

THE GROWTH OF CRACKS AND CRAZES IN POLYMERS

- A FRACTURE MECHANICS APPROACH

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ABSTRACT

A study has been made of the use of fracture mechanics in describing crack and craze growth phenomena in plastics. The thesis which follows has been divided into three main parts.

Part I has two component chapters. The first (Ch. 2), outlines the basis of the fracture mechanics concepts used in the analysis of results and the second chapter (Ch. 3) contains a literature survey of the state of knowledge on crazing and environmental stress cracking in plastics.

Part II describes experimental work which has been undertaken to study crack growth phenomena in both air and liquid environments. Chapter 4 gives results obtained from slow crack propagation tests in PMMA in air and shows that there is a unique relationship between the fracture toughness measure K_{IC} and the crack speed. Analysing results on a K_{IC} /crack speed basis is shown to rationalise results from many different types of test and also accounts for the rate dependent material characteristics. This approach is extended in Chapter 5 to include the effects of crack propagation in polystyrene in air. For the first time, realistic values of fracture toughness have been obtained for the propagation of a single crack/craze system. The K_{IC} vs crack speed relationship is again found to provide a good basis against which results may be compared and discussed. A criterion of unnotched tensile failure is also given. In Chapter 6, the K_{IC} vs crack speed approach has been used to correlate data for the environmental stress cracking of polyethylene in alcohol environments. The approach is entirely successful and excellent reproducibility of data has been obtained.

Part III of the thesis describes a large volume of experimental work which describes craze propagation in PMMA in an alcohol environment. In Chapter 7

the craze growth behaviour in pre-notched specimens under constant load is analysed and a model is presented which provides a good description of the kinetics of craze growth in terms of flow of the environment through the micro-structure of the craze. The model is couched in terms of the stress intensity factor based on the original crack dimensions, since it is found that macroscopically this parameter controls the rate of craze growth. The model has been successfully extended in Chapter 8 to account for the effects of cyclic loading on environmental craze growth in PMMA. Excellent correlation of data has been achieved for low cyclic frequencies. The effects of higher test frequency have been examined in a tentative manner and a qualitative description of the results is given.

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NOTATION

a_I	Inherent flaw size.
a_o	Initial crack length.
a_f	Crack length at instability.
a_1	Crack + craze + plastic zone length.
a_2	Crack + craze length.
$x (X)$	Craze length.
$\dot{a}$	Crack speed.
$\dot{x}$	Craze speed.
B	Specimen thickness.
W	Specimen width.
γ	Surface energy.
γ_p	'Surface work'.
G	Strain energy release rate.
G_c	Fracture Toughness.
K	Stress Intensity Factor (S.I.F.).
K_c	Critical S.I.F. for crack growth.
K_{Ic}	Value of S.I.F. at crack instability.
K_o	S.I.F. calculated using initial crack length.
K_m	S.I.F. at craze initiation.
K_n	Critical S.I.F. for transition 'end flow' to 'side flow'.
K_z	Critical S.I.F. for maximum 'end flow'.
$\bar{K}_o$	Equivalent value of static K_o in fatigue test.
$\check{K}_o$	Minimum value of (K_o) in fatigue test.
$\hat{K}_o$	Maximum value of (K_o) in fatigue test.
l_o	Process zone size (void spacing).

l	Reduced size of material in process zone.
$\delta_{(y)}$	Crack opening displacement.
δ_c	Craze tip displacement.
r_p	Plastic zone size.
β	Void size.
ψ	Void area.
σ	Applied stress.
σ_y	Yield stress.
σ_c	Craze stress.
σ_t	Craze ligament yield stress (wet craze).
σ_f	Failure stress.
S	Stress amplitude-fatigue.
N	Cycles.
E	Young's Modulus.
$E(t)$	Time-dependent modulus.
ρ	Density.
Δ	Solubility parameter.
M_v	Viscosity-average molecular weight.
μ	Viscosity.
T_g	Glass transition temperature.
$\bar{p}$	Atmospheric pressure.
$t()$	Time.
(A, C, m, n, ϕ)	Constants.

ABBREVIATIONS

MFI	Melt Flow Index.
ESC	Environmental stress cracking.
COD	Crack opening displacement.
PMMA	Poly (methyl methacrylate).
HIPS	High impact polystyrene.
PS	Polystyrene.
PPO	Poly (2,6-dimethyl 1-1, 4-phenylene oxide).
PE	Polyethylene.
PVC	Poly (vinyl chloride)
PC	Polycarbonate
SEN	Single edge notch(ed) specimen
SIF	Stress Intensity Factor

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CONCLUSIONS

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CHAPTER 1. INTRODUCTION

1.1 FRACTURE OF PLASTICS

For many years, the study of the properties of plastics was the exclusive province of the chemist and the physicist. However, because of the potential use of plastics as engineering materials, the nature of their behaviour has come under close scrutiny by materials scientists and engineers. Since many plastics have an excellent strength/weight ratio, high impact resistance and low processing costs, they are now being used in many applications where they act as load-bearing members.

At the present time, the most impressive advances have been made in the exploitation of fibre-reinforced plastics, particularly in applications for aircraft components and boat and motor car shells. Their use is somewhat limited because this type of composite cannot be readily adapted to mass production techniques; accordingly the manufacturing costs are high and the materials succeed mainly in applications where weight savings and corrosion resistance are of paramount importance. Thermoplastics, on the other hand, are ideally suited for mass production, and it is with these materials that the most promising advances are likely to be made in the future.

Many engineering applications require a material to be able to sustain considerable loads - often for long times. With plastics, there are many problems associated with creep, and to meet design requirements much effort is expended in documenting deformation characteristics. Of equal importance is a knowledge of the fracture behaviour of the materials - for obvious reasons. It is at this stage that problems arise, because information on fracture processes is more elusive to

obtain than creep data, since it is not yet clear what type of information gives the best indication of service performance. The assessment of impact resistance, and the problems of environmental stress cracking and crazing, are all cases where there is insufficient understanding of the fundamental processes involved to be able to recommend acceptable standards of performance. There is also the additional complication, that in some cases - in particular where cyclic loading is involved - there is no indication of what practical problems might exist, since plastics have not been rigorously field tested in such applications.

In practice, the most serious fracture problems are met when materials fail in a brittle manner under very low loading conditions. Some plastics are always susceptible to this kind of failure - prime examples being the thermosetting resins, polymethyl-methacrylate (PMMA) and polystyrene. In all these cases the "toughness" of the materials can be greatly improved by adding reinforcing agents to the plastics. The thermosetting resins are usually reinforced by glass fibres whereas the thermoplastics are more often "toughened" by the addition of rubber which is included to help improve their impact resistance. Polystyrene is the material most commonly reinforced in this way - the new material being known as high impact polystyrene or HIPS. In an air environment the toughening works well and cracks only grow with difficulty and the material tears rather than 'breaks'. This type of tearing fracture is accompanied by large scale deformation at the crack tip and is typical of failure in many other rigid plastics - notably PVC and polycarbonate. In all these materials, however, brittle fracture will occur if the temperature is lowered ($\sim 250^{\circ}\text{K}$) or if certain environments are present.

A classical example of a material which changes its mode of failure completely when liquid environments are present is polyethylene. In air, low stress

fracture just does not exist as a practical problem and yet in many seemingly innocuous environments - where there is no chemical reaction with polyethylene - the material breaks in a brittle manner at a fraction of its normal tensile strength.

Most of the problems concerning temperature and environment are not particularly new; environmental stress cracking has been a problem now since plastics have been in common usage and much effort has been expended in trying to understand the phenomenon. However, as yet, there is still no clear understanding of environmental effects, mainly because there is no test/analysis combination which gives consistent and reproducible data. Indeed previous investigations have been unable to classify the brittle fracture of PMMA precisely and this material is regarded as being a model brittle plastic.

The problems encountered in fracture testing of plastics are thus not simple to define in an all-embracing manner - nor are they particularly easy to solve. However, in many cases, these problems are not entirely new, because over the last twenty years, people working with metals, rubber and glass have encountered and overcome many of the fundamental difficulties. Test methods for these materials normally use pre-notched specimens since it is postulated that most practical failures are caused by the propagation of inherent material flaws under low applied stresses. The tests therefore measure the critical conditions for the growth of flaws of known size, failure criteria being produced via the analysis of the crack tip environment. The subject of fracture mechanics as it is known, has proved to be highly successful in the metals field in particular, and solutions are now available for the characterization of not only brittle fracture but also of cases where there is large scale plasticity prior to final fracture. An excellent review of these solutions is given by HAYES [1971] .

1.2 SCOPE OF THE PROJECT

The main object of this project was to examine the potential of fracture mechanics parameters and test methods in describing the fracture of plastics. More specifically, it was hoped that by a careful study of crack and craze propagation rates, many of the previous difficulties encountered in interpreting the effects of straining rate, time dependence, temperature, etc., could be overcome. Although no pre-set programme was specifically laid down, the general intention was to start by developing test methods and procedures using PMMA and polystyrene: it was then hoped that a major contribution could be made by extending the work to a full investigation of the environmental stress cracking [ESC] of polyethylene.

In the event, this plan was amended considerably since attention was diverted from stress cracking to an analysis of the mechanics of environmental craze growth in PMMA. Thus, the section devoted to the stress cracking of polyethylene is not quite so comprehensive as had been hoped - the tests being restricted to an examination of low density material only.

The craze growth work has taken precedence, mainly because it is now recognised that crazing plays an important role in the fracture of many plastics. In the PMMA situation which was investigated, there was an ideal opportunity for a comprehensive study of the mechanisms of the initiation, growth and breakdown of a single craze. Although this type of study leans rather more towards physics than engineering, the imbalance has been slightly offset by extending the project to examine the effects

of environment and fatigue in PMMA - a topic on which there is no background work available at all in the literature.

1.3 PLAN OF THESIS

Part I of the thesis follows this introductory section and is devoted to a literature review of:

- (i) Fracture mechanics concepts which are used in the analysis of experimental data and
- (ii) The general nature of crazing and environmental stress cracking in plastics.

The fracture mechanics section of Chapter 2 is purposefully brief since excellent, comprehensive surveys already exist elsewhere - notably HAYES [1971].

In Chapter 3, more attention has been paid to a detailed review of crazing physics and environmental effects since no such survey exists in the literature. The review is general in nature and does not cover any given material's particular characteristics in detail. Where such information is relevant to any of the plastics which are discussed in this report, it is to be found embodied within the main text.

Part II of the thesis deals with aspects of crack propagation in plastics - the three constituent chapters dealing with the effects of crack speed on failure in PMMA and polystyrene in air and polyethylene in alcohols. This section contains a large amount of experimental work and in the interests of brevity and conciseness, details of techniques etc. have been kept to a minimum - the reader being referred for further details to the two papers enclosed in the back.

Part III, the last section of the report, is devoted to a description of the work on environmental craze growth mechanics in PMMA. There are two component chapters; in the first chapter, (Ch.7), the growth of crazes under constant loads is discussed and a model proposed to account for the observed craze behaviour, and in the second, (Ch. 8), the work is extended to include the interactions of cyclic fatigue and environment in PMMA.

PART I.

LITERATURE SURVEY

CHAPTER 2 : FRACTURE MECHANICS CONCEPTS

CHAPTER 3 : CRACKING AND CRAZING IN PLASTICS

CHAPTER 2. REVIEW OF FRACTURE MECHANICS CONCEPTS

Practical experience with many materials has shown that design based on yield strengths alone is often inadequate because materials frequently fracture at much lower stress levels. The subject of fracture mechanics has evolved as the study of low stress fracture problems, in an attempt to provide more realistic design information.

The review of fracture mechanics concepts which follows is by no means exhaustive. The purpose of the chapter is to provide a short summary of the derivations of parameters which are used in the main body of the thesis to describe fracture processes in plastics.

2.1 THE GRIFFITH APPROACH

The fundamental concepts of fracture theory were proposed in the early 1920's by A.A. GRIFFITH [1921] who carried out a series of studies of brittle fracture using glass as a model material. GRIFFITH [1921] calculated that the theoretical value of the tensile strength of glass was $1.4 \times 10^4 \frac{MN}{m^2}$ by presuming that the ultimate strength was the sum total of the individual bond strengths. He ran a series of tests on glass rods but was unable to realise this value, only getting strengths around $170 \frac{MN}{m^2}$. He concluded that glass is not a perfectly homogeneous material (as the theory assumes) but contains flaws which act as localised stress raisers and cause successive bond breakage. Having realised that flaws were the main cause of trouble, Griffith then derived a solution for predicting the tensile strengths of flawed bodies. He reasoned that the magnitude of the stress to extend a crack, and cause subsequent specimen rupture, could be calculated from the condition that the elastic strain energy which is released by a small extension of the crack, must be at least equal to the energy of the new fracture surfaces which are created.

i.e. the fracture condition is given by:

$$\frac{\partial U}{\partial a} \geq \frac{\partial \gamma}{\partial a} \quad (2.1)$$

where U is the elastic strain energy, γ is the surface energy and a is the crack length.

This hypothesis led to a critical stress criterion of failure for a centrally notched plate of infinite dimensions - figure 2.1

$$\sigma_f = \left\{ \frac{2E\gamma}{\pi a} \right\}^{\frac{1}{2}} \quad (2.2)$$

where σ_f is the critical fracture stress, and E is Young's Modulus.

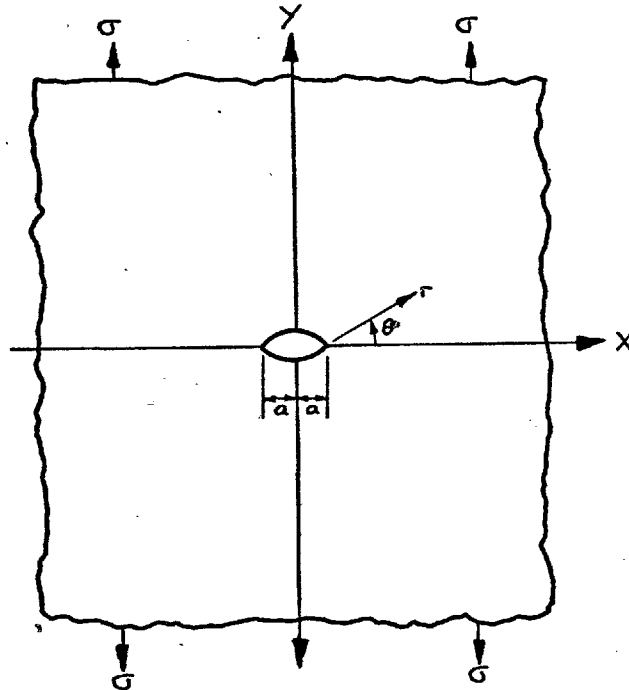


figure 2.1: Centre Notched Infinite Plate

2.2 SURFACE ENERGY AND SURFACE WORK

GRIFFITH [1921] verified his theory by producing microscopic flaws in glass tubes which were subsequently burst under internal pressure. However the γ value measured by experiment for glass, was much larger than the surface work calculated from the reversible work necessary to separate two atomic planes in the material. It is now known that the discrepancy is due to plastic deformation occurring at the crack tip, for although glass is usually regarded as being a

perfectly elastic material, MARSH [1964] has shown that plastic flow can occur, when he permanently deformed glass by means of hardness indentations. OROWAN [1955] has also demonstrated that similar conditions of plastic flow are responsible for the huge discrepancies found between γ as measured in experiments on steels [$\sim 10^3 \text{ Joules/m}^2$] and calculated values [$\sim 10 \text{ Joules/m}^2$]. He suggested, however, that the Griffith criterion might be applied to metals fracture if a plastic work term were added to the surface energy - the new parameter being the surface work γ_p .

This was precisely the argument which had been previously proposed by IRWIN [1947] who had realised that for metals, at least, the Griffith criterion had to be modified to include a plastic work term.

2.3 STRAIN ENERGY RELEASE RATE

IRWIN [1947] extended the range of the Griffith criterion by proposing that cracking occurs when the strain energy release rate $\{\partial U/\partial a \text{ in equation 2.2}\}$ reaches a critical value. According to Irwin's interpretation of the criterion, the strain energy can be dissipated as surface energy (γ), non reversible plastic work, kinetic energy etc. - no restriction being placed on how it is spent, providing only limited plasticity occurs at the crack tip. He named the energy release rate as G (after Griffith) and the critical value at fracture (G_c) is known as the "fracture toughness". Because two new surfaces are formed at fracture - each requiring surface work γ_p - the relation between G_c and γ_p (for a purely brittle fracture) is given by:

$$G_c = 2\gamma_p \quad (2.3)$$

2.4 CRACK EXTENSION FORCE

IRWIN and KIES [1954] were the first to note that the strain energy released when a crack extended a short distance had to equal the work that would be required to close this crack extension. Figure 2.2 shows a diagrammatic representation of the load/deflection curve for a test on a specimen with a crack of length a and a repeat test with crack length $a + \delta a$.

