equal to $P.S/4$ and Y is a geometrical calibration factor which in the absence of an external flaw or crack Y assumes a value of 1.93.

The Irwin relationship can be rewritten in terms of K_{Ic}, the unnotched fracture strength and the flaw size:

$$a^* = \left(\frac{K_{Ic}}{Y\sigma_f}\right)^2$$

3.6. Scanning electron microscopy

Fracture surfaces of all the materials tested were examined in a stereoscan scanning electron microscope. The surfaces were prepared for examination by depositing thin layers of gold–palladium

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†Grants Instruments Ltd, Bannington, Cambridge, UK.

TABLE II Comparison of the values obtained of the critical stress intensity factor, K_{Ic} ($MN\,m^{-3/2}$) in air and in water at 19 ± 2° C

Material	Air		Water	
	Mean	S.D. ($n = 10$)	Mean	S.D. ($n = 5$)
Perspex	1.28	0.04	2.25	0.06
TS 1195	1.50	0.09	2.18	0.07
TS 1195 XL	1.56	0.02	2.36	0.18
Lucitone	3.00	0.05	2.63†	0.12

†Stable fracture.

TABLE IV Comparison of the calculated values for the flaw size a^* (mm) in air and in water at 19 ± 2° C

Material	Air	Water
Perspex	0.050	0.225
TSS 1195	0.079	0.216
TS 1195 XL	0.078	0.242
Lucitone	0.338	0.372

alloy on the fracture surfaces. A silver colloid was applied to the sides of the samples to conduct heat away from the fracture surface to prevent the breakdown of material to be examined.

4. Discussion

Previous work [26] established the validity of applying fracture mechanics to the fracture in air at room temperature of denture base materials and Perspex.

In this paper, flaw sizes have been calculated routinely; it is recognized that assumptions on which these calculations are based may be invalid, but it is felt that the values indicate what is happening to the craze size and are, therefore, justified.

4.1. The effect of water

The value for the fracture toughness of Perspex almost doubles on testing in water and crack propagation becomes stick–slip (Table II). This agrees with the results of Mai [16] and Benbow [14]. The materials TS 1195 and TS 1195 XL behave in an identical manner to Perspex. The results are in marked disagreement with Williams' model for environmental fracture and it is suggested that water increases the crack opening displacement thereby bluntening the crack tip and increasing the fracture toughness. The results for the rubber-toughened material Lucitone, the only material to exhibit stable fracture, show a reduction on testing in water. In this material, the crack opening displacement and craze at the crack tip are already large due to the presence of rubber particles. As a result, water has a minimal effect in reducing the craze stress through its plasticizing action.

The unnotched fracture strength shown in Table III falls on testing in water. This is because water promotes crazing which increases the flaw size, thus lowering the unnotched fracture strength.

The flaw size shown in Table IV increases dramatically on testing in water. This flaw size is approximately the size of the fibrillar zones associated with crack initiation found on double torsion specimens fractured in water.

There is no significant difference in elastic modulus (Table V) between materials tested in air at room temperature and in water at room temperature.

4.2. Effect of raising the temperature

The values for K_{Ic} at 37° C in water at a crosshead displacement rate of $1\,mm\,min^{-1}$ (Fig. 7), compared to the values at 19° C (Table II) are significantly lower for Perspex TS 1195 and TS 1195 XL, whilst the result for Lucitone is not significantly different. The value for K_{Ic} would be

TABLE III Comparison of the values for the unnotched fracture strength, σ_f ($MN\,m^{-2}$) in air and in water at 19 ± 2° C. Specimens were stored in water for 1 month prior to testing

Material	Air		Water	
	Mean	S.D. ($n = 10$)	Mean	S.D. ($n = 10$)
Perspex	93	6.27	78	2.10
TS 1195	87	9.16	77	2.51
TS 1195 XL	91	4.10	79	4.10
Lucitone	85	3.47	71	3.00

TABLE V Comparison of the values obtained for the modulus E ($MN\,m^{-2}$) in air and in water at 19 ± 2° C. Specimens were stored in water for 1 month prior to testing

Material	Air		Water	
	Mean	S.D. ($n = 10$)	Mean	S.D. ($n = 10$)
Perspex	2640	34	2750	63
TS 1195	2560	82	2670	96
TS 1195 XL	2510	55	2590	88
Lucitone	2280	63	2460	49

