Eur. Polym. J. Vol. 23, No. 1, pp. 41–50, 1987
Printed in Great Britain

0014-3057/87 $3.00 + 0.00
Pergamon Journals Ltd

THE EFFECT OF MOLECULAR PROPERTIES ON THE MECHANICAL BEHAVIOUR OF PMMA—II. ENVIRONMENTAL STRESS CRACKING IN METHANOL

V. T. TRUONG,[1]* D. R. G. WILLIAMS[2] and P. E. M. ALLEN[1]
Departments of Physical and Inorganic Chemistry[1] and Chemical Engineering,[2] University of Adelaide, South Australia 5001, Australia

(*Received* 26 *May* 1986)

Abstract—The fracture process of low molecular weight PMMA in the presence of methanol is a crack predominant mechanism (Regime II). The activation energy of the cracking process calculated by Zhurkov's rate theory suggested that the failure mechanism is governed by a process where the slippage of chain molecules over each other results in the secondary bond breakage. Analysis based on a linear elastic fracture mechanics approach demonstrated the dependence of the crack opening displacement and the craze length on temperature and the stress intensity factor (SIF). Agreement between values of the diffusion coefficient at zero applied stress derived from the cracking data and those from methanol-equilibration of bulk PMMA indicated the role of diffusional behaviour of methanol in the failure mechanism. Increasing craze length with temperature or the SIF can be related to the enhancement of the diffusion coefficient at elevated temperature or increased SIF. The Williams–Marshall theory demonstrated quantitatively more rapid decay of the crazing stress as larger amounts of methanol are absorbed at the crack tip.

INTRODUCTION

Fracture of a polymer can, in general, be said to occur due to a combination of the processes, namely stress cracking and stress crazing. For example, the fracture of PMMA in air occurs predominantly by a stress cracking process whilst fracture of PMMA in an active environment such as methanol occurs by a subtle combination of stress cracking and crazing—the contribution of each mechanism depending upon the molecular weight characteristics of the polymer and environmental conditions, e.g. failure of a high molecular weight PMMA in methanol occurs predominantly by craze growth with subsequent fibril breakdown.

There has been a considerable number of studies concerned with the mechanisms of craze initiation and craze propagation [1–9] of glassy polymers in active environments. Correlation between the solubility parameter and the critical strain predicting crazing or cracking was suggested by Benier and Kambour [1] and later modified by Vincent and Raha [3]. Temperature effect on the crazing fracture energy in alcohols has been investigated by Andrews and Bevan [8]. Williams and Marshall [10] developed a theoretical treatment using the linear elastic fracture mechanics (LEFM) approach to demonstrate the effect of environments on the kinetics of crack and craze growth, the crack opening displacement (COD) and the stress intensity factor (SIF), K_c.

There have been few papers, however, relating to the effect of molecular weight (MW), molecular weight distribution (MWD) and tacticity on the failure mechanism of polymers in active environments. This is partly attributed to the fact that the establishment of mechanical properties and basic molecular parameters (MW, MWD and tacticity) has been seriously impeded by scarcity of well defined samples for testing. Reliable synthetic techniques are now available, at least in the laboratory, to produce relatively narrow MWD PMMA of known tacticity. In our previous study [11] the effect of tacticity on the failure mechanism was observed in the significant enhancement of fracture toughness of low MW atactic PMMA, in the presence of methanol, by blending in isotactic PMMA. It was also demonstrated that the enhancement in the fracture toughness of isotactic and atactic PMMA blends in active environments is strongly dependent on the complexing ability of the cracking/crazing solvent in promoting the crystallization of stereocomplexes at the crack tip thus facilitating the stabilization of craze fibrils. In the first paper of the series [12] the effect of MW on fracture energy of narrow and broad MWD PMMA has been studied in depth and a theory has been proposed to predict the sigmoidal curve of MW and fracture energy relationship.

Fracture toughness of PMMA in the presence of methanol exhibited strong dependence on the MW. The failure mechanism showed two distinct fracture behaviours: crazing in high MW samples and cracking in low MW samples [13]. In this paper the environmental stress cracking of low MW PMMA in methanol is investigated using Zhurkov's rate process relationship and the LEFM approach. Diffusional behaviour of methanol at the crack-tip and analysis based on the Williams–Marshall (WM) theory [10] are also discussed.

---

*Now at Australian Dental Standards Laboratory, Abbotsford, Victoria.

EXPERIMENTAL

Narrow MWD samples of PMMA were prepared by anionic polymerization and details are described elsewhere [11, 13]. A commercially supplied sample (Polysciences) of low molecular weight PMMA is included for comparison.

Molecular weights (MW) and molecular weight distribution (MWD) were determined by GPC. Sample designations and ratios $\bar{M}_w/\bar{M}_n$ are listed in Table 1.

Fracture toughness measurements

The test specimen configuration was double torsion (DT) geometry. The details of the technique have been previously described [12]. The whole specimen could be immersed in a constant temperature bath of methanol. The specimen was initially loaded in the range 0.5–1.2 kg and over a period of approximately 15 min this relaxed to the same constant value. This initial relaxation was attributed to some settling-in plastic flow around the supports. Methanol was then introduced into the bath to fully immerse the specimen. The temperature of the methanol was controlled to $\pm 1°C$ over a range from 0 to 40°C.

The stress intensity function at fracture, K_c, was determined utilizing the general compliance method [12, 15] and the crack or craze velocity, **v**, determined by measuring the time elapsed for the crack to travel between prescribed 2 mm incremental marks on the top surface. The corresponding average load, P, can be found directly from the Instron recorder. The crack velocity, **v**, could also be calculated from the rate of load relaxation, dP/dt, the initial value of load and the initial crack length [15]. However, it was often more convenient to find **v** by direct observation of the front tip propagation than from the dP/dt method, e.g. at $v \simeq 10^{-6}$ m/sec it was especially difficult to determine dP/dt as the change in slope approached zero.

Specimen configuration used in the presence of methanol was the protected geometry i.e. two sides of specimen were protected by silicone grease. Methanol entered the crack from the end but not the sides of the specimen and was termed by Marshall *et al.* as end flow [10]. This configuration basically simplified the crazing kinetics by eliminating the complicating effects of methanol entering from the sides.

RESULTS

The log K_c vs log **v** plots (Fig. 1) show a strong dependence on MW and can be divided into three Regimes: Regime I, Transition Regime and Regime II. Regime I is a mature craze growth region (high MW samples) and is associated with a honeycomb fracture surface as observed under a scanning electron microscope [16]. In contrast, Regime II is a rapid crack propagation regime (low MW samples) and is characterized by a featureless fractured surface. The transition Regime is intermediate between Regimes I and II, characterized by a mixture of crack and craze on the fractured surface. This paper will concentrate on analysis of experimental data in Regime II. Regime I and the Transition Regime are discussed elsewhere [16].