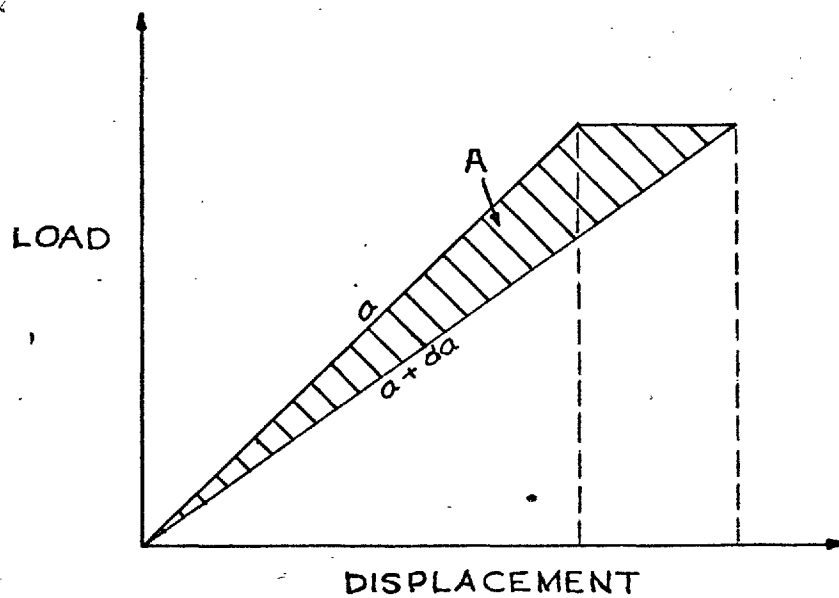


figure 2.2: Load/Displacement for Notched Specimen

The specimen compliance is given by:

$$C = l/P$$

where P is the load and l the elongation between the loading points.

The shaded triangular area (A) represents the non-recoverable strain energy which is lost for the crack extension δa , i.e., the energy which Griffith assumed must exceed the gain in surface energy as a condition for crack propagation.

The resistance to crack extension is always the non-recoverable strain energy loss, regardless of where this energy goes and so the crack extension force (or strain energy released) G can be defined by equating $G \cdot da$ to the area A in figure 2.2.

A simple calculation shows that:

$$G = \frac{P^2}{2B} \cdot \frac{dc}{da} \quad (2.4)$$

where B is the specimen thickness and P the load.

This solution for G is general and is not restricted to any particular specimen shape or dimension. Providing a calibration test can be performed to measure the quantity dc/da , equation (2.4) offers the facility of calculating G for complex specimen shapes.

2.5 STRESS INTENSITY FACTOR APPROACH

Some years later, IRWIN [1957] produced an equivalent fracture criterion via an analysis of the stress field in the vicinity of the crack. He considered that fracture can also be regarded as occurring when critical conditions are attained in the material at the crack tip, and he produced an analysis of the stress and displacement fields in this region. Using the solution for an elastic cracked sheet obtained by WESTERGAARD [1939], Irwin derived the solution for the stresses in the vicinity of the crack tip of a centrally notched plate (figure 2.1) as:

$$\sigma_{ij} = K(2\pi r)^{-\frac{1}{2}} \cdot f_{ij}(\theta) \quad (2.5)$$

where r and θ are polar co-ordinates with an origin at the crack tip: $f_{ij}(\theta)$ is dependent upon the particular stress component but not on geometry or applied load: K is called the "stress intensity factor" and is the same for all stress components.

The parameter K is the only factor relating the elastic stress field in the vicinity of the crack tip to the loading and geometry of the system. If a description of fracture is possible from this approach, it must be characterised by a function of the applied stress, σ , or the parameter, K . Experience shows that σ , based on either the gross or net area, is not constant at fracture and it is therefore postulated that a critical value of $K = K_c$ provides the required criterion. The particular

value of K which results in rapid, uncontrollable fracture is conventionally known as K_{IC} - the "crack toughness" - the subscript I referring to the mode of crack face motion.

2.5.1 Fracture modes

When crack propagation occurs, three modes of crack face motion can be envisaged and these are shown in figure 2.3.

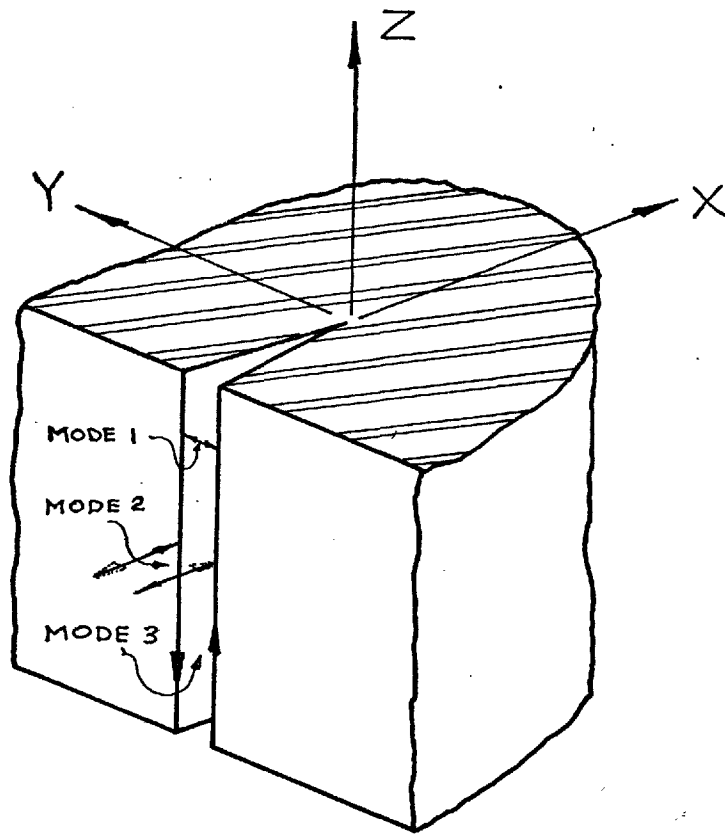


figure 2.3: Fracture Modes

- (i) Separation of the crack faces normal to each other is called MODE 1 - or "Opening Mode".
- (ii) Relative shear motion of the faces perpendicular to the leading edge of the crack is called MODE 2 or "Sliding Mode".
- (iii) Relative shear motion of the faces parallel to the leading edge is called MODE 3 or "Screw Sliding Mode".

In glassy plastics, at least, it would appear that only Mode I exists as a practical failure mode, and so hereafter the discussion will be solely about cracking in this manner, and the critical values of K will be referred to as K_c .

2.5.2 Derivation of stress intensity factor

The solution for obtaining the K value needs to be determined for the particular system being considered - for the centre-notched tension specimens of infinite width shown in figure 2.1, the solution is:

$$K^2 = \pi \sigma^2 a \quad (2.6)$$

where σ is the applied stress and $2a$ the crack length.

When small specimens - whose widths are very much finite - are used, the solutions are often more complicated than equation (2.6) because of correction factors which are introduced to allow for either bending effects or the presence of the free edge.

The solution for K is then given by:

$$K^2 = \sigma^2 Y^2 a \quad (2.7)$$

where Y^2 is the finite plate correction factor.

It is not worthwhile tabulating solutions here because data on other configurations are scattered throughout the literature. Reference should be made in particular to PARIS and SIH [1965], and BROWN and SRAWLEY [1966].

The relationship of K_c to the applied K is analogous to the relation of applied stress and yield stress. The applied stress and K values are mechanics concepts dependent upon the loading and specimen geometry whereas the yield stress and K_c are supposedly material properties dependent upon such variables as temperature, strain rate etc. In particular, the value of K_c obtained from experiments must be shown to be independent of the specimen geometry.

It is worth noting at this stage that the G_c and K_c criteria are not unrelated. Rearranging equation 2.2 and substituting G_c for 2γ gives:

$$G_c = E\pi\sigma^2 a$$

which when combined with equation (2.6) (for the same specimen geometry) gives:

$$K_c^2 = EG_c \quad (2.8)$$

The physical interpretation of the quantity K as a stress field intensity or some function of the strain energy release rate is really irrelevant because it is doubtful whether one concept is more fundamental than the other. The important point is that they both lead to equivalent equations for describing the fracture process.

In the present work, the K approach has been adopted out of expediency, since it was the intention to carry out long-term loading tests which would have led to difficulties assessing the value of E to use for evaluating G . { - Hence the bias on K in this survey!! }

2.6 PLASTIC ZONES

One of the consequences of using the linear elasticity solution for a sharp crack (equation 2.5) is that the theory predicts infinite values of the stresses at the crack tip - where the radius of curvature is "zero". In reality, however, the deformed shape of the crack assumes some finite radius of curvature, yielding occurs and the stress level always remains finite. If the zone of plastic deformation is small in comparison with the crack length and other planar dimensions of the body, then the stress distribution will not be seriously disturbed and the elasticity solutions represent a reasonably accurate approximation of the stress and displacement fields near the crack tip.

IRWIN [1960] has proposed that the influence of local yielding near the leading edge of the crack may be thought of as having the same influence upon the surrounding stress field as would be caused by a larger crack size. He deduced that the plastic zone 'radius' is given by:

$$r_p = \frac{m \cdot K^2}{2\pi\sigma_y^2} \quad (2.9)$$

where K is the stress intensity factor, σ_y is the yield stress and 'm' is a proportionality factor with values between 0.75 and 1.3 - depending on the amount of stress relaxation in the plastic zone.

2.6.1 The Dugdale model

A model of a crack with line plasticity, which does not have a stress infinity at the crack tip has been proposed by DUGDALE [1960]. His analysis assumes that the following conditions are satisfied:

- (1) Yielding is confined to a narrow band along the line of the crack.
- (2) The stress across the plane of the crack is constant and equal to the uniaxial yield stress.

- (3) The yielded zone is of such a length that the stress at the end of it is finite.

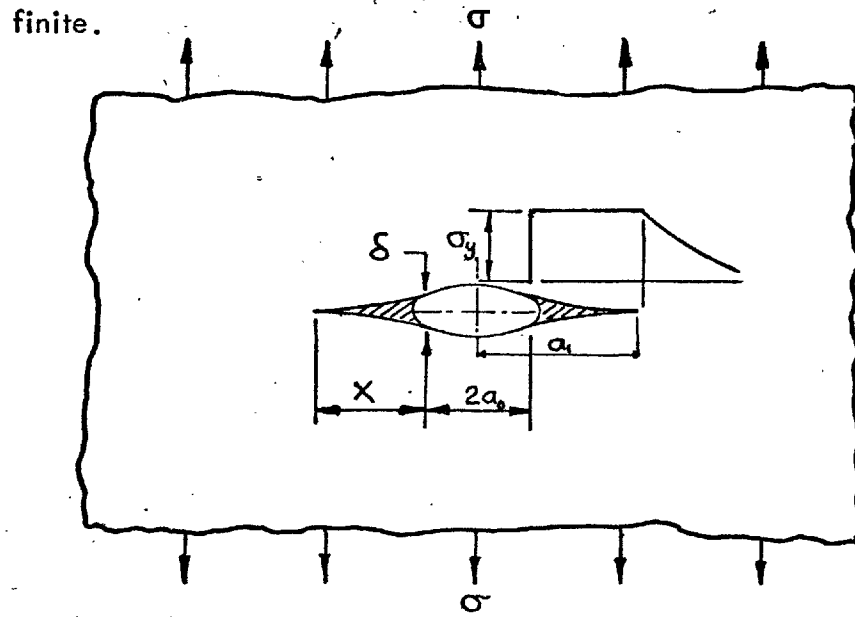


figure 2.4: Dugdale Model for Line Plasticity

A schematic diagram of the proposed situation is shown in figure 2.4. For the problem of a plate with a central crack of length $2a$, Dugdale's model gives the zone size (X) as:

$$X = a \{ \sec(\pi\sigma/2\sigma_y) - 1 \} \quad (2.10)$$

OR:

$$a/a_1 = 2/\pi \cos^{-1} (\sigma/\sigma_y) \quad (2.11)$$

Dugdale's own measurements of plastic zone sizes in notched steel plates confirmed the validity of equation 2.10 and others have since used the model to give good correlation of results for many other materials (e.g. WIEDERHORN [1969] (glass), BRINSON [1969] polycarbonate).

2.6.2 Crack opening displacement

The presence of a plastic zone at the tip of a 'real' crack enables the faces of the crack to move apart without extending the crack length. This relative motion between the flanks of the crack is termed the crack opening displacement (often abbreviated as COD).

A critical value of COD, implying the attainment of critical conditions in the crack tip plastic zone was originally proposed by WELLS [1963] as a fracture criterion. He measured the COD at crack tips in steels and obtained 'satisfactory' correlation of data.

The COD has been related to the stress intensity factor, K , by BURDEKIN and STONE [1966] who used a Dugdale model to calculate tensile strains on gauge lengths normal to the crack plane. The derived solution was:

$$COD(\delta) = \frac{K^2}{\sigma_y \cdot E} \quad (2.12)$$

where σ_y is the yield stress and E is Young's Modulus.

CHAPTER 3. CRACKING AND CRAZING IN PLASTICS - LITERATURE REVIEW

3.1 INTRODUCTION

Before a real understanding of fracture processes in plastics can be obtained, the nature of craze formation, deformation and breakdown must be fully understood. Also, the ways in which environments cause crazing or cracking must be studied in greater detail than hitherto. Since environmental effects and crazing are so closely tied to many of the failure problems which are encountered in service, a review of the current state of knowledge on these subjects is of direct relevance to the work presented in this thesis.

The review on crazing which follows has been kept as general as possible and does not specifically refer to the characteristics of any particular plastic. Where previous work on any of the plastics used in this project is pertinent to the discussion, it is discussed in the appropriate chapter or section which is devoted to the investigation of the material concerned.

Because the problems of environmental stress cracking are more specific, in that they generally concern only the polyolefins, a short review of the general background is given in this chapter and a more detailed experimental survey is given in the introduction to Chapter 6.

3.2 CRAZING IN GLASSY PLASTICS

It has been known for many years that when glassy plastics are loaded they have a tendency to form large numbers of small shiny surface defects which have every appearance of being cracks. Because of the similarity with the micro-cracking which is found in the glaze of many pottery articles, the term crazing was borrowed from the potters and used to describe the defects in plastics.

That crazing should occur in the glassy plastics was rather unfortunate, because not only does a sheet of plastic smothered with small defects look unsafe, but the crazes do nothing to improve the optical qualities of the material - for example see the crazes produced in the articles shown in figure 3.1.



figure 3 1: Examples of Crazing in Practice

In the early days, the two plastics which were most severely affected were PMMA and polystyrene – although it is now known that virtually all amorphous glassy plastics are susceptible to crazing. Polystyrene is particularly prone to crazing even in air; with many other materials, however, there is often no problem until they are stressed in a mild solvent vapour/liquid environment. Crazes not only spoil the optical properties, but are virtually always responsible for low stress failures in glassy plastics. For instance, in PMMA and polystyrene it is impossible to realise a yield stress in a conventional tensile test. At a stress value of approximately half the compressive yield stress, the materials craze and then break.

During the last twenty years there has been a considerable amount of research effort dissipated in trying to elucidate the nature and properties of crazes and a review of this literature now follows:

3.2.1 Nature of the craze

Most of the early studies into the nature of crazing were quick to point out that crazes only formed under tensile stress: compressive stresses giving no sign of crazing – SAUER, MARIN and HSAIO [1949] – (a further confirmation of the reluctance to yield in tension being solely due to crazing.) It was also noted that the stress did not have to be provided by an external loading – residual stresses can cause crazes of their own accord – Warburton-Hall and Russell [1953] – and also increase the severity when external loads are applied. The problem of residual stresses is particularly important with polystyrene because shrinkage during cooling of moulded articles often leaves a residual stress pattern which can cause crazing.

Besides needing tensile stress, crazes also require some site from which to initiate. Usually they are formed on the material surface at stress concentrations, such as voids, scratches, dust particles or inclusions – Spurr and Neigish [1962] – although there is some evidence that internal crazing is possible – again in poly-

styrene HOWARD and MANN [1964] - the sites in these cases presumably being internal micro-voids in the chain structure or inclusions formed during material production.