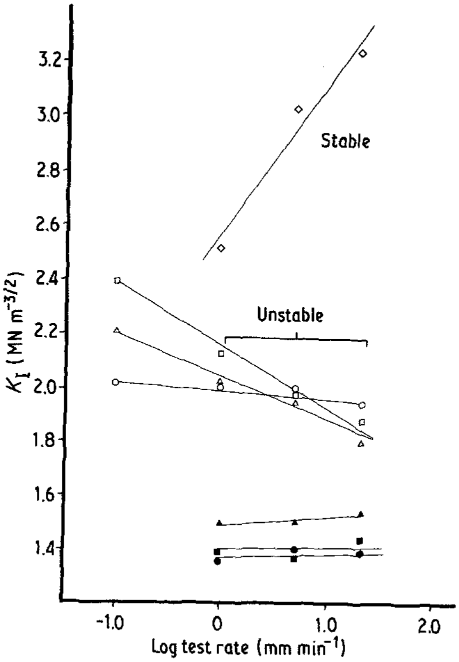

Figure 7 Plot of stress intensity factor against logarithm of the test rate for acrylic materials tested in water. Filled in symbols indicate values for K_{IA} and open symbols values for K_{Ic}. ○ = Perspex, △ = TS 1195, □ = TS 1195 XL and ◇ = Lucitone. Note that the negative slopes of K_{Ic} give rise to unstable crack propagation whilst the positive slope gives rise to stable crack propagation.

expected to fall since the modulus is reduced as the temperature is raised. Another contributing factor might be that of craze stress. Morgan and Ward [9] have shown that the craze stress falls appreciably over the temperature range 15 to 40° C for Perspex in air and it would seem likely that a similar reduction of craze stress would take place in water.

The unnotched fracture strength falls on raising the temperature to 37° C. This is probably due to the reduced fracture toughness and possible increased crazing taking place. However, the flaw size remains approximately constant and appears to be independent of temperature.

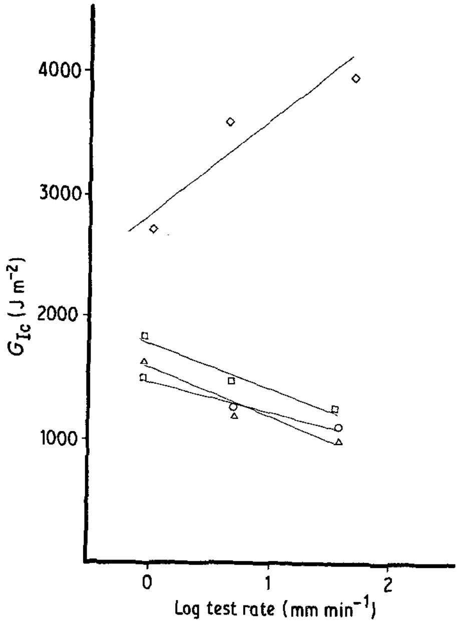

Figure 8 Plot of strain energy release rate against logarithm of the test rate. ○ = Perspex, △ = TS 1195, □ = TS 1195 XL and ◇ = Lucitone. Note again how the negative slopes of G_{Ic} give rise to unstable crack propagation whilst the positive slope results in stable crack propagation.

4.3. The effect of changing the test rate

4.3.1. The critical stress intensity factor

The critical stress intensity factor (Fig. 7) tends to decrease with increasing test rate for all the materials except Lucitone, which shows an increase in K_{Ic} with increasing crosshead displacement rate. (Lucitone was the only material to exhibit stable crack growth at 1, 5 and 20 mm min^{-1} crosshead displacement rates.) The value for K_{Ic} would have been expected to rise as the cross-head displacement rate rises since the modulus increases with increasing test rate (Table VI). The only explanation, therefore, is that G_{Ic} must be decreasing as the test rate is increased. This is confirmed by calculating values for G_{Ic} at different test rates (Fig. 8). The values for G_{Ic} fall due to reduced crazing taking place at the crack tip. One of the

TABLE VI Mean and standard deviation values of E (MN m^{-2}), obtained in water using the three-point bend test at different crosshead speeds. Specimens were tested in water at 37° C