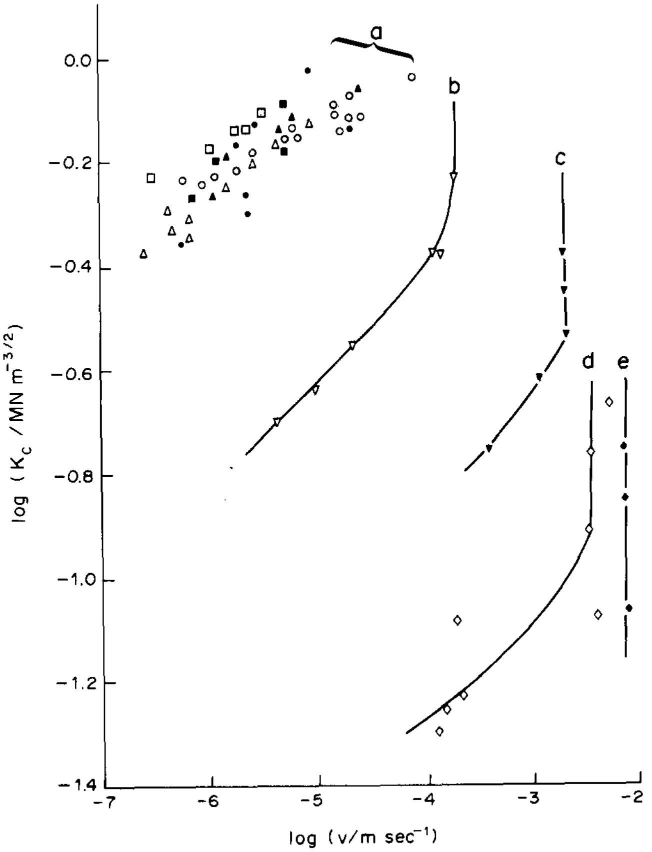

Fig. 1. The effect of MW on fracture toughness in methanol ($T = 20°C$) expressed as log K_c vs log v diagram for narrow MWD PMMA. (a) Regime I: A1 ($\bar{M}_w = 550{,}000$, □), A3 ($\bar{M}_w = 380{,}000$, ▲), A4 ($\bar{M}_w = 150{,}000$, ○), A5 ($\bar{M}_w = 97{,}000$, △) and A6 ($\bar{M}_w = 84{,}000$, ●). (b) Transition Regime: A7 ($\bar{M}_w = 71{,}000$). (c, d, e) Regime II: A8 ($\bar{M}_w = 36{,}000$), A9 ($\bar{M}_w = 31{,}000$) and A10 ($\bar{M}_w = 23{,}500$).

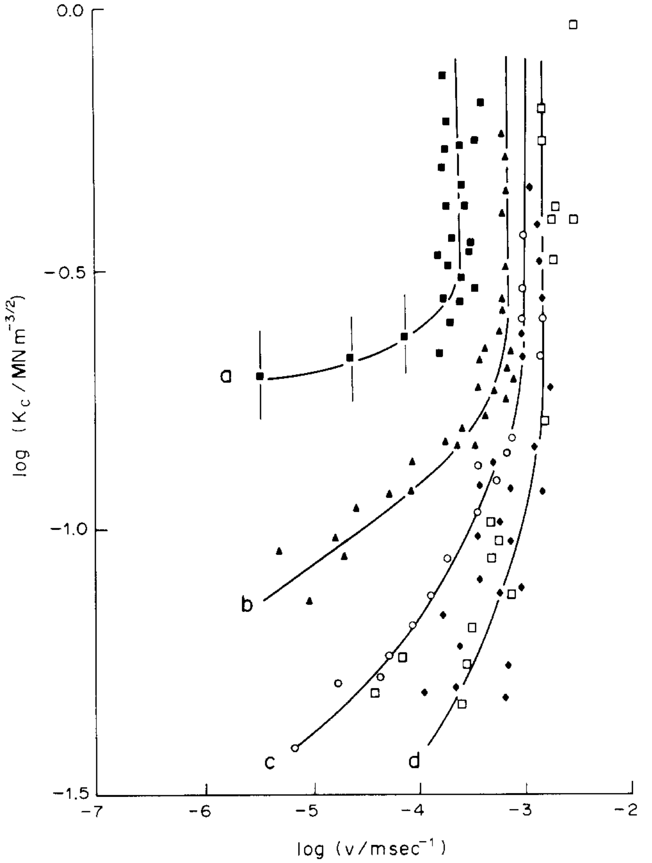

Fig. 2. Plot of log K_c vs log **v** for LWM at various temperatures, (a) $T = 0°C$, (b) $T = 10°C$, (c) $T = 20°C$, (d) $T = 30°C$ (□) and $T = 40°C$ (◆).

The log K vs log **v** plots of Regime II can be divided into two sections: (a) a vertical section specified by a limiting velocity, $\mathbf{v}_0$, and (b) a sloping section at $\mathbf{v} < \mathbf{v}_0$. A commercial low molecular weight sample, LMW, shows rapid crack propagation with a fracture surface devoid of feature and thereby belongs to Regime II. Comparison of the log K_c vs log **v** plots for various MW polymers (Regime II in Fig. 1) and for a LMW polymer at various temperatures (Fig. 2) indicate that increasing the MW has an equivalent effect to decreasing the temperature.

The temperature dependence of the log K_c vs log **v** relation can be analyzed in terms of Zhurkov's theory to provide an understanding of the process via the magnitude of the activation energy (Section 1). Furthermore, application of LEFM to the analysis of experimental data provides an insight into the important variables such as the crack opening displacement, COD, and the craze length in the presence of solvent (Section 2). The diffusion coefficient which can be deduced from the cracking data will be compared with the experimental values of the diffusion coefficient of methanol to clarify the effect of the rate of diffusion on the cracking mechanism. Furthermore, by comparing the stress and temperature dependence of the diffusion coefficient and that of the craze length, it is interesting to see how the rate of diffusion will affect the geometry of the crack tip (Section 3). Lastly, the Williams–Marshall [18] theory will be applied to clarify the time dependent deformation process at the crack tip (Section 4).