Because craze surfaces are highly reflective, they look exactly like cracks in glassy plastics, and for many years this is precisely what they were taken to be; even though there was a certain amount of experimental evidence which suggested otherwise. As early as 1949 Sauer et al. had noted that specimens of polystyrene which had been crazed across the whole section still managed to remain intact and carried loads without breaking. At the time this was regarded as being something of a curiosity and the evidence was not followed up.

WARBURTON-HALL and RUSSELL [1953] provided a second paradox, in the testing of PMMA, when they found that crazes apparently healed themselves and disappeared when samples were heated for a period at temperatures greater than 373°K . They were still convinced that crazes were true cracks and they proposed that the heating had expanded the material close to the crack which then closed up. It is somewhat surprising that they did not test their theory by inserting their own crack in a sample and repeating the test. If they had done so they would certainly have changed their minds since true cracks in PMMA do not heal at temperatures $\sim 373^{\circ}\text{K}$. The craze healing experiment was later repeated by BESSONOV and KUVSHINSKII in 1958 and they put forward a rather different explanation. They proposed that it was possible that the crack faces were "strengthened"* by a system of filaments, which contract on heating and thus cause the 'crack' to close. The filament idea also explained Sauer's results because it was noted that as the 'crack' opened up under stress, the filaments would cold work and thus provide strength. Direct confirmation of this theory came a few years later when SPURR and

* (their word - not mine!)

NIEGISCH [1962] looked at microtomed cross sections of crazed material on the electron microscope. To their surprise (since they do not seem to have read Bessonov's paper) they found that sections taken from long polycarbonate crazes showed the craze to be composed of voided material which was highly oriented in the direction of the applied stress. They were unable to make any detailed measurements from their micrographs and they did not pursue the topic any further.

3.2.2 Craze structure

Matters did not remain static for long, because around this time Kambour was embarking on a series of highly elegant experiments which were to go a long way towards explaining the true nature of the craze. He too, was convinced that there was material inside the craze and he reasoned that light is strongly reflected solely because the density and hence the refractive index is much less than that of the bulk polymer. In optical terms the craze - which is surrounded by normal polymer - may be likened to a thin layer of liquid of low refractive index between two pieces of 'glass' of high refractive index. Thinking of crazing in these terms he further reasoned that by measuring the critical angle for total light reflection at the craze/polymer interface, the refractive index and hence the density of the craze could be calculated. He confirmed his theory by measuring the density of crazes in PMMA and polystyrene, and, allowing for some margin of error in measuring the critical angles, he found that in both materials there was a 40% ($\pm 10\%$) void content in the craze, KAMBOUR [1964c]. Both these sets of crazes had been grown in air and in subsequent tests he repeated the measurements for a PMMA craze grown in ethanol and found that the density remained unchanged.

Because of the errors involved in the measurement of the critical angle in a thin craze, Kambour carried out a more precise series of tests on thick crazes in polycarbonate (grown in both air and alcohol) and decided that the upper limit of 50% void : 50% polymer was the most "accurate" value - KAMBOUR [1964b]. He

later verified this by a more direct method when he infused sulphur into a poly-phenylene oxide (PPO) craze and measured the void content from electron micrographs of the cross section - KAMBOUR and HOLIK [1969]. From all these measurements Kambour was able to show that the density of the craze is seemingly independent of either the parent polymer or the way in which the craze has been formed.

Having thus satisfied himself that crazes are indeed voided regions of oriented polymer, Kambour then concentrated on measuring the size of the voids within the craze. To do this, he grew crazes in PMMA in ethanol and then attempted to interchange the ethanol with silver nitrate, an electron dense substance which would show up the voids in the electron microscope. Because of photo-reduction of the silver solution his results were not as good as he had hoped, although he was able to see that the holes were spheroidal, with diameters in the range $20 \text{ \AA} \rightarrow 200 \text{ \AA}$ - KAMBOUR [1964b]. He repeated the tests using sulfur in a PPO craze and this time was able to get excellent micrographs which showed that at the tip of the craze the voids are approximately $20 \text{ \AA}$ in size and that they increase in size as the craze thickens behind the tip - eventually reaching an average size of approximately $200 \text{ \AA}$ - KAMBOUR and HOLIK [1969].

As a secondary facet to both these projects, the ease with which the liquids were able to be interchanged with the crazing agents showed that the voids do not exist as discrete holes within the polymer - they are instead, connected by a complex system of channels.

3.2.3 Craze initiation

When crazes are initiated, they are generated at the tips of flaws and other such inhomogeneities. In these locations the local stresses are much higher than those in the bulk material and when the stress is sufficient to overcome the secondary bonding forces holding the molecular chains together, separation occurs and a craze

is born. In effect, the material changes from a glassy to a softer rubbery phase which is easily cavitated by the dilational action of the triaxial stress system at the flaw tip.

In any test system where resistance to crazing is being measured, it is obviously of crucial importance to have some realistic parameter which can be measured at the onset of crazing and which can then be used as a comparator for assessing the material, environment etc. The two most common parameters proposed in the literature are the macroscopic values of stress and strain. Neither of these parameters takes any account of the size of defects at which the crazes start and are therefore susceptible to variations in material preparation, condition, handling etc.

In most of the early studies, the critical stress criterion held sway mainly because most of the tests were performed on rather primitive apparatus where stress was the only quantity which could be monitored with any precision. Indeed STUART et al. [1964] when proposing a critical stress criterion for the onset of crazing in polyethylene glycol terephthalate { "Terylene" } noted that there were considerable fluctuations in the values obtained. STERNSTEIN and ONGCHIN [1961] were able to obtain greater precision however, when they examined the effects of biaxial loading on crazing in PMMA. They subjected tapered cylinders of PMMA to internal pressure and then noted the section on the taper where crazing started - from this observation they computed a craze initiation stress.

More recently the pendulum seems to have swung away from critical stresses and strain is very much in vogue. Most of the more popular tests involve a method similar to that of Sternstein's, in that they involve measuring the point at which crazes appear on a plate specimen which is strapped to an elliptical former. Such a technique has been successfully used by DEMPSEY [1967] on HIPS in air and by Kambour when testing PPO and polycarbonate in a multitude of environments BERNIER and KAMBOUR [1969]. The quality of the data which they have

obtained seems to suggest that critical strain is probably a much more reliable measure than is stress.

3.2.4 Craze growth

Once they have initiated, crazes continue to grow as long as there is a concentration of stress at the craze tip which is sufficient for void formation, because there is a triaxial stress system at the craze tip - in the same way as at the tip of a true crack. Superficially, the craze appears to grow in a direction perpendicular to the direction of the applied stress {an observation which has since become commonplace}. However, this is not quite the whole story; STERNSTEIN et al. [1968] have examined the crazing patterns produced around a hole drilled in the centre of a tensile strip specimen of PMMA tested at elevated temperature { 343°K } in air, and they noted that the crazes did not always form perpendicular to the applied stress. They compared the pattern of crazing with the photoelastic fringe pattern obtained in separate tests and concluded that craze growth occurs along a path such that the major principal stress always acts perpendicular to the craze plane. BEVIS and HULL [1970] also came to the same conclusion as a result of an analysis of the stress and craze trajectories around a crack tip in polystyrene.

3.3 DEFORMATIONAL RESPONSE OF CRAZES

When crazes are formed, the constituent material undergoes considerable deformation. SPURR and NEIGISCH [1962] in their electron microscope study of sections of the polycarbonate craze estimated that even in the unloaded state the material inside the craze was extended 100% more than the surrounding bulk material. Because of this permanent deformation, the results of creep tests on materials which have crazed always show a non recoverable strain when the specimens are unloaded - MENGES [1969].

The main source of information on the ways in which the crazes themselves respond to different loading situations is due to KAMBOUR and KOPP [1967]. They grew crazes across the whole cross section of bars of polycarbonate by stressing the material in ethanol. They removed the ethanol and allowed the craze to dry under load for three months before testing under repeated cyclic loading. In order to measure the deformation response of the craze they used a cine camera/microscope unit to film the craze edges. When interpreting the results they had to presume that all the deformation of the craze was due to stretching of the craze itself and that no new material was created. This is not an unreasonable assumption, since there is no stress concentration along the craze/matrix interface sufficient to result in the production of new craze.

During the first cycle (which lasted 1 minute) they managed to obtain a very definite yield stress which was followed by a period of 'cold drawing'. They reversed the cycle at approximately 40% strain and noted that there was a considerable amount of hysteresis which resulted in a 28% residual strain at zero stress.

On the second and subsequent cycles, the yield stress dropped slightly and became markedly less pronounced as did the hysteresis and amount of non recoverable strain. By the fifth cycle, the craze deformation was found to be almost totally

elastic. They found that it was a little difficult to ascribe an accurate value to the craze modulus because of strain hardening effects caused by orientation, but they settled on a value of approximately 25% of the elastic modulus of the normal polymer as a reasonable estimate of the 'true' value.

3.4 EFFECT OF STRAIN RATE

In general, most of the crazing studies have tended to ignore the effects of strain rate on craze initiation and growth, even though plastics are notoriously rate sensitive materials. The tests have usually been conducted under constant load conditions or else on an Instron-type machine at some arbitrary strain rate. The sole exception was the work reported by MUARRY and HULL [1970] who looked at the strain rate dependence of the nucleation of cracks and crazes in polystyrene at room temperature. They conducted a series of tensile tests and noted that when crazes first appeared - at approximately half the final fracture stress (σ_f) - the load deflection curve became non-linear. At about $0.9 \sigma_f$ several of the crazes suddenly grew rapidly - final fracture eventually occurring at one of these crazes.

For strain rates $< 2 \times 10^{-6} \text{sec}^{-1}$, a small number of long crazes were formed during the initiation period. At higher rates the number of crazes increased whilst the average length decreased. They proposed that in any given test, the first crazes which appear are initiated by cavity formation around large 'particles' or other such inhomogeneities. As stress is increased in the test, extra crazes are formed around smaller and smaller 'particles'. At low straining rates, the cavities/crazes which initiate at the larger particles have plenty of time to grow before subsidiary crazes are activated and the large crazes tend to dominate the scene. The large circular crazes which are formed during this process eventually intersect, the voids coalesce and start slow crack propagation. At higher strain rates, although many crazes are formed around all sizes of 'particles', there is insufficient time for the crazes to coalesce before fracture occurs - this failure usually starting at the edge of the specimen.

From an examination of the fractured crazes they also noted that the craze thickness decreases with increasing strain rate - thus supporting their time dependence explanation - above.

3.5 EFFECT OF TEMPERATURE

Because craze formation intrinsically relies on the ease with which the polymer can be made to 'flow', it would be expected that increasing the temperature of the material would make for easier craze formation. In one of the early crazing studies by WARBURTON-HALL and RUSSELL [1953], this was in fact confirmed, as they found that the critical stress values for craze initiation in PMMA were much lower at high temperatures. The effects of temperature were analysed in much more detail by MENGES [1969] when he measured the critical strains for crazing (ϵ_c) as a function of temperature - using sophisticated creep machines. He was able to show that for polypropylene and polyoxymethylene, ϵ_c is unchanged by varying the temperatures - although the time to craze decreased as temperature was increased. These results seem to support the argument that critical strain is a much the better measure of craze initiation.

SPURR and NEIGISCH [1962] also noted, in passing, that as temperature is increased there is an increase in both the number of crazes and also the growth rates at any given level of applied stress.

On a slightly different tack, ANDREWS and BEVAN [1966] used pre-notched specimens to investigate the effects of temperature on craze initiation in PMMA soaked in Methylated Spirits (essentially a 9:1 ethanol/methanol mixture). (In the paper they talk about crack initiation but it is now virtually certain that they were measuring crazes.) They showed that for pre-notched tests, initiation can be characterised by a critical value of an energy parameter (T_c) - essentially akin to the surface work, γ_p (see page 21). Below 293°K the values of T_c increased dramatically with decreasing temperature whereas above 293°K, T_c was essentially constant. STERNSTEIN and SIMS [1964] also used similar tests to examine temperature effects in PMMA in an ethanol and water mixture. They pre-soaked their specimens for 24 hrs before testing, so it is not easy to compare their

results with those of Andrews et al., but they seem to be slightly at variance.

Sternstein et al. found that for temperatures greater than 293°K the crazes were easier to form and that the growth rates for any given loading condition increased in proportion to the temperature increase.

More recent results which have been obtained in the laboratories at Imperial College, contradict the results of both Andrews and Sternstein because it has been found that craze growth rates decrease as the temperature is raised above 293°K - WEBBER [1971]. The reasons for the above disparities are not yet fully understood, although it does appear that for higher temperatures the rate at which the polymer absorbs the environment is drastically increased and this can change the nature of the bulk material and hence the crazing behaviour. It would be expected that the rates of absorption of the various liquids used in the three investigations would be different and this may be the reason for the apparently contradictory results.

3.6 CRAZES AND FRACTURE OF GLASSY PLASTICS

3.6.1 Molecular orientation at crack tips

During the last twenty years there have been many investigations into the modes of fracture of plastics - particularly with PMMA and polystyrene. Most of these studies have involved the use of pre-notched specimens and have sought to interpret the results in terms of the Griffith criterion, by measuring the "surface energy" (γ) experimentally, and then comparing this with a theoretical value based on the reversible work necessary to separate two atomic planes of the material.

Credit is usually given to BERRY [1961a] for the first studies of this kind although, in fact, he was preceded by KIES [1953] who had made a very brief study on PMMA some years previously. Although there were some differences in experimental techniques and in the measured values of γ , they nevertheless came to the conclusion that the experimentally determined values of the surface work for glassy plastics are approximately $1000 \times$ greater than those predicted by theory. Berry calculated γ to be $4.5 \times 10^{-1} \text{ Joules/m}^2$ and measured values in the range $1.5 \rightarrow 3 (10^2) \text{ Joules/m}^2$. This large discrepancy was attributed by both Berry and Kies (plus everyone else who has since tried to measure γ) to be due to the dissipation of energy in plastic flow at the crack tip. Although the plasticity in PMMA is on too small a scale to be seen by the naked eye, there is direct evidence that material has been plastically deformed. When fracture surfaces of PMMA are examined, interference colours can be seen and it was HIGUCHI [1958] who first suggested that these colours are caused by molecular orientation and plastic flow at the crack tip producing a change in the refractive index of the broken material. BERRY [1962] later made a much more detailed study of the PMMA fracture surfaces and came to essentially the same conclusion as Higuchi. He did, however, go one step further by explaining the presence of different colours as being due to level

differences on the surface caused by the irregular nature of crack propagation at low crack speeds. He measured the thickness of the 'oriented' layer as $5 \rightarrow 6 \times 10^3 \text{ \AA}$ and said that this was constant all over the slow-growth surface.

3.6.2 Crazing at crack tips

Although the interference effect could be plausibly explained by Berry's model, there were however, a number of phenomena which the orientation hypothesis could not explain. The colours were found to be very sensitive to high vacuum. - NEWMAN and WOLOCK [1958] and also to inert liquids such as water and silicone oil. Kambour clarified the issue when he actually measured the refractive index of the surface layers in PMMA and found the value of the index to be compatible with that obtained for a craze with a 40% void content. He therefore concluded that not only is the material oriented but is also voided and has every optical characteristics of a 'normal' craze - KAMBOUR [1964(a)]. In a later test series he also measured the thickness of the layer and got thickness values in the range $2 \rightarrow 5 \times 10^3 \text{ \AA}$, KAMBOUR [1965]. (He later corrected himself when he was able to make more accurate measurements on other surfaces and got a value of $5800 \text{ \AA}$ which compares well with Berry's measurements, KAMBOUR [1966].)

In this latter series of tests, Kambour used a cleavage type specimen and set up a microscope so that he could view the crack tip during crack propagation and also measure the interference fringes produced by the deformation of the craze prior to fracture. He found that the interference bands extended for 25μ in front of the crack tip and he took this to be the length of the craze. From the various fringe patterns, he built up a model of what the craze looks like at the crack tip - this is shown in figure 3.2.

The shape of Kambour's proposed craze has since been confirmed by VAN DEN BOOGAART [1966] who used a high powered microscope to view the crack

tip in PMMA from the side rather than above (as Kambour). Because of this new evidence, BERRY [1964] later modified his orientation model to include the presence of voids in the fracture surface layer and was able to provide a much better explanation for the observed fracture surface features.