Material	0.1 mm min^{-1}	S.D. (n = 10)	1 mm min^{-1}	S.D. (n = 10)	5 mm min^{-1}	S.D. (n = 10)	20 mm min^{-1}	S.D. (n = 10)
Perspex (3 mm)	2260	31	2510	54	2560	31	2800	23
TS 1195	2240	59	2450	68	2520	52	2690	76
TS 1195 XL	2280	97	2360	84	2460	71	2580	69
Lucitone	2020	57	2210	93	2400	57	2390	77

TABLE VII Unnotched fracture (σ_f) for some denture base polymers tested in water at 37° C at a variety of strain rates. Specimens were stored in water for 1 month prior to testing

Material	1 mm min^{-1} (MN m^{-2})	S.D. ($n = 10$)	5 mm min^{-1} (MN m^{-2})	S.D. ($n = 10$)	20 mm min^{-1} (MN m^{-2})	S.D. ($n = 10$)	50 mm min^{-1} (MN m^{-2})	S.D. ($n = 10$)
Perspex (3 mm)	69	0.62	76	1.79	90	1.54	97	1.73
TS 1195	67	1.44	76	3.05	81	2.28	89	3.22
TS 1195 XL	70	1.78	77	4.59	83	2.82	91	3.04
Lucitone	62	1.68	68	3.22	75	3.04	82	3.05

criteria for unstable fracture is that dG_{Ic}/dV, i.e. the rate of change of G_{Ic} with crack velocity, is negative explaining the unstable stick–slip fracture. Crack propagation becomes stable at the 0.1 mm min^{-1} rate because dG_{Ic}/dV is positive. Crazing in water is probably a time-dependent mechanism. Evidence for this can be obtained from the fracture surfaces; as the test speed was increased, the roughened fibrillar zone associated with the first crack jump decreased in size, indicating that the degree of crazing at the crack tip falls on increasing the test rate.

Stable crack growth would then occur when the test rate was slow enough to allow full development of the crazing process. An alternative mechanism is that the rate of flow of water into the crazed crack tip could be the rate-determining step. Low test rates would provide more time for the water to flow into the crack tip and promote crazing, the velocity of stable crack growth in water at the 0.1 mm min^{-1} test rate would then correspond to the rate of flow of water into the crack tip craze. Typical crack velocities were 1.0 to 3.0×10^{-5} m sec^{-1}.

Loading specimens at 95% of the load to initiate fracture for 10 min caused a small amount of stable propagation at a higher K_{Ic} value to occur. Subsequent crack jumps took place at lower values for K_{Ic}.

The critical stress intensity factor at crack arrest is unaffected by the test rate, suggesting that crack arrest occurs at an approximately constant strain rate or crack velocity. The results showing K_{Ic} to increase with falling test rate, whilst K_{IA} remains constant are in general agreement with the results for testing epoxy resin in distilled water by Yamini and Young [27], and in agreement with Phillips' [28] results on Perspex in water at room temperature. Phillips has only achieved stable crack propagation in water at high crosshead displacement rates where the rate of propagation of the crack is faster than the diffusion of water into the crack tip. Under these conditions the test is effectively being carried out in air. The results are also in general agreement with the work of Phillips and Hakeem [12] for which methanol was used as the environmental medium. They showed a decreasing K_{Ic} with increasing test rate in methanol. Mai [16], however, found that K_{Ic} rose with increasing test rate for Perspex in ethanol. Phillips and Hakeem suggest two explanations: the first is that the five-fold difference in crosshead displacement rate between their tests and that of Mai could bring about the inversion of K_{Ic} (liquid environment) $> K_{Ic}$ (air), to K_{Ic} (liquid environment) $< K_{Ic}$ (air); the second is that methanol and ethanol are anomalous in their behaviour towards polymethyl methacrylate. Our results indicate that the second explanation is the more likely one.