1. Temperature dependence from the viewpoint of Zhurkov's theory

Zhurkov [19] carried out a rigorous study of the fracture kinetics of solids including metals and polymers and found that a wide range of materials followed a stress-biased Rhee-Eyring equation

$$t = t_0 \exp\left(\frac{U_0 - \gamma_F' \sigma_c}{RT}\right) \qquad (1)$$

where t = the time to failure measured from the moment of loading, t_0 = the limiting time, U_0 = the activation energy, σ_c = the crazing stress and γ_F' = constant [19, 20]. The crack velocity, **v**, is in-

Table 1. Molecular weights and molecular weight distributions

Sample	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A1	550,000	1.25
A3	380,000	1.20
A5	97,000	1.20
A6	84,000	1.20
A7	71,000	1.20
A8	36,000	1.20
A9	31,000	1.25
A10	23,500	1.25
LMW	160,000	2.10

versely proportional to the fracture time, t, and therefore

$$\mathrm{v} = \mathrm{v}_0 \exp\left(-\frac{U_0 - \gamma'_F \sigma_c}{RT}\right) \quad (2)$$

where v_0 = the limiting crack velocity.

The energy release rate, G_c, is related to the crazing stress, σ_c, and the COD, u_c, by [15]

$$G_c = \sigma_c u_c$$

and substituting σ_c in Eqn 2 gives

$$\mathrm{v} = \mathrm{v}_0 \exp -\left(\frac{U_0 - \gamma_F G_c}{RT}\right) \quad (3)$$

where $\gamma_F = \gamma'_F / u_c$.

This equation has been applied successfully to the fracture process in air for glass by Schonert *et al.* [21], Kies and Clark [22], for PMMA by Atkins *et al.* [23] and for polystyrene by Mai and Atkins [24]. Rewriting Eqn 3 by substituting $G_c = K_c^2/E$, where E is the modulus:

$$\mathrm{v} = \mathrm{v}_0 \exp -\left(\frac{U_0 - \gamma_F (K_c^2/E)}{RT}\right). \quad (4)$$

As can be seen from Fig. 2, the log K_c vs log v curves for LMW at various temperatures approach a limiting velocity v_0, characterized by the vertical part of the curve. By applying Eqn 4, the activation energy, U_0, and the constant, γ_F, can be evaluated. Eqn 4 can be rewritten as

$$RT \ln \frac{\mathrm{v}_0}{\mathrm{v}} = U_0 - \gamma_F \frac{K_c^2}{E} \quad (5)$$

and this equation suggests that $RT \ln \mathrm{v}_0/\mathrm{v}$ vs K_c^2/E will give a straight line (Fig. 3) where U_0 is the intersection and γ_F is the slope and $E = 3.5\,G\mathrm{Nm}^{-2}$ [25]. The results are shown in Table 2.

As shown in Table 2, the activation energy, U_0, of crack propagation in the presence of methanol varies from 18.2 to 11.4 kJ mol^{-1} as the temperature increases from 0 to 40°C. The values of U_0 are of the order of secondary bond energies and suggests that the breakdown does not occur by the rupture of the main chain but rather by the rupture of intermolecular secondary bonds. The temperature dependence of the activation energy also suggests the breakdown mechanism is governed by a viscous flow process [26]. The magnitude of U_0 is five to ten times smaller than that reported by Atkins *et al.* [23] and Marshall *et al.* [17] for the stable crack propagation of PMMA ($\mathrm{v} < 10^{-1}$ m/sec) in air.

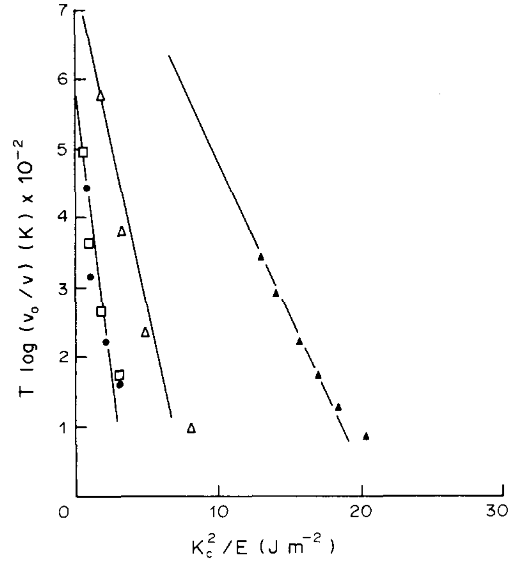

Fig. 3. Plot of fracture toughness–velocity relationship for LMW PMMA in methanol in terms of Zhurkov's theory [T log (v_0/v) vs K_c^2/E]. $T = 0$°C (▲), $T = 10$°C (△), $T = 20$°C (□), $T = 40$°C (●).

Table 2. Calculated values of U_0 and γ_F at $T = 0$ to 40°C for the cracking process in methanol

T (°C)	U_0 (kJ mol^{-1})	γ_F(m^2 mol^{-1})	γ_F(m^2) × 10^{21}*
0	18.2	866	1.41
10	15.3	1912	3.19
20–40	11.4	2870	4.78

*Dimensions of γ_F are changed from m^2 mol^{-1} to m^2 by using Avogadro's number, N_A: γ_F(m^2 mol^{-1}) = γ_F(m^2)N_A.

Furthermore, the magnitude of γ_F for the cracking of PMMA in methanol is larger by two decades (Table 2) than the γ_F for the cracking of PMMA in air ($\gamma_F = 8.9 \times 10^{-23}$ m^2) [23], and for the cracking of polystyrene and glass-filled polystyrene ($\gamma_F = 1 \times 10^{-23}$ to 6×10^{-23} m^2) [24]. According to Zhurkov [19], the value of γ_F (or γ'_F) describes the strength of solids and is sensitive to the molecular orientation of the solids. Zhurkov believed that γ_F was inversely proportional to the fracture resistance of materials. In this sense, the γ_F values obviously suggest that PMMA is more prone to cracking in methanol than in air. This prediction can also be observed in the log K_c vs log v diagram where values of K_c in methanol cracking are always lower than K_c in air cracking at a given crack velocity (Fig. 4).

Zhurkov's suggestion, however, lacks molecular significance. Kies and Clark [22] suggested that

$$\gamma_F = \beta \lambda^2 \quad (6)$$

where β = the fraction of the fracture energy required in breaking bonds to create surfaces and λ = the spacing distance for the intermolecular bond (λ = 0.7 nm). Now the energy release rate at fracture, G_c may be defined in terms of the total surface energy γ_c, where

$$G_c = 2\gamma_c.$$

The total surface energy can then be divided into that part which is related to plastic deformation, γ_{c2} and that part which is related to surface energy only, γ_{c1}, that is

$$G_c = 2(\gamma_{c1} + \gamma_{c2})$$

therefore

$$G_c \beta = 2\gamma_{c1}. \quad (7)$$

The values of β can be calculated from Eqn 7 where $G_c = K^2/E$ and $E = 3.5\,G\mathrm{Nm}^{-2}$ [25]. Values of G_c and $G_c\beta$ at $\mathrm{v} = 10^{-4}$ and 10^{-5} msec^{-1} are shown in Table 3.