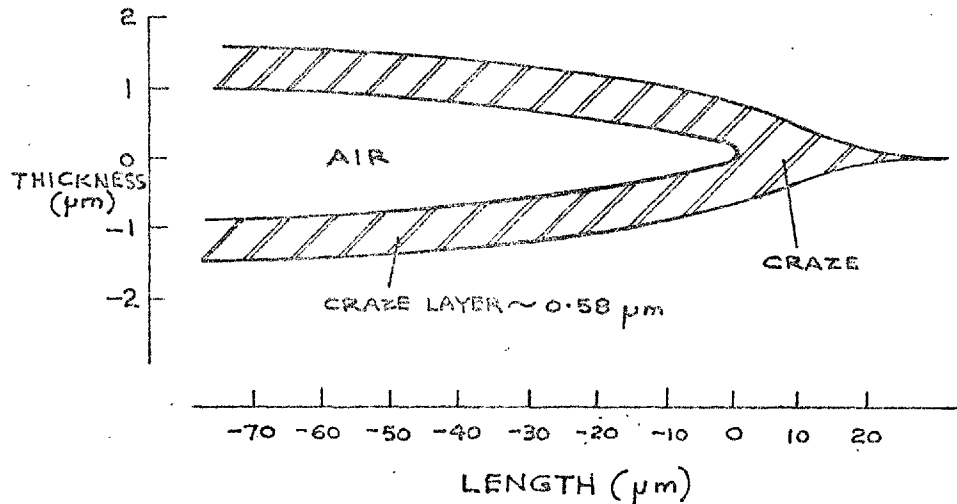


figure 3.2: Schematic Representation of Craze at Crack Tip in PMMA (KAMBOUR [1966])

KAMBOUR [1966] also extended his observations to include polystyrene and showed that crazing again occurs at the crack tip, although on a much larger scale than in PMMA, since the measured length ahead of the crack tip in polystyrene was 550μ and the layer thickness was $60,000 \text{ \AA}$! The crack tip in polystyrene, however, is not quite the same as in PMMA because there is a bunch of crazes surrounding the crack and these distort the measurements. (They also have a profound effect on γ_p values, as will be discussed in Chapter 5.)

3.6.3 Energy contributions to surface work (γ_p)

Having established that the 'plastic zone' at the crack tip in glassy plastics is really a craze, Kambour became involved in trying to account for the various factors which make the experimental values of γ_p much greater than the theoretical predictions (γ). In a series of papers {KAMBOUR [1965/6/7]} he assessed the relative merits of three main contributions as being:-

- (1) The energy required to create voids in the craze $\sim 2\% \gamma_p$
- (2) The energy associated with 'elastic' deformation of the craze
 $\sim 80-90\% \gamma_p$
- (3) The energy associated with 'plastic' deformation of the craze
 $\sim 15\% \gamma_p$.

The numbers tend to vary between each of the references quoted because he was unsure what value of Young's Modulus (E) he should ascribe to the craze.

(As a result of the cyclic tests on polycarbonate - see section 3.3 - he eventually used $E_{craze} = 25\% E_{bulk}$ and the numbers quoted above were obtained using this value.)

3.7 CRAZE BREAKDOWN AND FRACTURE

3.7.1 Slow speed fracture

In glassy plastics, there are two common types of failure. In the first case, under relatively slow loading conditions, cracks can start to grow slowly at low load levels. If the loads are either maintained or increased then catastrophic 'fast' fracture will ultimately take place. Alternatively, when loading takes place over a very short time scale (e.g. impact loading), the slow growth region is often not apparent and the material instantaneously splits because of 'fast' fracture.

BERRY [1964] has proposed that the failure process is initiated within the craze by means of void coalescence - new craze being generated at the crack-craze tip as the 'old' craze is broken. This is obviously an appealing theory because it conveniently explains the way in which the slow growth can occur - it is by no means a new theory for fracture because direct visual observation of fracture in thin sheets of zinc has shown that voids opening and coalescing to form the growing crack are a common fracture in metals, McCLEAN et al.

[1954]. In plastics too, there is some direct evidence for void coalescence.

MURRAY and HULL [1970c] used a microscope to look at crazes in polystyrene and were able to observe that very small 'marks' appeared inside the craze at low stress values, these 'marks' growing and eventually coalescing to form the main crack as the load on the specimen was increased. In a somewhat different experiment, ZHURKOV et al. [1969] used X-ray diffraction techniques to measure flaw contents of a number of thermoplastics. Prior to rupture, they found that there was a sudden change in the scattering pattern - suggesting that more and more large cracks were appearing in the material, due to either slow crack growth or void coalescence (or both). In measurements of the void concentrations at a crack tip in polycapromide they noted that at the moment of fracture the concentration was always constant. This correlates well with the results of KAMBOUR's [1966] fringe measurements in the PMMA craze because he too noted that at the instant of craze fracture the fringe order was always the same, and was indicative of a 100% strain within the craze. In effect, both pieces of evidence seem to point towards a constant crack opening displacement (C O D) criterion of failure.

Thus, void coalescence within the craze can have serious consequences and can cause pre-mature failures, especially in cases where crazes have been formed at low stresses by environmental contact.

3.7.2 High speed fracture

Crazing is not only important in slow growth; there is a great deal of circumstantial evidence to suggest that crazes are produced (and then broken) for crack velocities $>1000 \text{ cm/s}$. For example, on PMMA 'fast' fracture surfaces the oft-observed hyperbolic markings are almost certainly due to the intersection of the main crack front and a radially expanding void within the craze. Interference colours are also apparent on the surfaces, indicating, as before, the pre-

sence of a crazed layer.

In PMMA, the normal mode of crack propagation appears to be by splitting through the centre of the craze since the oriented layers on opposite fracture surfaces are equally apparent. However in polystyrene this is not always the case.

MURRAY and HULL [1970b] have proposed that many of the observed surface fractures can best be explained by failures not only through the centre of the craze but also by splitting along the craze/matrix interface - especially when cracks are moving with a high velocity.

3.8 CRAZE TOUGHENING

In the preceding sections crazes have been considered to be defects which should be avoided at all costs. This is not always the case in practice however, because there is at least one situation where crazes are positively helpful in INCREASING material toughness.

The susceptibility of polystyrene to low-load impact failure has long been recognised, and in order to increase the toughness the manufacturers tried adding rubber to the material (= HIPS).^{*} It was thought that the rubber particles would absorb impact energy and would also serve to blunten cracks. The modified material is indeed much tougher than the base resin, though not quite for the reasons quoted. BUCKNALL and SMITH [1965] have shown that the main toughening role of the rubber particles is in acting as sites for internal craze formation. During loading many crazes are formed around each particle and because crazes are oriented material they act together in this case, as energy sinks. Much of the applied load/energy is absorbed in the production and subsequent deformation of the crazes - giving the characteristic "stress whitened" look to the material. This finding has been confirmed by BIGLIONE et al. [1969] who carried out a series of tensile tests on both types of polystyrene under various levels of external pressure. They found that for pressures $> 2kb$ crazing is not observed in plastics and that it was at this pressure that the tensile strengths of both polystyrenes became equal, i.e. when no crazing is possible, the rubber particles in HIPS do not have a toughening effect.

* HIPS - High Impact Polystyrene.

3.9 ENVIRONMENTAL STRESS CRAZING

In many cases where crazes are the cause of low-stress failures, it is found that it is the combination of stress and environment which has been responsible for craze initiation and growth. Liquid environments are particularly pernicious, causing crazes to initiate at much lower stress/strain levels than in air for example. This lowering of the critical limits is of vital importance in plastics usage because whatever the application, it is certain that at some stage in the life of an article it will be in contact with environments and trouble can occur.

The crazes which are produced by environmental attack do not appear to differ significantly in their structure from crazes produced in air. The void contents, void sizes etc. appear to be the same, KAMBOUR [1967]; although it is readily noticeable that much greater craze deflections can be sustained - so the stress/strain behaviour must be different. On this last point there is little further information, as yet, since no-one (not even Kambour!) has attempted to measure the stress/strain curve of a "wet" craze.

3.9.1 Role of the environment

Liquid environments which exert a corrosive action on glassy polymers and cause crazing, generally have two important properties. In the first case they must be able to 'wet' the plastic (i.e. spread easily on the material surface with essentially zero contact angle) thereby lowering the polymer surface energy and making void formation easier - STUART et al. [1964]. They must also be able to diffuse easily into the polymer structure causing the material to swell.

Swelling causes the glass transition temperature, T_g , to fall and this consequently means that low stresses can induce plastic flow more easily. Experiment suggests that both statements are essentially correct, crazing agents do wet the plastics and also have a considerable swelling action. Good solvents (which do not

swell) are not, in general, good crazing agents. A detailed examination of swelling, plasticization and adsorption has been made by BERNIER and KAMBOUR [1969].

They carried out a series of three-point bending tests on PPO*, measuring critical crazing strains (ϵ_c) in a large variety of liquid environments. They also performed a series of tests to measure the T_g 's of fully swollen films of PPO so as to provide cross checks on the plasticization theory. For a small-molecule liquid and a given polymer, the degree of swelling is known to be correlated approximately by the difference between the solubility parameter (Δ) of the liquid and that of the polymer. In the crazing tests they found that there was a very definite relation between ϵ_c and Δ for different polymer-environment systems - as is shown in figure 3.3. The minimum initiation strain occurred when $\Delta_{\text{polymer}} \rightarrow \Delta_{\text{liquid}}$. Liquids which had solubility parameters $\sim \Delta_{\text{polymer}}$ did not cause crazing, however; they caused cracking instead. (The crazing/cracking agents are indicated in figure 3.3.)

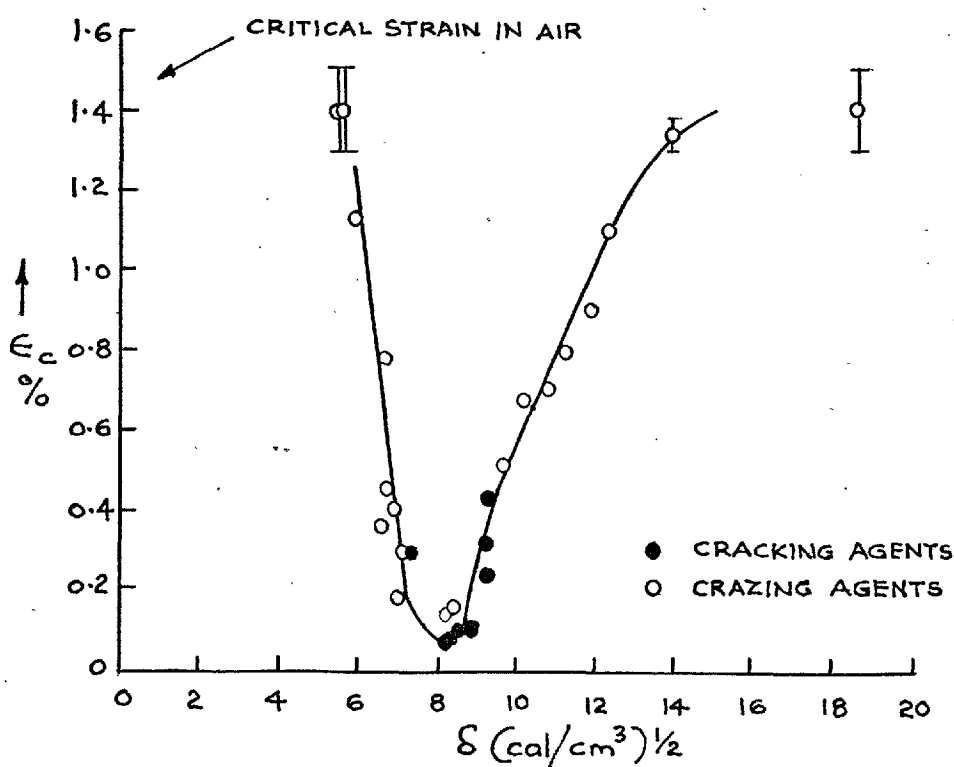


figure 3.3: Critical Crazing Strain vs Solubility Parameter
(BERNIER and KAMBOUR [1961])

* poly (2,6-dimethyl 1-1, 4-phenylene oxide).

From the tests on the equilibrated films, they were able to show that for cracking agents there had been sufficient plasticization to lower the T_g below room temperature thus setting up conditions for crack, rather than craze, formation. This latter data also showed that there was a reasonable correlation between ϵ_c and T_g . Although they were a little short on experimental data they, at least, were convinced that the case for plasticization being the main cause of reduced values of ϵ_c was proved.

Similar conclusions about the role of the environment, based more on hypothetical reasoning rather than hard experimental evidence, have been proposed by GENT [1970]. He postulated that when a flawed material is stressed, a transition occurs at the crack tip which causes the polymer to change from a glassy to a softer, rubbery state. Cavitation of the rubber-like material follows as a natural consequence of the hydrostatic stress system. He suggested that even in air (or vacuum) crazing would occur because the dilational stresses lower the secondary molecular bonding forces, producing molecular motion similar to that occurring at T_g . The effect of the environment in his model, is to cause a drastic drop in T_g thus allowing cavitation at much lower stress levels. He backed up his argument with some rather empirical equations which he derived using "reasonable" values of many of the unknowns. Using his equations he predicted a relation between a critical applied stress for crazing and the solubility parameter - the relationship showing the same sort of trends which Bernier and Kambour had measured experimentally. KAMBOUR et al. [1969] had shown that even agents which are poor swelling agents for PPO can cause crazing in stressed material. Gent has plotted curves which confirm that this is entirely possible - it being due to the remarkable increase in swelling power induced by high dilational stresses.

3.10 ENVIRONMENTAL STRESS CRACKING OF POLYETHYLENE

3.10.1 Nature of the problem

One of the major problems of fracture in plastics is the susceptibility of the polyolefins (polyethylene in particular) to the phenomenon of environmental stress cracking (hereafter called E S C). HOWARD [1964] has written an excellent summary of the published work on this problem and has given a concise definition of ESC as follows:-

"Environmental stress cracking is the failure, in surface initiated brittle fracture of a polyethylene specimen or part, under polyaxial stress in contact with a medium in the absence of which fracture does not occur under the same conditions of stress. Combinations of external and/or internal stresses may be involved and the sensitising medium may be gaseous, liquid, semi-solid or solid."

The problem thus has a number of curious features, especially the absolute need for both stress and environment. If only one of these is present, cracking does not occur and there is no problem. (In practice most manufactured articles have considerable residual stresses and hence the danger of ESC is always present.) Indeed, cracking agents, far from being solvents for polyethylene (as with crazing agents) are often precipitants even at high temperatures. There are numerous types of environment which are hostile to polyethylene and, although no complete classification exists, it is known that polar liquids (those with their electrical and mass centre displaced) such as alcohols and detergents are particularly pernicious.

Before continuing with a brief survey of the large volume of literature which has been published on this phenomenon, it is worth setting down some pertinent features about the rather special structure of polyethylene.

3.10.2 Structure of polyethylene

Most of the glassy plastics which are susceptible to crazing are amorphous polymers although one or two, e.g. polycarbonate and PPO are slightly crystalline. Polyethylene is rather exceptional in that some grades can be highly crystalline and can also have considerable short range ordering of the molecular chains. The degree of crystallinity is a strong function of the density of the material as might be expected. Low density polyethylene ($\rho \sim 0.92$) has a highly branched structure and is usually 40-60% crystalline whereas high density material ($\rho \sim 0.95$) - with only small amounts of branching - is typically 60-80% crystalline. During the crystallisation process, the individual crystallites form in clusters or aggregates known as spherulites; - something of a misnomer, since the clusters can be rod or sheaf-like bunches of molecular chains as well as spheroids.

One of the main complicating factors about the structure is that polyethylenes do not consist of single, discrete molecular species but rather they are polydisperse systems made up of distributions of species of varying molecular weight. This dispersion is again a function of material density, low density material having by far the greater spread of molecular weights. During polymerization, the crystal growth rates are high enough to prohibit the high molecular weight chains from disentangling themselves from the melt, and chains tend to have their two ends embedded in different crystals - forming 'intercrystalline links' - KEITH and PADDEN [1959]. Because the high molecular weight fraction remains within the crystals, the low molecular weight fractions are pushed to the edge of the spherulites where this material has difficulty in crystallising. There are only a few chains extending between the spherulites and there tends to be a concentration of chain ends in these regions - thus forming a kind of built-in inhomogeneity CLEGG et al. [1959]. The small amount of material which is rejected in this

way can find itself the object of competition between adjacent spherulites, thereby producing a system of internal stresses which can result in microvoiding - HEISS and LANZEN [1958].

The boundaries of the spherulites therefore exist as weak points in the material and ISAKSEN et al. [1963] have noted that the locus of environmental stress cracks tends to follow the boundaries of the spherulites or else cracks go along spherulite radii.

3.10.3 Crack initiation

As with most other fracture processes, ESC is initiated at inherent material flaws or inhomogeneities - generally on the material surface because the liquid agents are not usually absorbed by the bulk polymer. CAREY [1950] claims to have confirmed this by running comparison tests on "notch-free" injection moulded material and on die-cut samples. The former had far superior resistance to ESC (although orientation effects cannot be discounted here). Others have carried out similar types of test and come to essentially the same conclusions as Carey - for example O'CONNOR and TURNER [1962] found that there was a marked improvement in ESC resistance in flame polished specimens.