4.3.2. Unnotched fracture strength

The unnotched fracture strength falls on reducing the crosshead displacement rate (Table VII), and is probably a result of increased crazing taking place at lower test rates. The ranking order for the unnotched fracture strengths changes on increas-

TABLE VIII Calculated values of flaw size (mm) using the Irwin SEN method using K_{Ic} from DT tests in water at 37° C at different crosshead speeds

Material	Crosshead speed		
	1 mm min^{-1}	5 mm min^{-1}	20 mm min^{-1}
Perspex (3 mm)	0.218	0.181	0.124
TS 1195	0.249	0.177	0.135
TS 1195 XL	0.248	0.181	0.143
Lucitone	0.443	0.525	0.477

TABLE IX Some values for Perspex under different conditions of critical stress intensity factor, K_{Ic} ($\mathrm{MN\,m^{-3/2}}$), modulus, E ($\mathrm{MN\,m^{-2}}$), yield stress σ_y ($\mathrm{MN\,m^{-2}}$), and crack opening displacement, δ_c (μm). Values for σ_y are taken from the work of Bauwens-Crowet [29]

Test condition	Specimen geometry	Cross-head speed ($\mathrm{mm\,min^{-1}}$)	K_{Ic}	E	σ_y	δ_c
Air 19 ± 2° C	CT	1	1.14	2640	94	5.2
Air 19 ± 2° C	DT	1	1.28	2640	94	6.6
Water 19 ± 2° C	DT	1	2.25	2750	94	19.6
Water 37 ± 1° C	DT	1	1.97	2260	72	23.8
Water 37 ± 1° C	DT	5	1.98	2510	94	16.6
Water 37 ± 1° C	DT	20	1.93	2560	110	13.2

ing the test rate. As the flaw size reduces due to decreasing crazing taking place, real flaws within the materials will have a more pronounced effect. Thus Perspex has an almost identical unnotched fracture strength, σ_f, to that of TS 1195 XL at a test rate of $1\,\mathrm{mm\,min^{-1}}$, whilst at $50\,\mathrm{mm\,min^{-1}}$ Perspex has a considerably higher σ_f due probably to its more homogeneous structure.

4.3.3. *Flaw size and crack opening displacement*

The values for the flaw size increase as the test rate is reduced (Table VIII) due to crazing being time-dependent but whether the flaw size corresponds accurately to the craze size cannot be determined. Crazing in water might be expected to increase the craze length, R, alter the craze stress, σ_0, and increase the crack opening displacement. These values have been measured for Perspex in air by Morgan and Ward [8]. The methods used to obtain these values directly would be exceedingly difficult to apply to cracks which were unstable. Values of δ_c can, however, be easily calculated using Equation 1. They are also useful to determine where the load–deflection plot is non-linear and where the craze at the crack tip is sufficiently large to modify the elastic stress distribution around the crack tip. Table IX shows some calculated values for δ_c obtained by substituting measured values for E and K_{Ic}, along with values for the yield stress, σ_y, taken from the work of Bauwens–Crowet [29], into Equation 1.

The value for δ_c for Perspex in air (Table IX) calculated from both CT and DT tests is markedly larger than directly measured values of δ_c. This is probably a result of water plasticizing the crack tip, errors in measurement of K_{Ic}, E and σ_y, and no correction factor for the Poisson's ratio being used. The δ_c is increased markedly on testing in water, and increases as the temperature is increased to 37° C with the values at 37° C showing an increase in δ_c with reducing test rate. It would be interesting to establish if the crack opening displacement was constant during the stable crack growth region in water, as it has been found to be during the stable crack growth region in air.

Kinloch and Williams [30] have proposed a model for crack stability in epoxy resins based on yield stresses and plastic zone sizes, and that it is the presence of a plastic zone due to yielding at

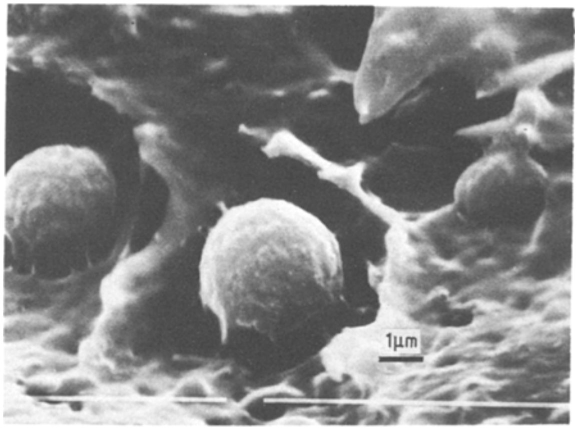

Figure 9 Rubber particle exposed in the fracture surface of Lucitone as seen under the scanning electron microscope. Note the cavitation and flow that has occurred around the rubber particle and the fibrils connecting the particle to the matrix.