The average of the $G_c\beta$ values is approximately 0.02 Jm^{-2} and is of the order of magnitude of the surface energy of PMMA/methanol

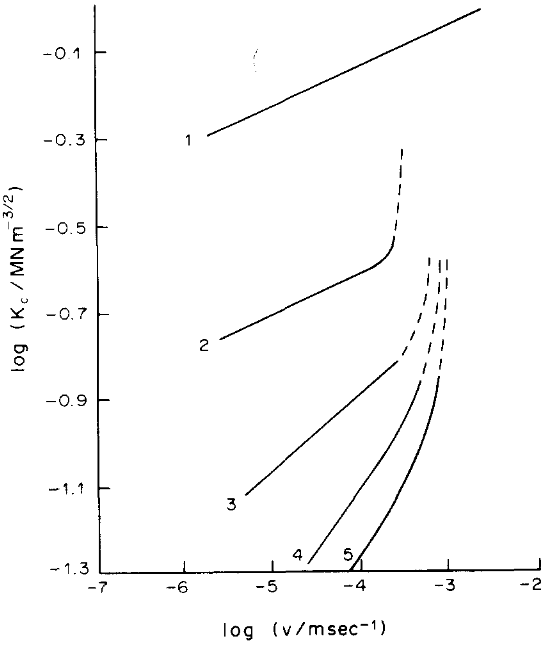

Fig. 4. Comparison of fracture toughness in air and in methanol. (1) In air ($T = 20°C$). (2) In methanol ($T = 0°C$). (3) In methanol ($T = 10°C$). (4) In methanol ($T = 20°C$). (5) In methanol ($T = 30$–$40°C$).

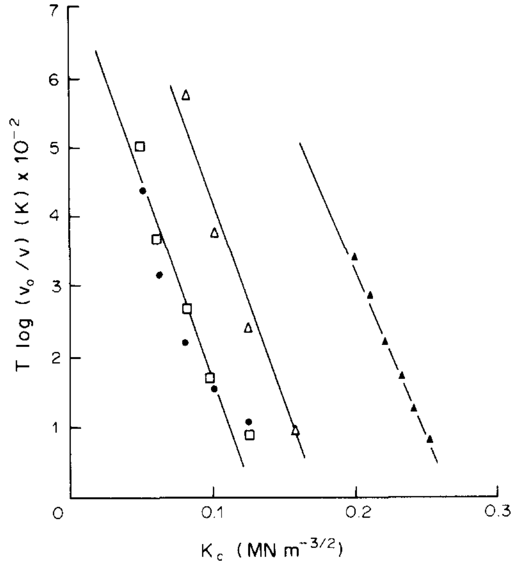

Fig. 5. Plot of fracture toughness–velocity relationship for LMW PMMA in methanol in terms of Zhurkov's theory [T log (v_0/v) vs K_c]. The points deviating from the straight line have values of crack velocity close to the limiting velocity, v_0. $T = 0°C$ (▲), $T = 10°C$ (△), $T = 20°C$ (□), $T = 40°C$ (●).

($2\gamma_{cl} = 0.04\ \mathrm{J m^{-2}}$) [27]. This agreement suggests that the van der Waals bonds are broken to create new surface rather than by main chain rupture. The remaining energy, ($G_c - G_c\beta$) is expended by plastic deformation and void formation. Comparing with the Atkins *et al.* data in air [23], the remaining energy of the fracture process in methanol is over ten times smaller and suggests that there is less craze formation in the presence of methanol than in air. On the other hand, the remaining energy ($G_c - G_c\beta$) decreases with increasing temperature, i.e. less craze matter is formed at elevated temperature.

From fracture mechanics theory [15], K_c can be expressed by

$$K_c = (u_c\epsilon_y)^{1/2}E \qquad (8)$$

where ϵ_y is the yield strain. Substituting Eqn (8) in Eqn (5) gives

$$RT\ln\frac{v_0}{v} = U_0 - \gamma_F(u_c\epsilon_y)^{1/2}K_c. \qquad (9)$$

Table 3. Values of G_c and $G_c\beta$ at various temperatures and crack velocities

v (m/sec)	T (°C)	K_c ($\mathrm{MNm^{-3/2}}$)	G_c ($\mathrm{Jm^{-2}}$)	$G_c\beta$ ($\mathrm{Jm^{-2}}$)
10^{-4}	0	0.224	14.3	0.04
	10	0.112	3.6	0.02
	20–40	0.056	0.9	0.01
10^{-5}	0	0.199	11.4	0.03
	10	0.089	2.3	0.02
	20	0.045	0.6	0.01

The yield strain, ϵ_y, is independent of strain rate and of the COD, u_c, and is assumed to be constant at a given temperature so the product $u_c\epsilon_y$ is also a constant. Thus a plot of T log (v_0/v) vs K_c will give a straight line with the intersection v_0 and slope $-\gamma_F(u_c\epsilon_y)^{1/2}$ (Fig. 5). Values of U_0 and $(u_c\epsilon_y)^{1/2}$ are shown in Table 4.

The U_0 values obtained from Eqn (9) are approximately 20% larger than those determined by Eqn (5). although these values can be considered reasonably close, the larger values of U_0 from Eqn (9) clearly point to an inadequacy of the constant COD assumption. Israel *et al.* [28] have confirmed that the COD for cracking in air increases with K_c and reaches a limit at $K_c \simeq 1\ \mathrm{MN\,m^{-3/2}}$. The magnitude of K_c may have the same effect on the COD for cracking in methanol. The possible K_c dependence of the values of u_c in methanol will be discussed from the LEFM viewpoint in the following section.

2. *Temperature dependence of crack propagation*

The deficiency in the analysis of experimental data using the Zhurkov theory can be overcome by em-

Table 4. Calculated values $(u_c\epsilon_y)^{1/2}$ and U_0 from Eqn 9

T (°C)	$\gamma_F(u_c\epsilon_y)^{1/2} \times 10^2$ ($\mathrm{m^{5/2}\,mol^{-1}}$)	$(u_c\epsilon_y)^{1/2} \times 10^4$ ($\mathrm{m^{1/2}}$)	U_0 ($\mathrm{kJ\,mol^{-1}}$)	U_0 ($\mathrm{kJ\,mol^{-1}}$) from Eqn (5)
0	9.75	1.12	25.8	18.2
10	11.24	0.59	19.1	15.2
20–40	11.45	0.40	14.3	11.4

Table 5. Effect of temperature on the reduction factor, α, at $v = 3.16 \times 10^{-4}$ m/sec