The ability of the cracking agent to 'wet' the plastic is a major consideration in ESC-as in crazing. Liquids such as water, which do not 'wet' polyethylene, are not good cracking agents - BERGEN [1968]. The absorption of the agent on the interface of a microfissure results in the liquid being able to penetrate the material along the weakened spherulite boundaries, thereby further weakening the polymer by exerting a "spreading pressure" on the spherulitic structure - ISAAKSEN et al. [1963]. What then happens is still a matter for conjecture because to date there is still no convincing answer as to what reaction takes place to cause cracking.

3.10.4 External variables

(a) Molecular weight

Because each grade of polyethylene is made up of chains of varying molecular weight, the parameter is usually expressed as an average value in terms of the Melt Flow Index (M F I). This is a reciprocal function, quoted in terms of flow rate under standard conditions and its numerical value therefore DECREASES as molecular weight increases.

Whatever the test method, it is always readily noticeable that as the MFI increases there is a marked decrease in resistance to cracking, RICHARDS [1946] (+ countless others). Richards found that there is not a gradual transition as might be expected; instead, at some value of MFI (variable grade to grade) there is a very sudden decrease in resistance. HOPKINS et al. [1950] also reported that even in a polymer of relatively low MFI the very low molecular weight species within the material can have a deleterious effect on the strength of the polymer. They were able to produce an impressive improvement in ESC resistance when they eliminated the low end of the molecular weight fraction.

(b) Density

As far as density is concerned, it is generally accepted that increasing the density (all other things being equal) produces an increased resistance to environmental attack because of the greater structural integrity of the material. Hence, by suitable adjustments of the density and the MFI it is possible to produce a polymer which is highly resistant to ESC. Some care needs to be taken in getting the correct balance of density and MFI, because it has been reported that a polyethylene of low density and low MFI is worse than a high density material with a high MFI. In low density polyethylene, the crystals are small and imperfect and increasing the MFI increases the number of chain ends in inter-spherulite regions

and hence the number of weak links susceptible to environmental attack. With high density material, the crystals are large and well formed, and it is hard to cause cracking through the crystal structure under any conditions - hence the influence of MFI is less apparent, McFEDRIES et al. [1962].

(c) Orientation

Besides raising the density and/or lowering the MFI, one of the other ways of improving the fracture resistance is to induce orientation into the material.

Oriented polyethylene is extremely resistant to cracking when stresses are applied parallel to the direction of chain alignment and a considerable increase in strength can be obtained. If the stresses are applied perpendicular to the orientation direction the converse is unfortunately true, as was shown by DOLL and PLAHER [1961] who used specimens cut from injection moulded articles. Because of the strength improvement, it is often possible to take advantage of the orientation effect by carefully choosing the fabrication conditions of a given article. Particular care must be paid to extruded articles however, because this process can produce significant increases in the MFI - DAUES and EVANS [1967].

(d) Temperature

As a final comment on the effects of external variables, it is pertinent to note that ESC is very sensitive to the temperature of both the material and the environment. An increase in temperature produces a corresponding decrease in ESC resistance. (See HOWARD [1964] for references.) Because of this, many of the tests on ESC reported in the literature are often performed at elevated temperature (usually $\sim 320^{\circ}\text{K}$) so as to decrease testing times. As to whether the failure processes at high temperatures are the same as those at 293°K is a matter for conjecture although CLEGG et al. [1959] do consider this point and conclude that there is no conclusive evidence to suggest otherwise.

3.10.5 Finale

Although a great many people have expended a lot of effort in measuring the effects of external influence on ESC behaviour, there has been a certain amount of conflict in interpreting the test data. As yet, there is no universal test method for assessing ESC phenomena with any precision. Indeed some tests give completely contradictory results, particularly as regards the influence of material density.

A more detailed analysis of the commonly employed test procedures is to be found in the introduction to Chapter 6.

PART II

CRACK PROPAGATION IN PLASTICS

CHAPTER 4 : FRACTURE OF PMMA IN AIR AT 293°K

CHAPTER 5 : FRACTURE OF POLYSTYRENE IN AIR AT 293°K

CHAPTER 6 : ENVIRONMENTAL STRESS CRACKING OF
POLYETHYLENE

CHAPTER 4. FRACTURE OF POLY (METHYLMETHACRYLATE) (PMMA) - IN AIR AT 293°K

4.1 INTRODUCTION

Most of the previous attempts to correlate and explain the fracture behaviour of plastics have started by describing the failure of PMMA. During the past twenty years there have been at least seventeen reports on PMMA in the literature. Although the material is not a true engineering plastic and failure problems are not often encountered in practice, it has been studied mainly because (a) it is transparent - and hence cracks can easily be seen and (b) it breaks in a reasonably brittle manner - thus giving hope that theories developed previously for metals and glass can be easily adapted to provide criteria of failure. PMMA also has time and temperature dependent properties which allow for the study of strain rate and temperature effects on fracture behaviour - the idea being that experience gained on this 'model' plastic can be transposed and used to explain failure modes in other plastics where fracture processes are more complex.

Most of the previous people who worked with PMMA chose to apply the simple Griffith approach and attempts were made to measure the "surface energy", γ . Even though the values of γ which were measured were far greater than the surface tension because of plastic deformation at the crack tip, the Griffith criterion (equation 2.2, page 20) may still be used to predict a constant value of the "surface work", γ_p , at the onset of fracture - provided the plasticity is limited.

TABLE I. Fracture Toughness Values Quoted for PMMA in Air.

	Author(s)	Test Method	$\dot{a}$ mm/s	γ_p $\times 10^2$ Joules/m ²	$K_{(I)c}^{(calc)}$ MN/m ^{3/2}
1	BENBOW & ROESLER ('56)		$\sim 10^{-2}$	4.9	[1.69]
2	BENBOW ('61)		10^{-2}	4.2	[1.56]
3	BERRY ('61')		Instability	3.0	[1.12]
4	BERRY ('63)		10^{-3}	1.4	(0.76)
5	van den BOOGAART ('66)		$\sim 10^{-3}$	1.65	(0.83)
6	BROUTMAN & Mc.GARRY ('65)		1.25	1.25	(0.99)
7	BROUTMAN & KOBAYASHI*		1.25	2.0	(1.26)
8	DAVIDGE & TAPPIN ('68)		Instability	(3.65)	1.94
9	OLEAR & ERDOGAN ('68)		Instability	(1.39)	1.19
10	KEY, KATZ & PARKER ('69)		Instability	(1.15 → 2.7)	1.09 → 1.66
11	KIES ('53)		Instability	6.15	[1.9]
12	SVENNISON ('61')		$\sim 10^{-2}$	4.5	[1.61]
13	VINCENT & GOTHAM ('66)		$6.8 \times 10^{-2} \rightarrow$ 4.3×10^{-1}	1.5 → 3.4	[0.93 → 1.6]
14	WILLIAMS, RADON & TURNER ('68) (1)		$\sim 2.5 \times 10^{-3}$ ^{**}	(2.2 → 3.5)	1.13 → 1.43
15	WILLIAMS, RADON & TURNER ('68) (2)		Instability	(2.11 → 3.0)	1.48 → 1.75
16	IRWIN & KIES ('54)		Instability	4.4	[1.6]
17	FUJISHIRO ('71)		$\sim 10^{-2}$	0.923	(0.63)
18	HIGUCHI ('71)		Instability	3.6	[1.7]

N.B. () = Converted value - Using 'derived' E (via WILLIAMS [1972]).[] = De-converted value - Using quoted E .

* Private communication. ** 'Apparent' speed.

TABLE I shows the γ_p values which are quoted for PMMA in the literature and it can readily be seen that measured values of γ_p were by no means constant.

If all these results are correct, then it is difficult to explain the discrepancies on the basis of material property fluctuations - since the properties of cast PMMA do not vary much grade $\rightarrow$ grade and the implication is that simple 'brittle' fracture theory is invalid. However, a careful reading of the various references quoted indicates that many of the experimental techniques used were somewhat dubious - for example KIES [1953] generated his initial flaws by hammering a screwdriver into a plate of PMMA - giving a notch of doubtful form and hardly representative of the uniform, infinitely sharp cracks proposed by Griffith. Also, many of the higher values of γ_p can be dismissed as being irrelevant due to poor experimental technique (see page 91 for a more detailed critique).

The other source of difference between the results is that γ_p values are quoted for entirely different cracking situations. PMMA is a time-dependent material and can sustain very slowly moving, stable cracks which gradually accelerate to produce total fracture by unstable crack propagation. (In the present context a stable crack is defined as one which can be stopped by load reversal - vice-versa for an unstable crack.) The energy required to propagate cracks in these two situations would be expected to be different and this would naturally lead to variations in measured 'surface work' values since γ_p will be a function of crack speed. It can be seen from Table I that γ_p values where slow crack propagation occurred are generally less than for those measured at the onset of unstable 'fast' fracture. In work on rubber fracture, this fact has been recognised for many years and GREENSMITH and THOMAS [1955] have found that the 'tearing energy' (equivalent to ' G ') is a strong function of crack speed in vulcanised synthetic rubber.

In the literature on thermoplastics failure, there are very few references to the effects of slow crack velocities - although there is some fairly detailed work on the effects of very high crack speeds - COTTERELL [1965(a)], GREEN [1971]. The most notable attempt to correlate the slow cracking situation was made by VINCENT and GOTHAM [1966] who in a short note to "NATURE" gave a table of ' G ' ($\equiv 2\gamma_p$) values which they had measured as a function of crack velocity. They were able to show that there is definite evidence of a velocity dependence - but they did not really examine the subject in depth and the report is of only limited value because of its brevity. A much more detailed description of the possible effects and consequences of slow crack growth was provided by WILLIAMS et al. [1968] who reported on velocity effects in a comprehensive series of tests using a wide range of specimen geometries. However, again this report is of only limited use since no measurements were made of crack speeds - the velocities were 'inferred' indirectly from an analytical solution by IRWIN [1964].

The present project arose, in fact, as a consequence of this latter piece of work, since it was thought that a detailed description of slow fracture in PMMA could serve to explain many of the previous discrepancies in results obtained by other workers and confirm the usefulness of adopting a fracture mechanics approach to provide criteria of failure for glassy plastics.

This work will now be described. Experimental details have been kept to a minimum in the main text, the ardent experimentalist being referred to the paper on this subject, MARSHALL et al. [1969] - enclosed at the end of this thesis.

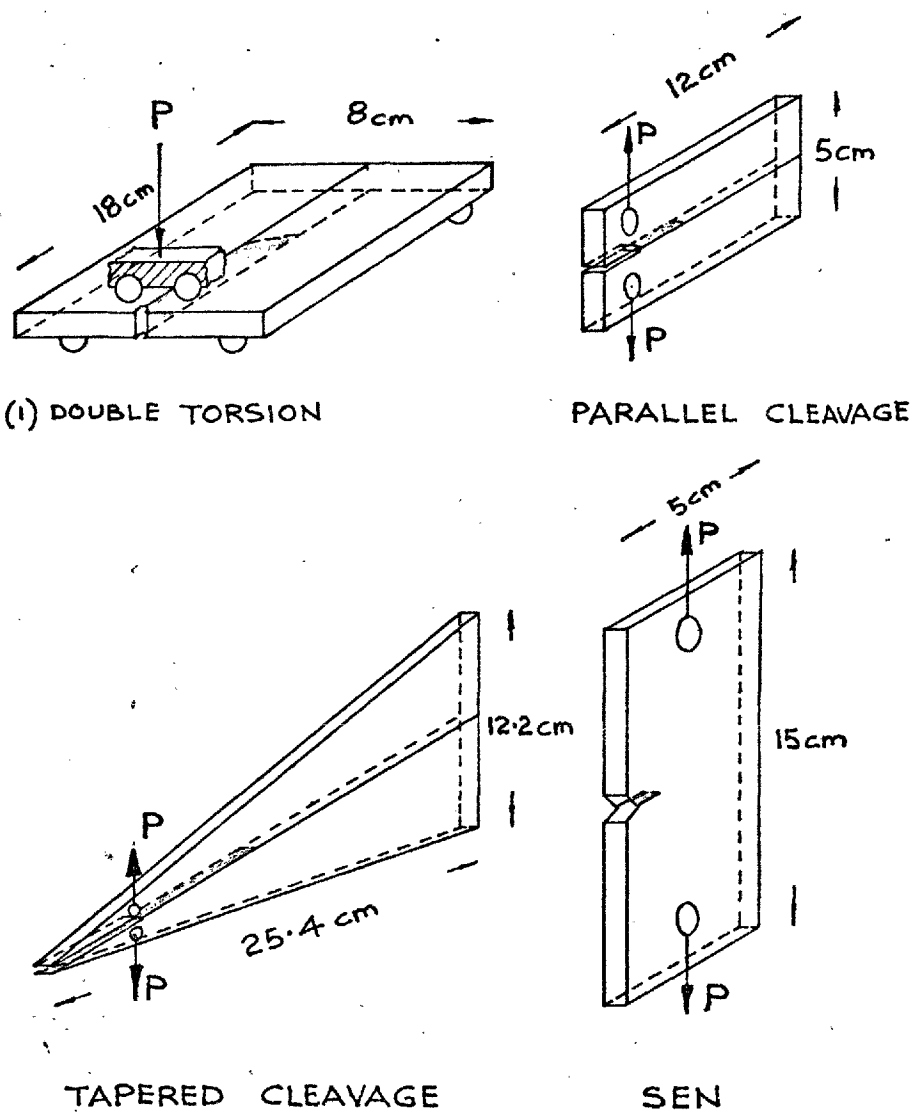


figure 4.1: Specimen Geometries

4.2 EXPERIMENTAL PROGRAMME

4.2.1 Specimen geometries

Most previous attempts to measure either γ_p or K_c values for PMMA have involved using many different types of specimen geometry and the results have often seemed to vary according to which specimen was used. In fact many people have explained the discrepancies in their numbers as being due to the choice of specimen geometry and claimed (of course) that theirs was the one best representative of a practical cracking situation. One of the fundamental maxims of fracture mechanics - which cannot be stressed too strongly - is that the results should be totally independent of geometrical effects - either in crack length or specimen shape. The solutions for calculating $\gamma_p/K_c/G_c$ or whatever, will of course vary, geometry to geometry, but the theory presumes and requires that the number obtained after calculation must be geometry independent.

Some specimens shapes are convenient for measuring slow crack propagation and others are more suitable for measuring instability points and it was thought that the only way to obtain true correlation of data was to plot the results on a K_c /crack speed (K_c vs $\dot{a}$) basis so that the results could be conveniently compared.

Hence a test programme was conceived, in which tests were made with four different types of specimen geometry, viz:

- (i) Single Edge Notched (SEN) (ii) Parallel Sided Cleavage
- (iii) Tapered Cleavage (iv) Double-Torsion - or "Outwater" - specimen.

The specimens and their respective dimensions are shown in figure 4.1.