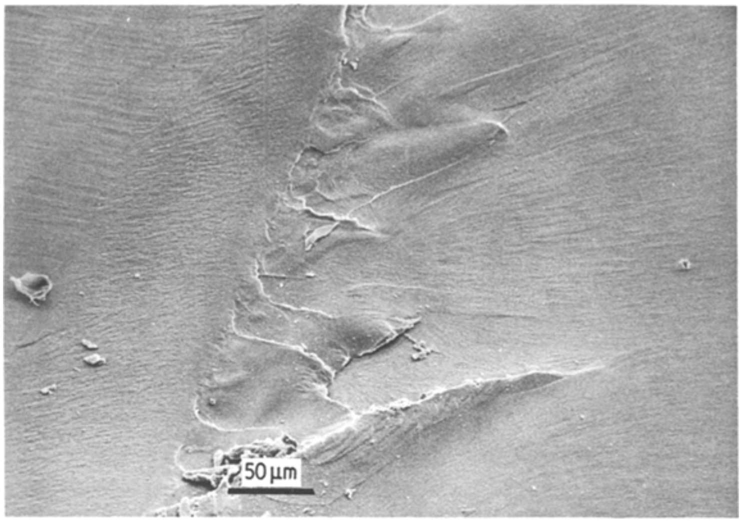

Figure 10 Fracture surface of Perspex tested in water. The roughened zone is associated with both crack initiation and arrest and is thought to be a result of an increased crack opening displacement due to plasticization by water.

the crack tip that causes stick–slip crack propagation. This work suggests that it is not simply the presence of a plastic zone and a resulting larger δ_c that causes unstable propagation, but a δ_c that is decreasing in size with increasing test rate or crack velocity. Thus if

$$\frac{\mathrm{d}(\delta_c)}{\mathrm{d}V} \leqslant 0$$

a crack is unstable, agreeing with the concept that unstable crack growth is determined by:

$$\frac{\mathrm{d}G_{\mathrm{Ic}}}{\mathrm{d}V} \leqslant 0$$

4.4. Fractography

4.4.1. Specimens fractured in air

The fracture surfaces of Perspex, TS 1195 and TS 1195 XL were smooth and featureless with the exception of ribmarks. Lucitone, the rubber-reinforced material, had parabolic markings on its fracture surfaces and at higher magnifications rubber particles could be seen (Fig. 9). The larger flaw size of Lucitone was due to the increased plastic flow and crazing associated with the rubber particles.

4.4.2. Specimens fractured in water

The fracture surfaces of Perspex, TS 1195 and TS 1195 XL had a roughened fibrillar zone associated with both crack initiation and arrest (Fig. 10). This roughened fibrillar zone increased in size as the test rate was reduced until stable fracture was achieved. Fracture surfaces are formed as a result of the crazing process which takes place at the crack tip. When a craze has a small crack opening displacement and its length is long, a relatively

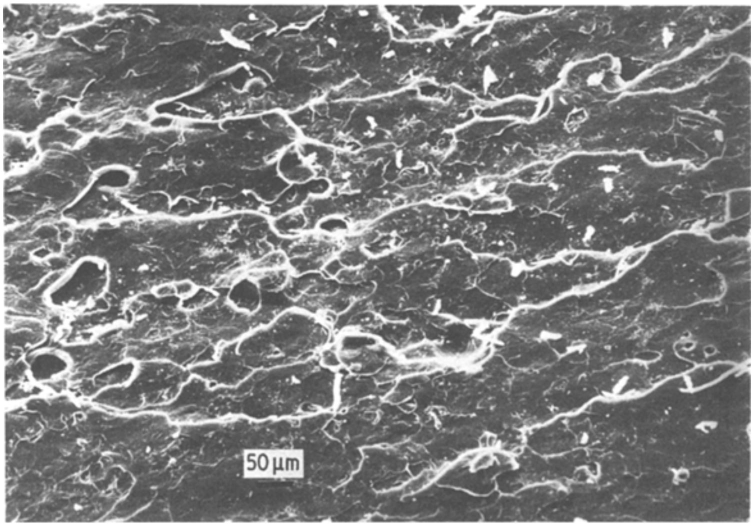

Figure 11 Fracture surface of TS 1195 tested in water. The fracture surface is much rougher than for specimens tested in air.