T (°C)	$\log(K_{\mathrm{air}}/K_{\mathrm{MeOH}})$	$\log[E(20^\circ)/E(T)]$ [14]	α	α from Zhurkov's theory [19, 20].)
0	0.47	0.06	0.090	0.13
10	0.70	0.03	0.035	0.03
20	0.85	0	0.020	0.03
30–40	1.00	−0.04	0.012	0.03

Table 6. Effect of temperature on the reduction factors α, α_ϵ, α_u and the craze length, Δ, at $v = 3.14 \times 10^{-5}$ m sec^{-1}

T (°C)	$\alpha = a_\epsilon \alpha_u$	α_ϵ*	α_u	u_c (μm)	$\Delta = \frac{\pi}{8}\frac{u_c}{\epsilon_y}$ (μm)†
0	0.090	0.090	1	2.56	320
10	0.022	0.035	0.63	1.61	600
20	0.008	0.020	0.41	1.05	590
30–40	0.0005	0.012	0.43	1.10	1020

*From Table 5 where $\alpha = \alpha_\epsilon$.
†$\Delta = 28\ \mu$m in air [25].

ploying LEFM concepts. At the crack tip, the critical crazing stress, σ_c, ($\sigma_c = E\epsilon_y$) is responsible for the load-carrying capacity of the material. In an aggressive environment, the craze at the tip, because of its porous nature, allows the fluid to diffuse through and eventually plasticize the craze fibrils. This process causes a drop in the critical stress from the value in air, σ_c, to $\alpha\sigma_c$ where α is the reduction factor for plasticization and $\alpha < 1$ [14]. Because the modulus E of the bulk polymer is not influenced by the environment, the drop of the critical stress to $\alpha\sigma_c$ is equivalent to the drop of the yield strain from the value in air, ϵ_y, to $\alpha\epsilon_y$. In air, the SIF, K_c, is given by Eqn (8) but, in the aggressive environment, K_c becomes

$$K_c = (u_c \epsilon_y \alpha)^{1/2} E \qquad (10)$$

where u_c and ϵ_y are the COD and the yield strain in air, respectively [14]. The reduction factor, α, can be calculated by taking the ratio of K_c in air and K_c in methanol at a given velocity.

Young and Beaumont [29] suggested that the value of $u_c\epsilon_y$ in air is insensitive to temperature and therefore the reduction factor, α, can be evaluated from

$$\frac{K_{\mathrm{air}}(20^\circ)}{K_{\mathrm{MeOH}}(T)} = \frac{(u_c\epsilon_y)^{1/2}E(20^\circ)}{(\alpha u_c \epsilon_y)^{1/2}E(T)} = \frac{E(20^\circ)}{\alpha^{1/2}E(T)} \qquad (11)$$

The LHS of Eqn 11 can be evaluated from experimental data at a particular velocity (Fig. 4). For example, at $v = 3.16 \times 10^{-4}$ m/sec $\log[K_{\mathrm{air}}(20^\circ)/K_{\mathrm{MeOH}}(0^\circ)] = 0.47$, from stress cracking in air data [12], and from Williams' data [14] $E(20^\circ) = 3.5\ G\mathrm{Nm}^{-2}$ and $E(0^\circ) = 4\ G\mathrm{Nm}^{-2}$. Thus α is calculated to be 0.090. Using the same method of calculation, the values of α at various temperatures are listed in Table 5.

Also listed in Table 5 are the values of α based on Zhurkov's theory, calculated as the ratio of $(u_c\epsilon_y)^{1/2}$ in methanol (Table 5) and in air. As seen in Table 5, calculated values from Zhurkov's theory are in reasonable agreement with those from LEFM theory. However, while the values of α from Zhurkov's theory remain constant from 10°C to 40°C, the values calculated by the LEFM show a systematic decrease with increasing temperature. This indicates that, as the temperature increases, more methanol is absorbed (the volume fraction of absorbed methanol increases from 0.15 to 0.33 as temperature increases from 0°C to 40°C [30]) and the more plasticization will occur at the crack tip. As already mentioned, α is also the reduction factor of the yield strain, therefore the yield strain is reduced with increasing absorbed solvent. The effect of solvent on the reduction in yield strain was confirmed by Kamei and Onogi's experiments on the mixture of polystyrene and solvent at various ratios [31].

The decrease in fracture toughness in environmental stress-cracking is attributed not only to a drop in σ_c but also to a reduction in u_c. The reduction factor, α, therefore is due to both the reduction of the crazing stress and the COD. Values of α as shown by experimental data decrease with the front tip velocity. For example, at $T = 20$°C we obtain

$$\alpha = 0.020 \text{ at } \log(v/\mathrm{m\,sec^{-1}}) = -3.5,$$
$$K_c = 0.112\ \mathrm{MNm^{-3/2}}$$

and

$$\alpha = 0.008 \text{ at } \log(v/\mathrm{m\,sec^{-1}}) = -4.5,$$
$$K_c = 0.068\ \mathrm{MNm^{-3/2}}.$$

Obviously, the smaller value of $\alpha = 0.008$ at $\log(v/\mathrm{m\,sec^{-1}}) = -4.5$ compared with $\alpha = 0.020$ at $\log(v/\mathrm{m\,sec^{-1}}) = -3.5$ indicates that the reduction factor, α, originates from two factors—the COD and the crazing stress (the yield strain). In brief, in air cracking, the product of the COD and the yield strain is expressed by

$$u_c \epsilon_y$$

and in methanol cracking,

$$(\alpha_u u_c)(\alpha_\epsilon \epsilon_y)$$

or

$$\alpha = \alpha_\epsilon \alpha_u$$

where

α_ϵ = the yield strain reduction factor
α_u = the COD reduction factor.

The results for other temperatures are listed in Table 6.

The above results have shown the temperature dependence of α_u is similar to that of α_ϵ. In other words, the effect of plasticization gives a smaller COD with increasing amount of solvent uptake at the crack tip (i.e. increasing temperature). At $T = 0$°C the COD still remains unchanged ($\alpha_u = 1$) whereas at $T = 20$–40°C the COD reduces to less than half value at $\log(v/\mathrm{m\,sec^{-1}}) = -4.5$.

The effect of the SIF, K_c, on the magnitude of the COD, u_c, and the craze length, Δ, at a constant temperature can be seen in Table 7.