4.2.2 Apparatus

The SEN and cleavage specimens were loaded on a batch of lever arm, dead weight loading rigs - see figure 4.2. The double torsion specimen requires a rather

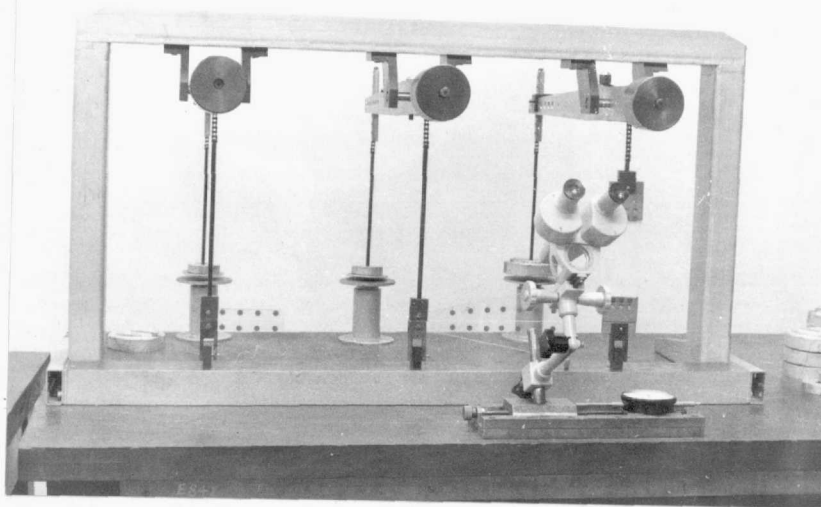


figure 4.2: Dead-weight Loading Stations

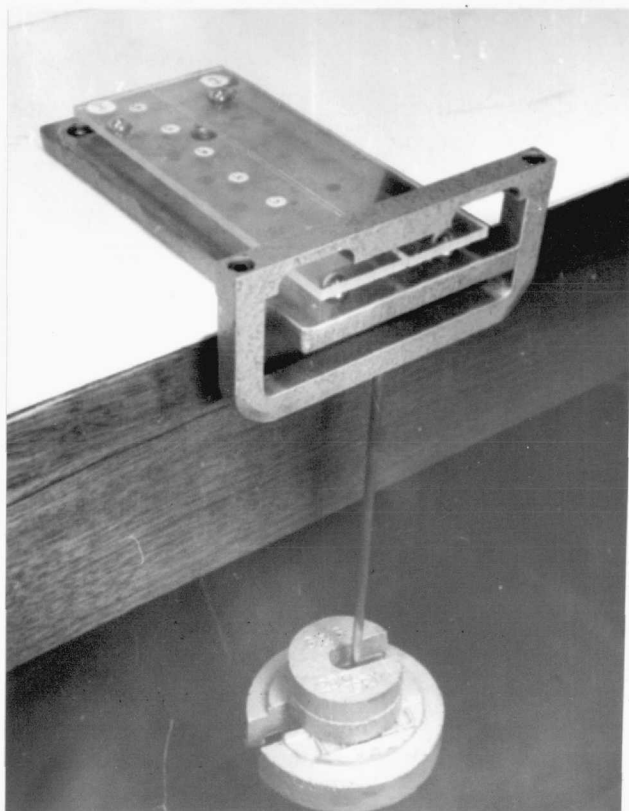


figure 4.3: Loading System for Double-torsion Specimens

more specialized form of loading and a special rig was made to test at constant load - see figure 4.3. The specimen is supported on four ball-bearings and the crack propagated down the central section by loading on either side of the control slots at one end of the specimen. As with the tapered cleavage specimen, the geometry is 'stable' in that the solution for K is independent of crack length. (For a 'proof' of this - see OUTWATER and GERRY [1967].)

A number of other tests were also made by loading specimens on an Instron Universal TT-D testing machine (hereafter called "the Instron") at various cross-head speeds.

Crack propagation was measured by either a travelling microscope or by cine-camera, depending on crack speed.

All tests were carried out in a temperature controlled laboratory - the ambient temperature being $293 \pm \frac{1}{2}^{\circ}\text{K}$ and the relative humidity being $50 \pm 5\%$.

The material used was I.C.I. "Perspex" (supplied as cast sheet).

4.2.3 Calculations

The infinite plate solution for the SEN specimen (equation 2.6 page 26) is invalid for the 50 mm wide specimen used here, and the boundary collocation solution of BROWN and SRAWLEY [1966] was used, since this equation takes account of finite plate effects. The solution was:

$$K = \sigma a_o^{\frac{1}{2}} \{ 1.99 - 0.41(a_o/W) + 18.70(a_o/W)^2 - 38.48(a_o/W)^3 + 53.85(a_o/W)^4 \} \quad (4.1)$$

where σ is the gross stress, a_o the crack length and W , the plate width.

The cleavage and double torsion specimens present more complex loading situations for deriving exact solutions for K ; although approximate solutions are given in the paper 1 - MARSHALL et al. [1969] (at end of thesis).

Also, because side slots had to be used to control the direction of the crack propagation, it was not known whether there would be a change in stress distribution which would invalidate analytical or numerical results. Hence, the solution for K was obtained from experimental calibration tests - using the Irwin-Kies solution of equation 2.4, viz:

$$K^2 = \frac{P^2 E}{2B_c} \cdot \frac{dc}{da} \quad (4.2)$$

By loading the specimens on the Instron, the compliance was easily measured as a function of crack length, thus giving dc/da . The modulus was measured on the same material - using the appropriate straining rate. The "correctness" of the derived solution was checked by calibration tests on a polyester resin - which does not have rate sensitive properties.

Comprehensive details of the test procedures and the results obtained are given in the enclosed paper 1.

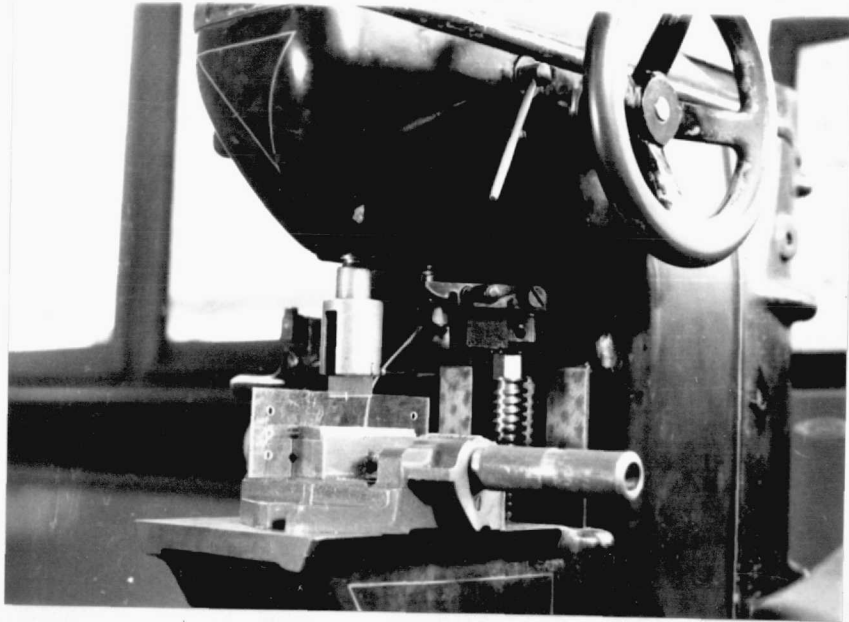


figure 4.4: Notching Apparatus

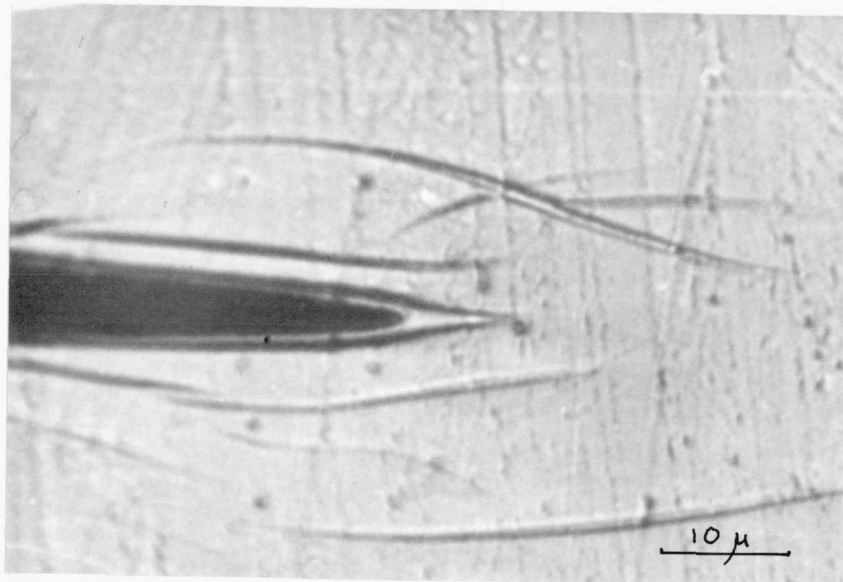


figure 4.5: Craze at Crack Tip - PMMA

4.2.4 Notching

One of the requirements of fracture theory is that artificial cracks should be made as sharp as possible - since the theory presumes zero tip radius.

(a) SEN

The notching of the SEN specimens was carried out using a razor blade mounted in a jig which was in turn fitted to a Vickers Hardness Testing Machine - as shown in figure 4.4. The cracks produced by this method were true and square across the section thickness and appeared 'sharp' to the naked eye - they were also independent of razor tip radius since the crack propagated ahead of the blade.

However on examination of such a crack under a high powered microscope, it could be seen that there was a distinct craze produced at the crack tip (see figure 4.5) - the main crack propagating through the centre of the craze. The main craze dimensions were exceedingly small compared with the other crack dimensions and so the theory ought to be valid. It can be seen from the photograph of figure 4.5 that a number of ancillary crazes were produced around the main craze. These have previously been noted by KAMBOUR [1965] and always appear to be produced when cracks are grown in PMMA. Kambour detected the presence of these ancillary crazes all the way across the section, although in the present case they could only be seen on the surfaces.

Kambour's measurements of the craze dimensions led him to the opinion that the unbroken craze extended 25μ in front of the crack tip. The cracks produced by the present notching technique had considerably smaller crazes - this probably being a reflection of the rather higher speed of crack initiation since Kambour's observations were all made on cracks propagating at very slow speeds ($\sim 10^{-1} \text{ mm/s}$) c.f. speeds of approximately 10^{-1} mm/s - immediately before crack arrest in the present case.

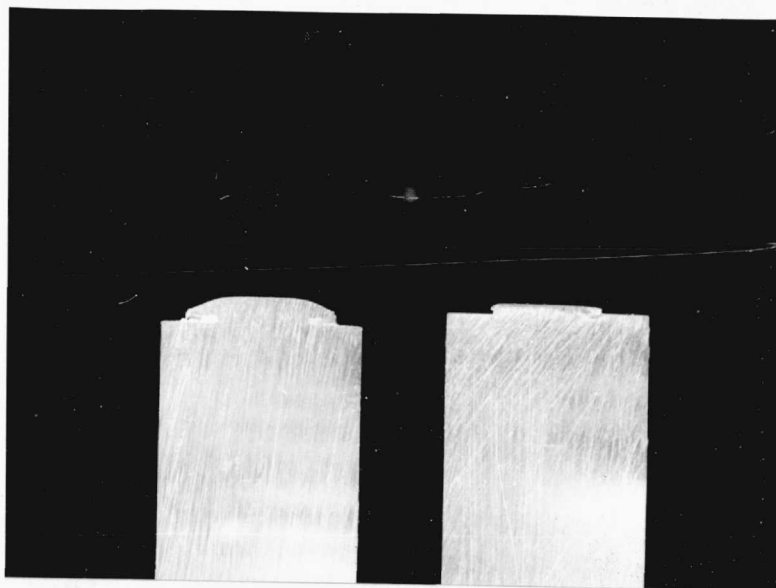


figure 4.6: Effects of Crack 'Wander' - Cleavage Tests

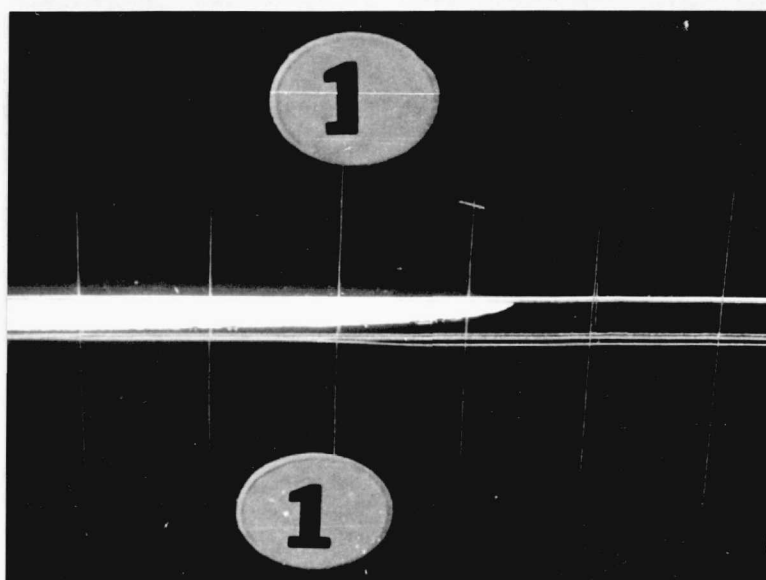


figure 4.7: Crack Geometry - Double Torsion Specimen

(b) Cleavage specimens

The cleavage specimens were unsuitable for razor notching and instead the saw slits were taken through to the central section at the point of loading - to produce a weakened section, from which a crack could be propagated by pre-loading either on the Instron or the constant load rigs. Cracks are not particularly easy to control in either type of cleavage specimen since they tended to 'wander' within the saw slits. Only specimens with well-formed cracks were accepted for testing - otherwise there was difficulty in assessing the crack width B_c in equation 4.2. The effect is shown in figure 4.6 which compares a particularly bad case of crack wander with the clean-flat surface which results from a well-formed crack

(c) Double torsion specimens

These specimens were pre-notched using the Vickers Machine and jig and then pre-loaded to produce a running crack. The pre-loading was necessary because a propagating crack in this geometry adopts a non-uniform crack front due to the bending action of the loading application - see figure 4.7. The craze produced at the tip of such a crack was found to be entirely commensurate in size and form with that shown in figure 4.5 for the SEN specimen.

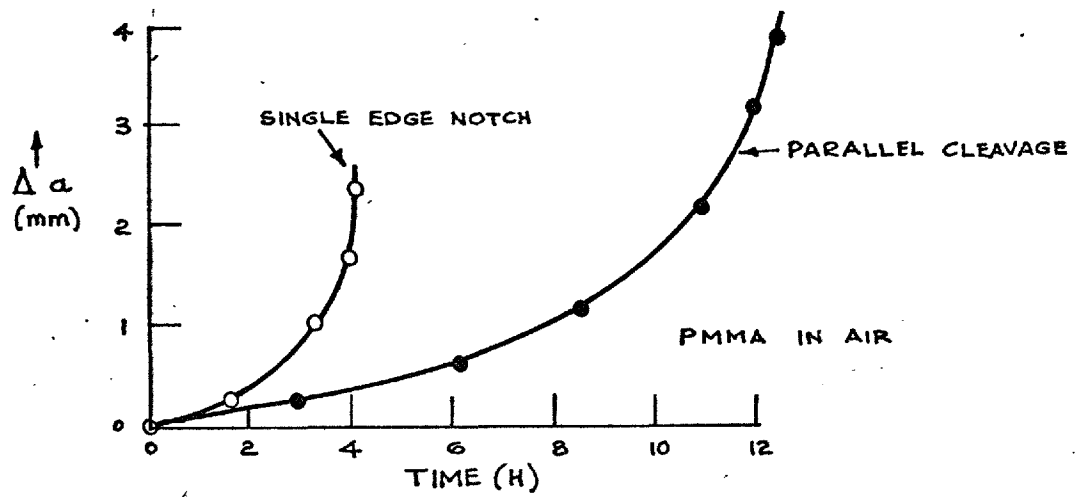


figure 4.8: Crack Length vs Time Curves - (SEN and parallel cleavage)

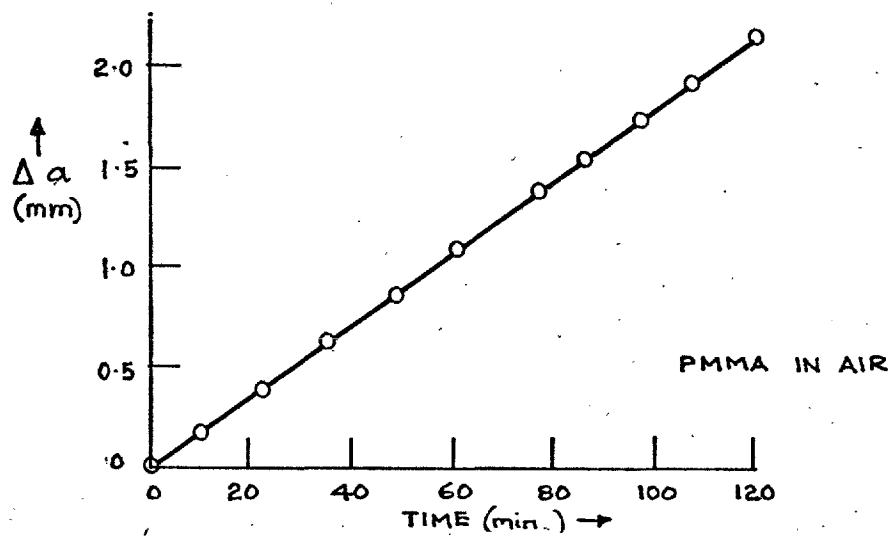


figure 4.9: Crack Length vs Time Graph - Tapered Cleavage

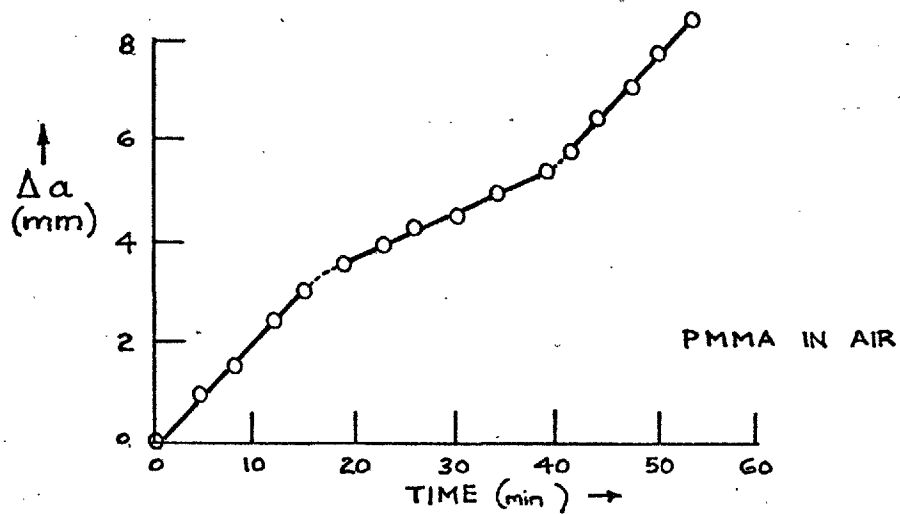


figure 4.10: Effects of Crack 'Wander' - Tapered Cleavage

4.3 EXPERIMENTAL RESULTS

4.3.1 Constant load tests

For all the specimen geometries, the experimental procedure was exactly the same, the specimens being subjected to a variety of dead weight loads and the crack growth measured as a function of time. To establish crack length independence in the SEN tests, specimens with initial lengths in the range $2.5 \rightarrow 12.5 \text{ mm}$ were tested in turn, three different thicknesses (1.5 mm , 3 mm , 6 mm) also being used to evaluate thickness effects on the results. Typical crack length versus time curves for each type of geometry are shown in figures 4.8 and 4.9.