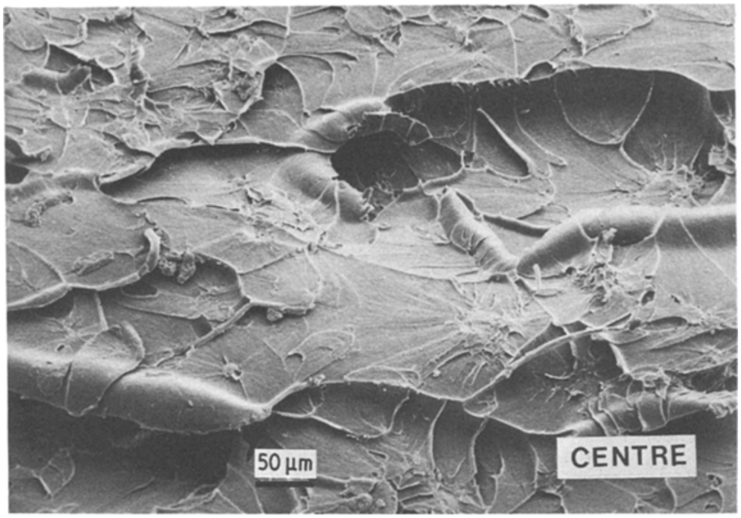

Figure 12 Fracture surfaces of Lucitone tested in water. Note the difference in structure between the centre and the edge indicative of non plain strain conditions throughout the specimen thickness.

smooth fracture surface will result. If, however, the craze has a large crack opening displacement and short length, the crack will wander from one void to another within the craze causing a rough fracture surface. Thus the crack tip in water, and the much rougher fracture surfaces of specimens that underwent stable crack propagation in water (Fig. 11) indicate that the crack opening displacement is larger in water and constant for stable crack propagation.

The fracture surfaces of Lucitone specimens tested in water at 37° C were markedly different from those tested in air. A large amount of plastic flow is seen on the fracture surface shown in Figs. 12 and 13, the morphology of the centre of the specimen being entirely different from the edge. No equatorial crazing, that was a characteristic feature of specimens tested in air, was seen around the rubber particles. It is possible that the plastic flow or yielding prevented craze formation. The thickness effect was clearly seen on examining the specimen visually with only the central region having been craze whitened. As the temperature was reduced to room temperature, or the crosshead displacement rate increased, this edge effect diminished. The ratio of crazing to yielding which occurs will depend on the test rate and temperature. Yielding is favoured compared with crazing at higher temperatures and lower test rates, and since yielded material cannot maintain high stresses, lower K_{Ic} values will therefore be obtained at higher temperatures and lower test rates. Fracture toughness measurements are no longer valid when applied to materials that

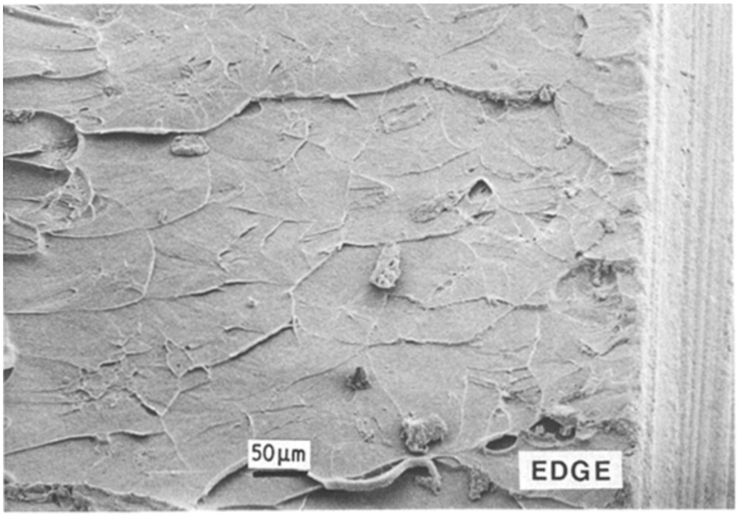

Figure 13 Fracture surfaces of Lucitone tested in water. Note the difference in structure between the centre and the edge indicative of non plain strain conditions throughout the specimen thickness.