The relationship of K_c vs u_c shows a straight line on a log–log plot (Fig. 6) and it was found that

$$u_c = 56.4\, K_c^{1.39}\ \mu\mathrm{m} \quad \text{at} \quad T = 20^\circ\mathrm{C}$$

and

$$u_c = 15.9\, K_c\ \mu\mathrm{m} \quad \text{at} \quad T = 10^\circ\mathrm{C}$$

Table 7. Effect of the SIF, K_c, on the reduction factors α, α_t, α_u and the craze length, Δ, at $T = 20°C$

$K_c (MNm^{-3/2})$	$\alpha = \alpha_t \alpha_u$	α_t	α_u	u_c (μm)	Δ (μm)
0.112	0.020	0.02	1	2.56	1436
0.100	0.017	0.02	0.87	2.23	1250
0.079	0.014	0.02	0.69	1.77	993
0.063	0.009	0.02	0.46	1.14	662
0.050	0.007	0.02	0.34	0.87	488

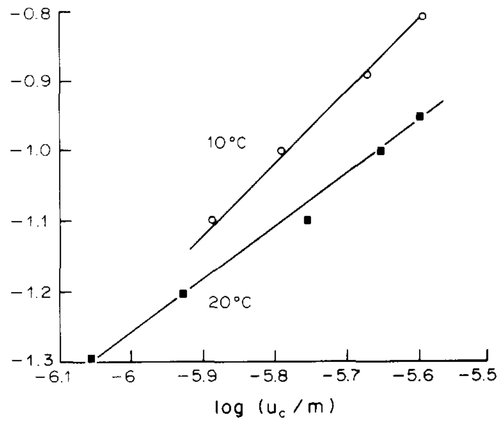

Fig. 6. The effect of the SIF, K_c on the COD, u_c.

whereas Israel *et al.* [28] found this relationship for air cracking to be

$$u_c \propto K_c^{2.14}$$

The temperature and the SIF, K_c, dependence of the craze length shown in Tables 6 and 7 reveal an interesting observation that the craze length increases with increasing temperature and SIF, K_c. The results can be understood in terms of the diffusion rate of methanol at various temperatures and stress at the crack tip. This problem will be discussed in the next Section.

3. *Effects of temperature and* K$_c$ *on the diffusion behaviour of methanol*

The basic factor which governs the plasticization and fracture mechanism in the aggressive environment is the diffusion of solvent molecules into bulk material at the crack tip. The plasticization of the crack tip of low MW PMMA is the only reason for a rapid crack propagation at low SIF, K_c, compared with the air cracking at the same velocity (Fig. 4). Also, the faster diffusion at higher temperature results in the higher limiting velocity v_0 (Fig. 2).

According to the mechanism suggested by Brown *et al.* [32–34], the penetrant acts as a wedge to open the crack by jumping a distance J into a cavity smaller than itself—the cavity then expands under stress. This is an early stage of the craze nucleation and they have concluded that the rate of diffusion of penetrant into the bulk material determines the velocity of crack propagation. Thus,

$$v = \frac{AD}{J} \tag{12}$$

where A which is related to the surface coverage, varies from zero to unity; D = the diffusion coefficient; J = the jump distance of a liquid molecule.

Because methanol wets PMMA completely, A is assumed to be unity, representing full surface coverage of methanol on the PMMA surface [35] so that

$$v = \frac{D}{J} \tag{13}$$

Thus, Eqn 3 can be rewritten as

$$v = \frac{D_0}{J} \exp \frac{\gamma'_F \sigma_c - U_0}{RT} \tag{14}$$

and

$$v_0 = \frac{D_0}{J} \tag{15}$$

where $\gamma'_F = \gamma_F u_c$ is the activation volume and D_0 the pre-exponential factor [32].

Brown [32] has suggested that the jump distance, J, can be estimated from the activation volume, where the product of J and the molecular cross-sectional area of the liquid molecule equals the activation volume. The molecular cross-sectional area calculated from

$$\text{molecular cross-sectional area} = \frac{\text{(molar volume)}}{\text{N}_A \text{ (length of the molecule)}}$$

is 0.209 nm^2 for methanol and therefore the diffusion coefficient at zero stress can be calculated from

$$D(\sigma_c = 0) = D_0 \exp -\frac{U_0}{RT}. \tag{16}$$

The calculated results are listed in Table 8, together with values of γ'_F and J at various temperatures. As previously stated, the COD, u_c, was assumed to have the values shown in Table 7. Values of γ_F and U_0 were the results discussed in Section 1 (Table 2).

The calculated values of the diffusion coefficient, D, obtained from data for methanol stress cracking of LMW and listed in Table 8 increase with temperature. The calculated values show reasonable agreement with experimental data obtained from methanol equilibration of bulk PMMA. The experimental values were 0.8×10^{-9} cm^2 sec^{-1} at $T = 20°C$ [35] and of the order 10^{-8} cm^2 sec^{-1} at $T = 42°C$ [36], compared with the calculated values of 2.2×10^{-9} cm^2 sec^{-1} and 5.2×10^{-8} cm^2 sec^{-1} (Table 8), respectively, obtained from data for methanol stress cracking of LMW.

It was demonstrated previously that the magnitude and temperature dependence of U_0 suggest that the breakdown process is governed by a viscous flow process where secondary bond rupture occurs. Now, the agreement between the experimental values of D and the values of D calculated by Eqn 13, reveal the other important point that solvent diffusion into bulk polymer is the basic factor controlling the kinetics of breakdown mechanism (Eqn 14).

Furthermore, the enhancement by stress of the diffusion coefficient D can be estimated from (combining Eqns 14 and 15)

$$D = D_0 \exp \frac{-U_0 + \gamma_F (K_c^2/E)}{RT}. \tag{17}$$

Table 8. Estimation of the diffusion coefficient at zero stress ($\sigma_c = 0$) from solvent-cracking data of LMW

T(°C)	γ_F(m^2) × 10^{21}	$\gamma'_F = \gamma_F u_c$(m^3) × 10^{27}	J (nm)	D_0 (cm^2 sec^{-1})	D (cm^2 sec^{-1})
0	1.41	3.61	17.3	4.3×10^{-8}	1.3×10^{-11}
10	3.19	5.15	24.6	1.7×10^{-7}	2.6×10^{-10}
20	4.78	5.02	24.0	2.4×10^{-7}	2.2×10^{-9}
40	4.78	5.26	25.2	4.3×10^{-6}	5.2×10^{-8}

Table 9. The effect of K_c on the diffusion coefficient at $T = 20$°C

K_c(MNm$^{-3/2}$)	α_u	J(nm)	D_0(cm^2 sec^{-1})	D(cm^2 sec^{-1})
0.112	1	58.6	5.9×10^{-7}	3.6×10^{-7}
0.100	0.87	51.0	5.1×10^{-7}	1.3×10^{-7}
0.079	0.069	40.4	4.0×10^{-7}	3.0×10^{-8}
0.063	0.46	27.0	2.7×10^{-7}	9.2×10^{-9}
0.05	0.34	9.9	2.0×10^{-7}	4.2×10^{-9}
0	—	—	—	2.0×10^{-9} (extrapolated)

The effect of the SIF, K_c, on the magnitude of D in methanol at $T = 20$°C is shown in Table 9.