The SEN specimen did not give much slow crack growth, since the stress intensity factor is very sensitive to crack length, and speeds in the higher range were consequently difficult to measure with any precision. The parallel cleavage specimens were also semi-unstable in that K increased with increasing crack length, but in this case the K /crack length sensitivity was less and more crack growth was obtained - thus allowing for more accurate determination of the speeds. For the tapered cleavage geometry, K is independent of crack length and constant speeds were obtained, making testing much easier and speed measurements more precise. The effect of crack "wander" in a tapered cleavage test is clearly indicated in figure 4.10. As the crack width increases due to the "wander", the effective K drops and the speed follows suit. Conversely, the subsequent change back to a uniform front produces an increase in speed - back to the initial value. The double torsion test was more successful in this respect, since the cracks stayed in the slits and variations in width due to "wander" were negligible.

The crack length vs time curves obtained in these tests were used to calculate crack speeds by taking slopes to various points on each curve - the corresponding value being calculated using the current value of crack length in each case (unnecessary in the tapered cleavage and double-torsion tests, of course, since $da/dt = \text{constant}$ and K is independent of crack length). The resulting $K_c/\dot{a}$ curves are shown as figures 4.11, 12, 13 and 14.

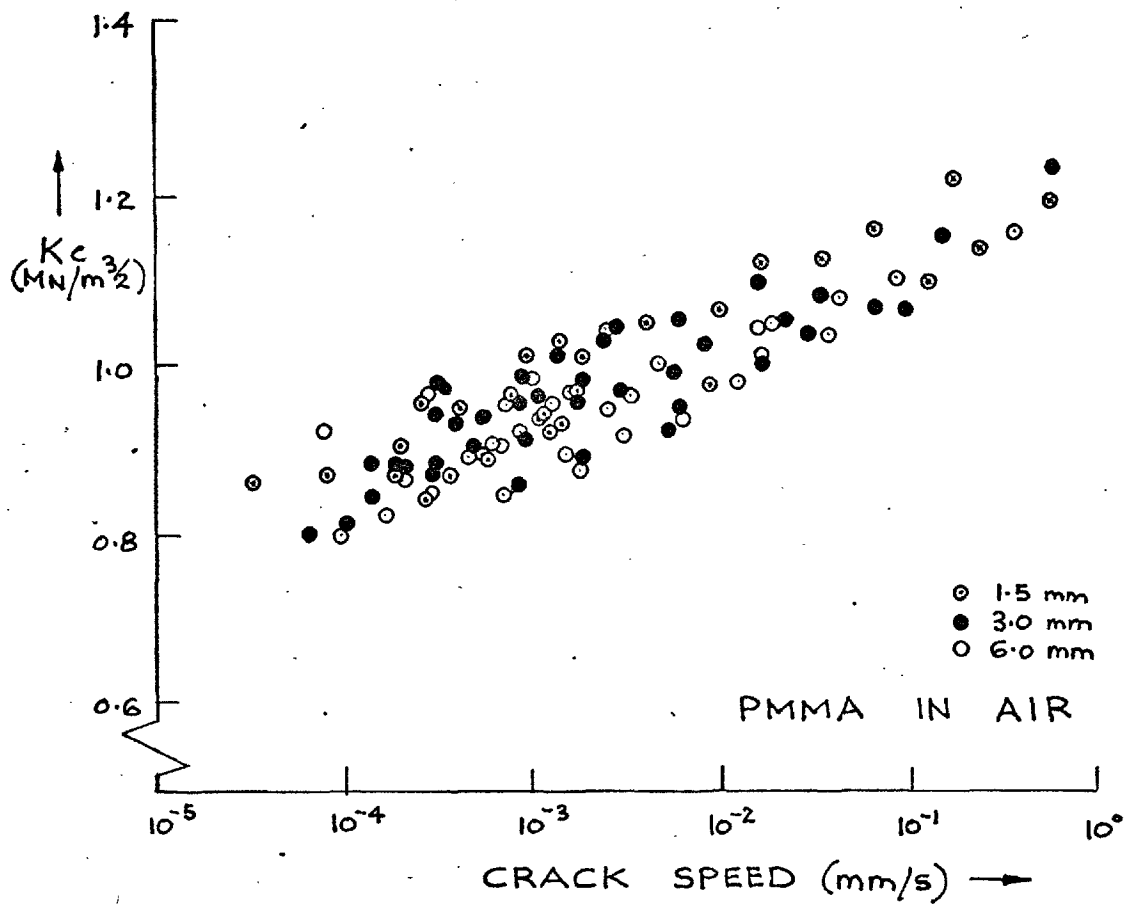


figure 4.11: K_c vs Crack Speed Curve for PMMA - SEN

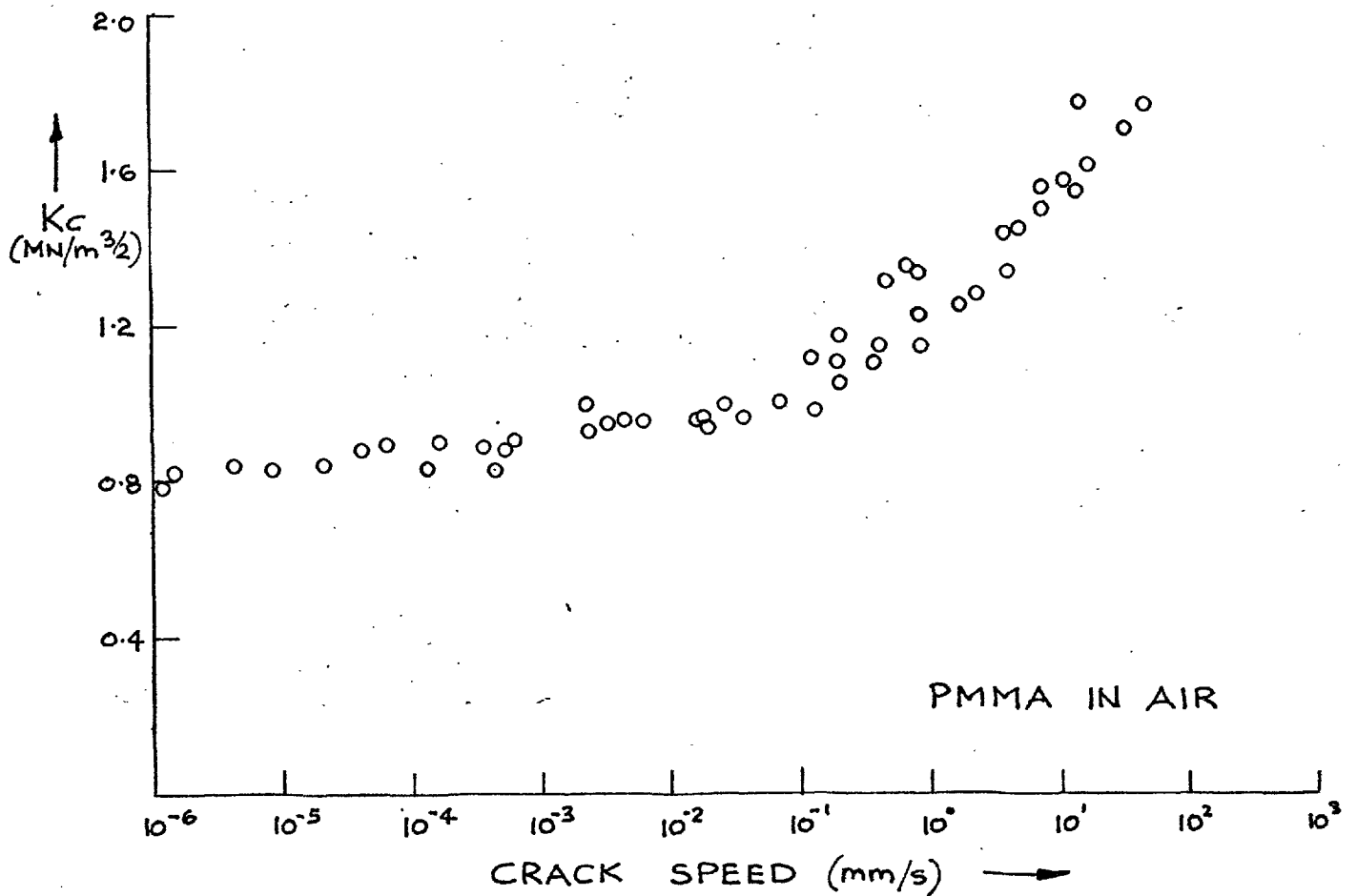


figure 4.12: K_c vs Crack Speed Curve for PMMA - Parallel Cleavage

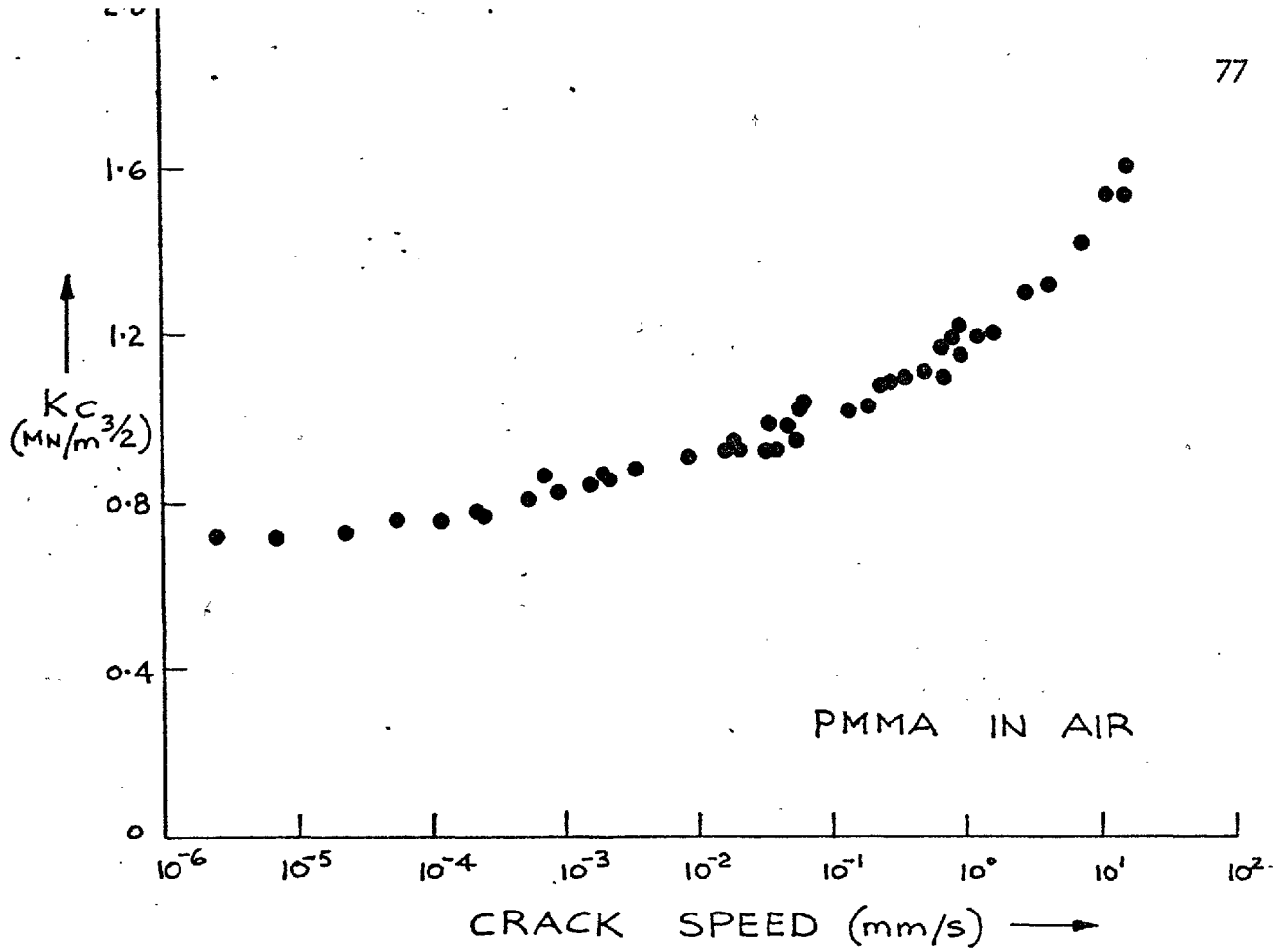


figure 4.13: K_c vs Crack Speed Curve for PMMA - Tapered Cleavage

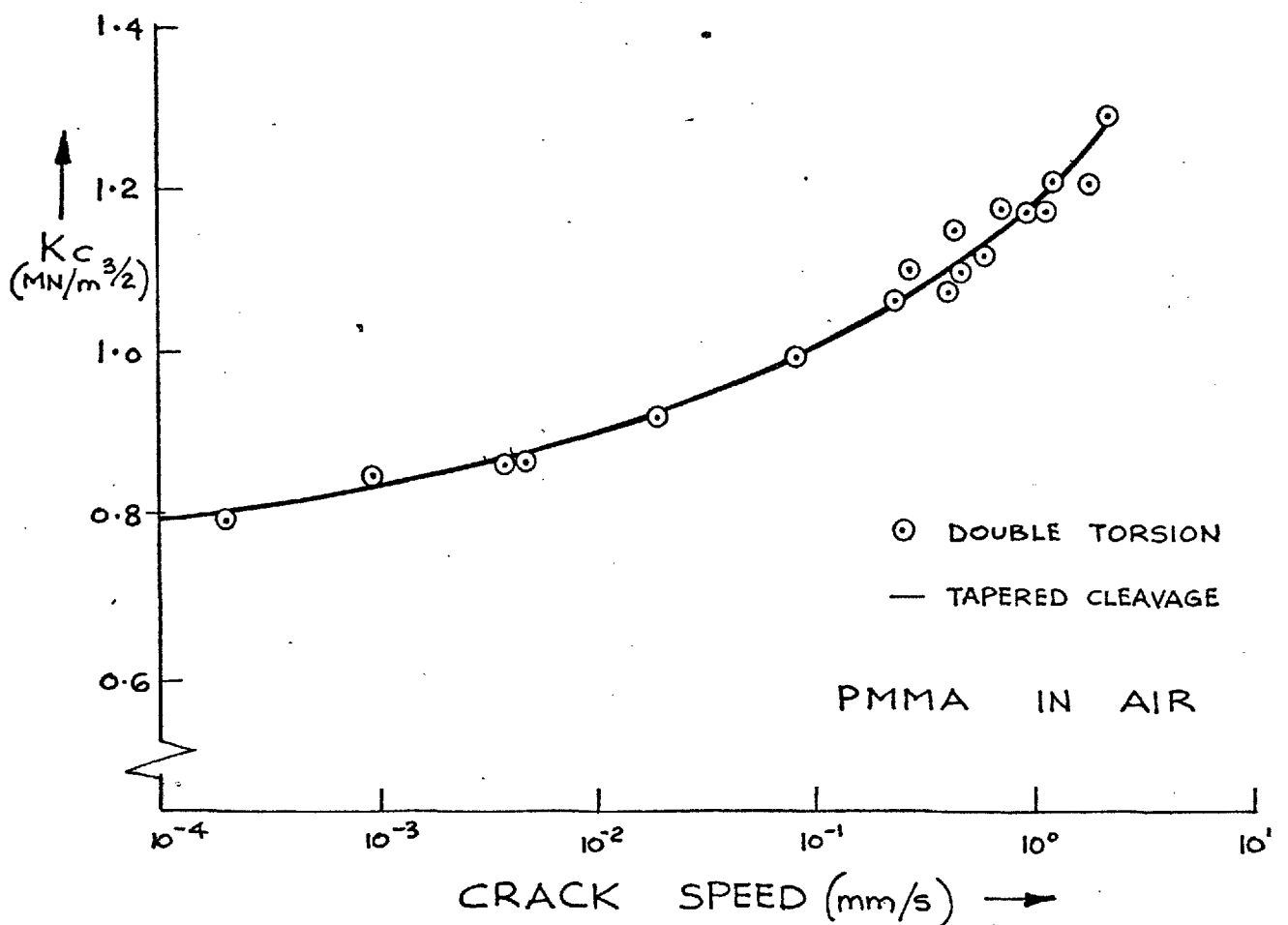


figure 4.14: K_c vs Crack Speed Curve for PMMA - Double Torsion

4.3.2 Instron tests: tapered cleavage and double torsion

To evaluate the effects of a change in loading condition, a number of tapered cleavage and double torsion specimens were tested at cross-head rates in the range $0.05 \text{ mm/min} \rightarrow 20 \text{ mm/min}$ on the Instron. Typical load/deflection curves on the tapered specimen at different rates are shown in figure 4.15 (the double torsion gave the same type of result). It can be seen that the constant value at which the load settles during crack propagation increases as cross-head rate increases - thereby giving higher K_c values and higher crack speeds.