TABLE X Comparison of values of K_{Ic} (MN m$^{-3/2}$), and G_{Ic} (J m^{-2}) for 3 and 6 mm thick compact tension specimens of Perspex and Lucitone tested in water at 37° C. Specimens were tested saturated at a cross-head speed of 1 mm min^{-1}

Material	Thickness	K_{Ic}		G_{Ic}	
		Mean	S.D. ($n = 5$)	Mean	S.D. ($n = 5$)
Perspex (6 mm)	3 mm	1.81	0.07	–	–
Perspex (6 mm)	6 mm	1.78	0.09	–	–
Lucitone	3 mm	2.54	0.11	4533	368
Lucitone	6 mm	2.65	0.13	3215	240

exhibit large amounts of plastic flow and edge effects.

4.5. The validity of fracture mechanics to the materials tested

The validity of linear elastic fracture mechanics applied to Perspex and Lucitone was ascertained using compact tension tests at 37° C in water. Table X shows the effect of specimen thickness on K_{Ic} and G_{Ic} for Perspex and Lucitone where there is clearly no significant difference in K_{Ic} for two different thicknesses of Perspex, no significant difference in K_{Ic} for 3 and 6 mm specimens of Lucitone, but there is a significant difference in the values of G_{Ic}.

The 3 mm specimens of Lucitone clearly no longer obey the linear elastic fracture mechanics theory since

$$\left(\frac{K_{Ic}}{EG_{Ic}}\right)^2 (1-\gamma^2) \neq 1$$

A 6 mm Perspex sheet tested using 6 mm thick DT specimens at 37° C at cross-head displacement rates from 0.05 to 50 mm min^{-1} gave very similar results to that of the 3 mm sheet (Fig. 14).

It seems reasonable to assume that Perspex TS 1195 and TS 1195 XL are being tested under plane strain conditions at 37° C in water with 3 mm specimens, whilst the material Lucitone is being tested in a plane stress condition or a condition in between that of plane strain and plane stress.

5. Conclusions and implications

Water has a dramatic effect on crack propagation in acrylic polymers. It is clear from the results that the mechanism for environmental fracture proposed by Williams is not applicable because of an increase in the crack opening displacement. Fracture in water is test-rate sensitive and this rate sensitivity may be due to the rate of flow of water into the crack tip. The fracture behaviour of acrylics in water is similar to that in methanol, but markedly different from that in ethanol; this difference might be a result of the bulkier ethanol molecules having a greater plasticizing action. Low molecular weight chemical species found in food stuffs and in body fluids would be likely to be of importance in the failure of dentures and bone cements.

High molecular weight species, such as proteins would probably be of less importance since

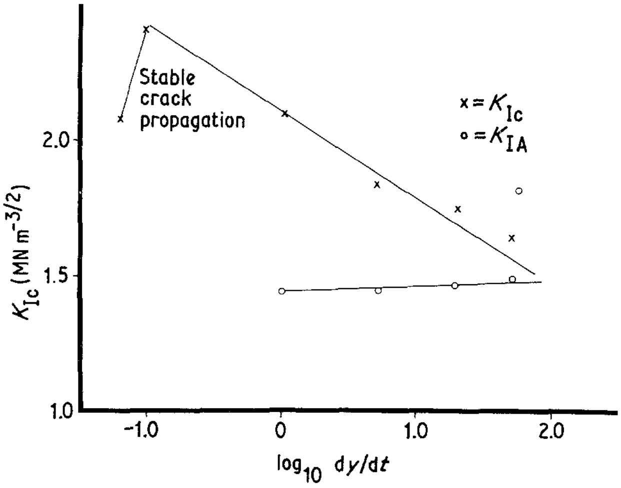

Figure 14 Plot of stress intensity factor against logarithm of the test rate for 6 mm thick Perspex specimens in water. The similarity of the plot to that for thinner specimens confirms that plain strain conditions were attained. The reduction in K_{Ic} at low test rates explains the stable fracture found.

they would be very low in diffusing into the crack tip.

All fatigue and fracture toughness testing of bone cements and denture base materials should be carried out in water. The fracture process of acrylic polymers in liquid environments is complex and worthy of further investigation to elucidate the fracture mechanism, particularly with respect to craze shape and structure at the crack tip.

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