The extrapolated value of $D = 2.0 \times 10^{-9}\,\text{cm}^2\,\text{sec}^{-1}$ at $K_c = 0$ obtained from the K_c^2 vs log D relationship is comparable to $2.2 \times 10^{-9}\,\text{cm}^2\,\text{sec}^{-1}$ as shown in Table 8.

The results clearly indicate a strong K_c dependence of the diffusion coefficient, D. The value of D increased two decades from $2.0 \times 10^{-9}\,\text{cm}^2\,\text{sec}^{-1}$ to $3.6 \times 10^{-7}\,\text{cm}^2\,\text{sec}^{-1}$ when K_c increased from 0 to 0.112 MNm$^{-3/2}$.

The diffusion coefficient, D, and the craze length, Δ, have similar dependence on the temperature and the SIF, K_c, they both increase with increasing temperature or K_c. This similarity confirms the role of the diffusion rate of solvent into bulk material at the crack tip as the controlling factor in environmental cracking mechanism. That is, the enhancement of the diffusion coefficient by temperature or by K_c will lead to an increase in the size of plasticized zone, namely an increase in the craze length, Δ.

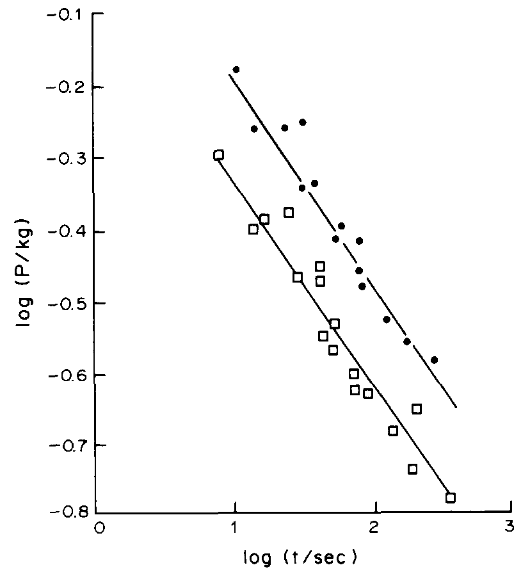

Fig. 7. Relaxation of the load P with time at two different initial P_i for the cracking of LMW PMMA in methanol. The slope is -0.3.

4. Analysis based on Williams–Marshall (WM) theory

The WM theory developed from the LEFM concept has provided an expression for the time dependence of viscoelastic deformation at the crack tip. The crazing stress, σ_c, and the modulus, E, relax with time, t, by

$$\sigma_c = \sigma_0 t^{-m} \tag{18}$$

and

$$E = E_0 t^{-n}. \tag{19}$$

Where σ_0 and E_0 are front factors, m and n are time factors for σ_c and E, respectively.

In air, m and n were found to be approximately 0.1 [14]. In an active environment, n remains unchanged because viscoelastic properties of bulk material embodied in modulus E are not affected, but the value of m will increase by plasticization of the crack tip. The relationship between the SIF, K_c, and the velocity, $\mathbf{v}$, is expressed by

$$K_c = C\mathbf{v}^{(m-n)/2(1-m+n)} \tag{20}$$

where

$$C = \left(\frac{8}{\pi}\right)^{(m+n)/2(1-m+n)} (u_c E_0)^{(1-2m)/2(1-m+n)} \times \sigma_c^{(1+2n)/2(1-m+n)}.$$

It is intended in this Section to estimate the value of m at different degrees of plasticization at the crack tip.

The relaxation of the load with time during the fracture test in methanol was recorded and has the following form (Fig. 7)

$$P \propto t^{-0.30}.$$

Converting P into K_c by using $K_c = A_g P$ (A_g is geometrical factor of specimen), the relaxation of K_c with time at 20°C can be expressed by

$$K_c = 0.25\, t^{-0.30}\ \text{MNm}^{-3/2}. \tag{21}$$

Also, the COD, u_c, is a function of K_c (Table 7, Fig. 6)

$$K_c = 0.055\, u_c^{0.72}\ \text{MNm}^{-3/2}\ (20°\text{C}) \tag{22}$$

or

$$u_c = 56.4\, K_c^{1.39}\,\mu\text{m}.$$

Combining Eqns 21 and 22 gives

$$u_c = 8.32\ t^{-0.42}\ \mu\text{m}. \qquad (23)$$

Substituting Eqn 23 into Eqn 20, we obtain

$$K_c \propto \mathbf{v}^{(m+n)/2(1-m+n)}\, t^{-i}$$

or

$$K_c t^i \propto \mathbf{v}^{(m+n)/2(1-m+n)} \qquad (24)$$

where $i = 0.42\ (1 - 2m)/2(1 - m + n)$. This equation indicates that, because of the factor t^{-i}, the log K_c vs log $\mathbf{v}$ curve is not a straight line (Figs 1, 2 and 4). However, plot of log $(K_c t^i)$ vs log $\mathbf{v}$ would give a linear relationship with a slope of $(m + n)/2(1 - m + n)$.

The time factor, m, for σ_c can be calculated by the following method. Firstly, using a trial value of m $(n = 0.1)$, a plot of log $(K_c t^i)$ vs log $\mathbf{v}$ can be drawn (Eqn 24). The value of the slope $(m + n)/2(1 - m + n)$, found from the straight line of log $(K_c t^i)$ vs log $\mathbf{v}$ can be used to calculate the value of m. The correct value of m is the value where the trial m value is equal or close to the calculated m.

The suitable trial value of m for crack propagation at 20°C is 0.18 and this value gives a slope of 0.14 (Fig. 8). The calculated value of m from $(m + n)/2(1 - m + n) = 0.14$, is found to be 0.16. Hence, it is reasonable to accept 0.18 as the value of m at 20°C. This trial method is sensitive to chosen trial value, e.g. if m is arbitrarily chosen at 0.3, then the calculated value will become 0.2.

At $T = 10°\text{C}$, using the following experimental data

$$K_c = 0.35\ t^{-0.25}\ \text{MNm}^{-3/2}$$

$$K_c = 0.063\ u_c\ \text{MNm}^{-3/2}$$

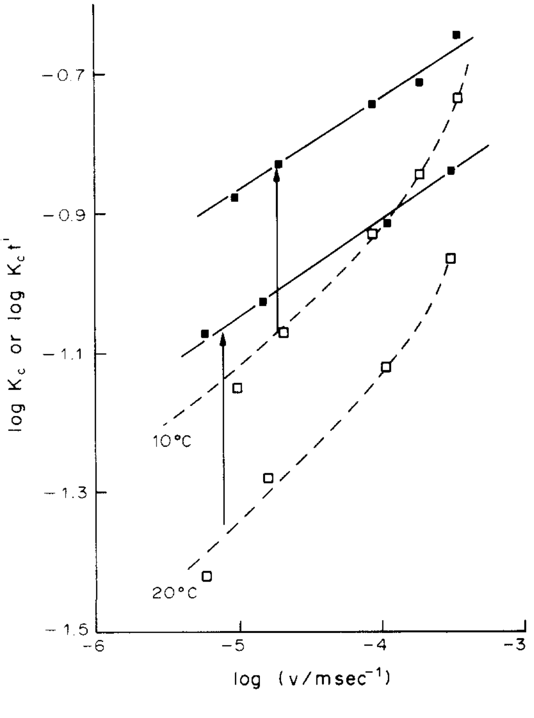

Fig. 8. Plots of log K_c vs log $\mathbf{v}$ (broken line) and log $K_c t^i$ vs log $\mathbf{v}$ (solid line). Plots of log $K_c t^i$ vs log $\mathbf{v}$ were drawn with $m = 0.18$ for $T = 20°\text{C}$ and $m = 0.15$ for $T = 10°\text{C}$.

and therefore

$$u_c = 5.55\ t^{-0.25}\ \mu\text{m}$$

m was determined to be 0.15 by the trial method.

The increase in m with temperature (higher solvent uptake) implies that the stress will decay more rapidly with higher degree of plasticization.

CONCLUSIONS

The fracture behaviour in the presence of methanol has been studied in the region of crack growth for low MW PMMA and the following conclusions can be drawn:

(1) The crack predominant Regime II was satisfactorily treated by the Zhurkov and fracture mechanics (LEFM) approaches. The calculated results of the activation energy of the cracking process established that the crack mechanism is governed by a viscous flow process where the slippage of chain molecules over each other results in the secondary bond breakage.

(2) The diffusion coefficient, D, of methanol at zero applied stress derived from the cracking data is in good agreement with reported values from the equilibration of bulk PMMA samples in methanol. This shows the role of methanol diffusion at the crack tip in failure mechanism. The COD, u_c, and the craze length, Δ, are dependent on the temperature, T, and the SIF, K_c. The increasing craze length with T and K_c can be attributed to the enhancement of diffusion coefficient at elevated temperature and/or high K_c resulting in a larger plasticized craze zone.

(3) The crazing stress, σ_c shows a more rapid decay with time as more methanol is absorbed at the crack tip.

Acknowledgement—The support of the Australian Research Grants Scheme is acknowledged.

REFERENCES

1. G. A. Bernier and R. P. Kambour, *Macromolecules* **1**, 393 (1968).
2. R. P. Kambour, C. L. Gruner and E. E. Romagosa, *J. Polym. Sci. Polym. Phys. Edn* **11**, 1879 (1973).
3. P. I. Vincent and S. Raha, *Polymer* **13**, 283 (1972).
4. Y. W. Mai and A. G. Atkins, *J. Mater. Sci.* **11**, 677 (1976).
5. E. J. Kramer, *Adv. Polym. Sci.* **52/53**, 1 (1983).
6. Y. W. Mai, *J. Mater Sci.* **14**, 2264 (1979).
7. E. H. Andrews, G. M. Levy and J. Willis, *J. Mater. Sci.* **8**, 1000 (1973).
8. E. H. Andrews and L. Bevan, *Polymer* **13**, 283 (1972).
9. H. R. Brown and E. J. Kramer, *Polymer* **22**, 687 (1981).
10. J. G. Williams and G. P. Marshall, *Proc. R. Soc. Lond.* **A319**, 165 (1970).
11. P. E. M. Allen, D. M. Host, V. T. Truong and D. R. G. Williams. *Eur. Polym. J.* **21**, 603 (1985).
12. V. T. Truong, P. E. M. Allen and D. R. G. Williams, *Eur. Polym. J.* **22**, 903–910 (1986).
13. V. T. Truong, Ph.D. Thesis, University of Adelaide (1981).
14. J. G. Williams, *Adv. Polym. Sci.* **27**, 67 (1978).
15. P. W. R. Beaumont and R. J. Young, *J. Mater. Sci.* **10**, 1334 (1975).
16. V. T. Truong, P. E. M. Allen and D. R. G. Williams, *Eur. Polym. J.* To be published.

17. G. P. Marshall, L. H. Coutts and J. G. Williams, *J. Mater. Sci.* **9,** 1409 (1974).
18. J. G. Williams and G. P. Marshall, *Proc. R. Soc. Lond.* **A342,** 55 (1975).
19. S. N. Zhurkov, *Int. J. Fract. Mech.* **1,** 311 (1965).
20. S. N. Zhurkov and V. E. Korsukov, *J. Polym. Sci. Polym. Phys. Edn* **12,** 385 (1974).
21. K. Schonert, H. Umhauer and W. Klemm, *Proc. 2nd Int. Conf. Fract.* p. 474. Brighton, England (1969).
22. J. A. Kies and A. B. J. Clark, *Proc. 2nd Int. Conf. Fract.* p. 483. Brighton, England (1969).
23. A. G. Atkins, C. S. Lee and R. M. Caddell, *J. Mater. Sci.* **10,** 1381 (1975).
24. Y. M. Mai and A. G. Atkins, *J. Mater. Sci.* **11,** 677 (1976).
25. J. G. Williams, *Int. J. Fract. Mech.* **8,** 393 (1972).
26. H. H. Krausch, *Polymer Fracture*. Springer-Verlag, Berlin (1978).
27. E. H. Andrews and L. Bevan, *Polymer* **13,** 337 (1972).
28. S. J. Israel, E. L. Thomas and W. W. Gerberich, *J. Mater. Sci.* **14,** 2128 (1979).
29. R. J. Young and P. W. R. Beaumont, *Polymer* **17,** 717 (1975).
30. E. H. Andrews, G. M. Levy and J. Willis, *J. Mater. Sci.* **8,** 1000 (1973).
31. E. Kamei and S. Onogi, *Polym. J.* **8,** 347 (1976).
32. N. Brown, *J. Polym. Sci. Polym. Phys. Edn* **11,** 2099 (1973).
33. N. Brown, and S. Fischer, *J. Polym. Sci. Polym. Phys. Edn* **13,** 1315 (1975).
34. N. Brown, B. D. Metzger and Y. Imai, *J. Polym. Sci. Polym. Phys. Edn* **16,** 1085 (1975).
35. K. Iisaka, Y. Nishimoto and K. Shibayama, *J. Polym. Sci. Polym. Phys. Edn* **17,** 791 (1979).
36. R. A. Ware and C. Cohen, *J. appl. Polym. Sci.* **25,** 717 (1980).