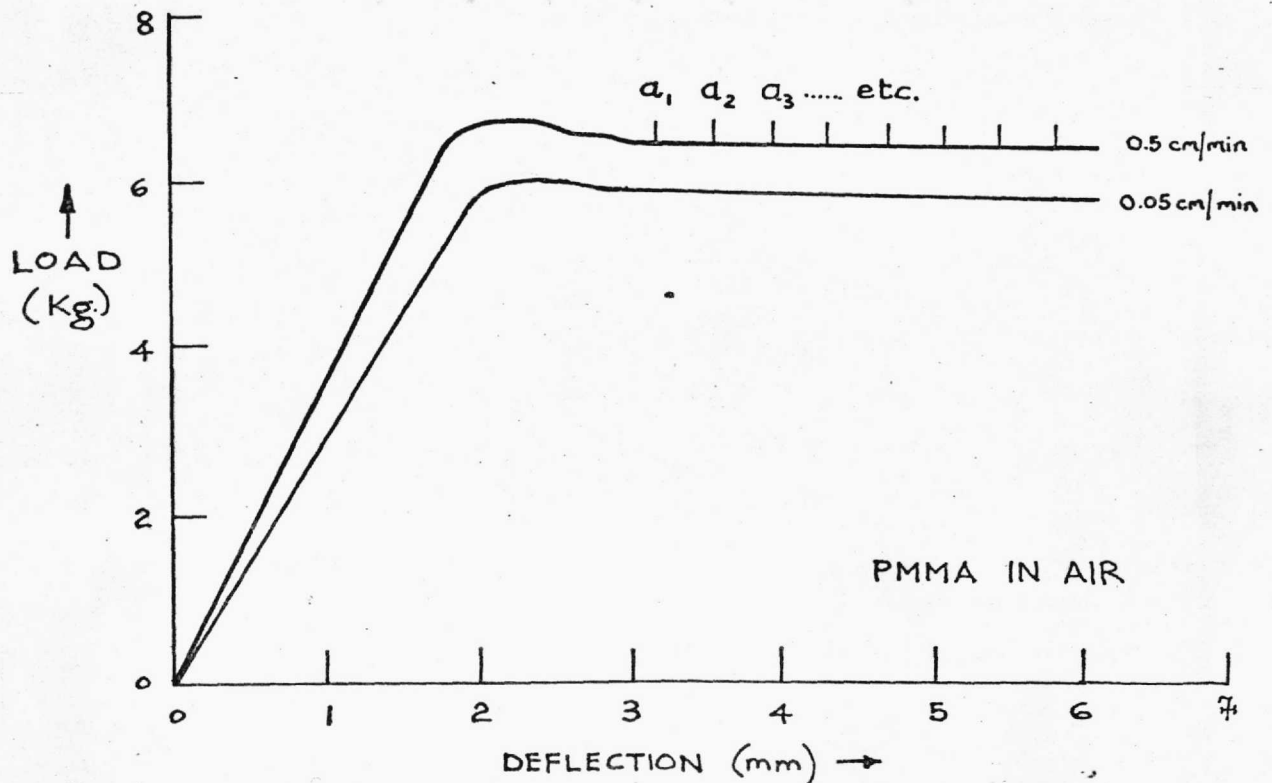


figure 4.15: Load vs Deflection Curve - Tapered Cleavage

The K_c and crack speed values obtained, are shown plotted with the constant load results in figures 4.13 and 1.14.

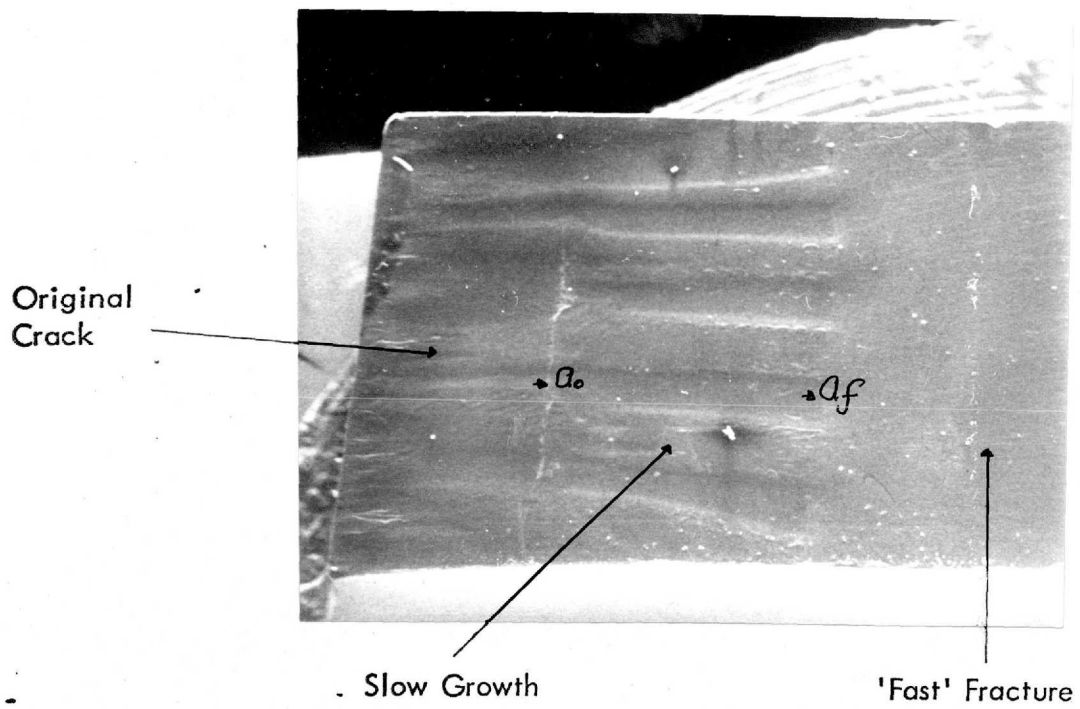


figure 4.16: Slow Growth Fracture Surface - PMMA (SEN)



5μ

figure 4.17: Markings on Fast Fracture Surface - PMMA

4.4 CRACK APPEARANCE

During the slow growth tests it was noted that the appearance of the cracks did not change radically with crack speed. The usual "river" pattern and fan markings were visible on the surfaces of all the cracks. Stereoscan micrographs of the details on the slow and fast fracture surfaces are illustrated in figures 4.16 and 4.17.

The transition point from slow to unstable fracture is clearly shown in figure 4.16.

The 'fan' markings are seen (in figure 4.16) to be caused by the crack propagating on slightly different levels across the section - as proposed earlier by BERRY [1962]. In the present case however, it would appear that the transitions between the different levels of crack propagation are considerably smoother than Berry had predicted.

The fast fracture surface appears, macroscopically, to be mirror smooth. Close examination, however, shows that the surface is covered by small hyperbolic markings - illustrated in figure 4.17. All the marks have a distinct focus and it has long been recognised that this represents the site of a secondary fracture initiated ahead of the main crack front - most probably caused by void growth in the craze at the crack tip. The hyperbolic shape results from the intersection of the main crack front with the radial front produced by the expanding void - KIES et al. [1950]. (Because open-form cracks are produced, the velocity of the main crack must necessarily be less than that of the secondary fracture.) The density of these markings has been shown by COTTERELL [1968] to be a function of crack speed, the density increasing for increasing crack speeds. This is presumably a consequence of the higher stress intensity at the crack tip at higher crack speeds causing more voids to expand in an unstable manner.

4.5 COMPARISON OF RESULTS

4.5.1 (a) K_{Ic} vs $\dot{a}$ (SEN)

The K_{Ic} vs $\dot{a}$ curve shown in figure 4.11 for the SEN specimens, has been drawn to a magnified scale to indicate the variation of results with specimen thickness. It can be seen that there is no appreciable variation - an expected result, since thickness variations should only have a significant effect when the plastic zone size at the crack tip is of the same order of magnitude as the specimen thickness HAHN et al. [1965]. In the present case the minimum thickness of 1.5 mm is three orders of magnitude greater than the plastic zone size and only plain strain fracture would be expected.

The scatter on the results is rather large - being of the order of $\pm 11\%$ - a reflection of the difficulty associated with measuring the crack speeds and the highly sensitive nature of the K -crack length relationship. Also the range of speeds which were measured is limited and it is concluded that the specimen is not very satisfactory for making this type of measurement in cases where the rate of change of K with crack speed is small - as it is over the range of speeds obtained here.

By measuring the extent of slow growth (e.g. a_f in figure 4.18) on each of the fracture surfaces, the value of K_{Ic} at the onset of 'fast' fracture (K_{Ic}) was found as $K_{Ic} = 1.65 \text{ MN/m}^{3/2}$ - this result being subject to a scatter of $\pm 6\%$.

(b) K_{Ic} vs $\dot{a}$ - parallel cleavage

The parallel cleavage results (figure 4.12) were much more consistent - scatter being of the order of $\pm 8\%$ and because K is not as sensitive to crack length changes, as in the SEN test, a wider range of crack speeds was obtained. The results indicate a lower limit of $K_{Ic} = 0.78 \text{ MN/m}^{3/2}$ for the onset of crack growth.

From the fracture surfaces it was again possible to observe the point at which there was a transition from slow to fast-unstable fracture and this was identified as occurring at $K_{Ic} = 1.77 \text{ MN/m}^{3/2}$ ($\pm 9\%$).

(c) K_c/a - tapered cleavage and double-torsion tests

The tapered cleavage results of figure 4.13 were even more consistent than for the parallel sided specimens - scatter being of the order of $\pm 5\%$. A lower limit of $K_c = 0.73 \text{ MN/m}^{3/2}$ and a fast fracture limit of $K_{Ic} = 1.71 \text{ MN/m}^{3/2}$ were established (the latter value by a separate test series) these values comparing favourably with the previous results.

The double-torsion results, shown plotted in figure 4.14, are compared there with the tapered cleavage curve, and it is readily evident that the two geometries give a satisfactory correlation of data.

As a final check on the geometry independence of the crack growth data, the results of all four test series are brought together in figure 4.18.

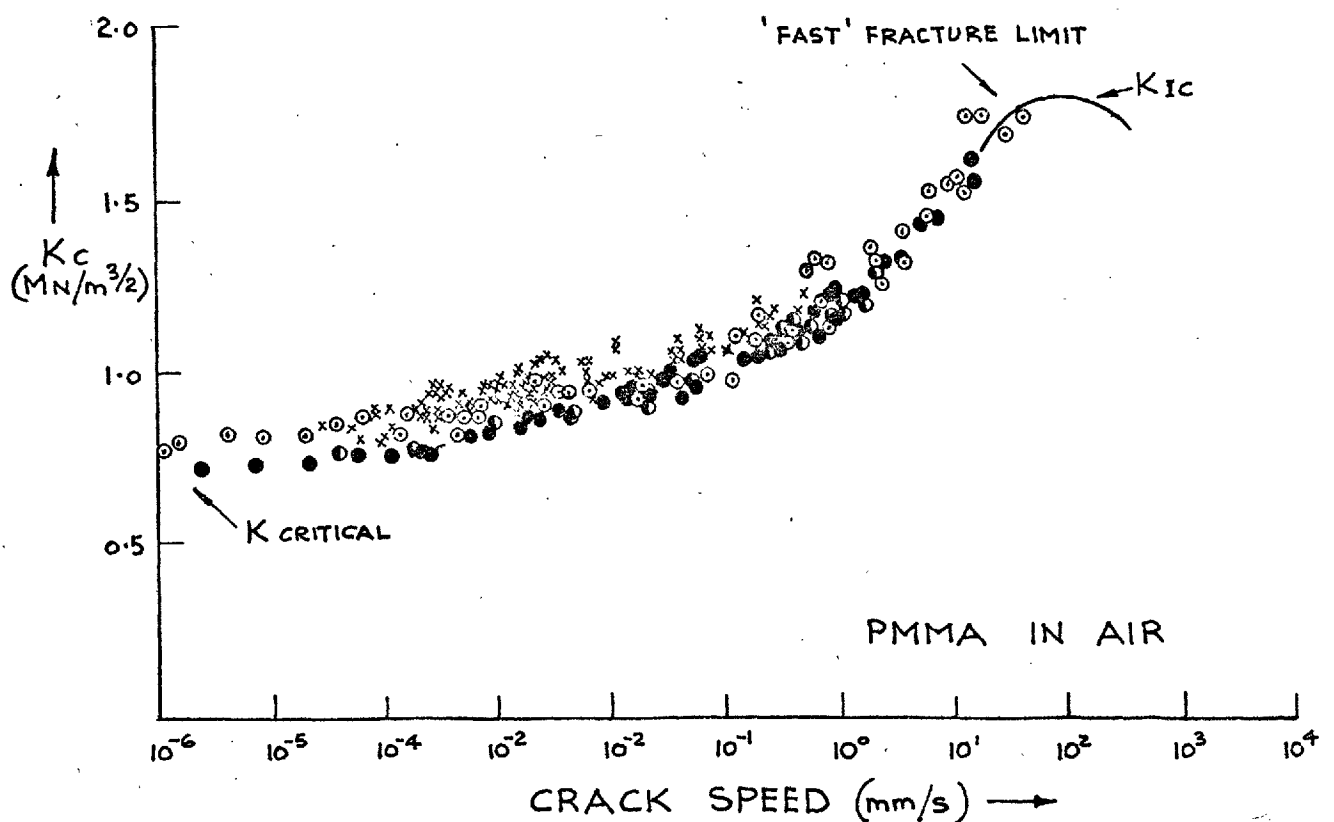


figure 4.18: K_c vs. Crack Speed - PMMA - All Specimens

The curve of figure 4.18 shows that to within acceptable limits, the results are sufficiently close as to verify the geometry independence of the K_{Ic} /crack speed relationship. The lower limit K_{Ic} value is $0.73 \text{ MN/m}^{3/2}$ and the transition from slow growth to fast fracture occurs at $K_{Ic} = 1.70 \text{ MN/m}^{3/2}$.

As a further check on the rate-dependence of the instability data for K_{Ic} obtained from the constant load tests a series of SEN specimens were tested on the Instron.

4.6 EFFECT OF STRAIN RATE ON K_{Ic}

Even though the SEN specimen is not ideal for testing on the constant load machines, it does have a number of advantages for fracture testing at different strain rates. The specimen is quickly (and hence cheaply) made, (cf. cleavage specimens) and by pulling a number of specimens on the Instron, the points of crack initiation and final fast fracture are easily measured.

A large number of these tests were carried out at machine cross-head rates varying from $0.005 \text{ cm/min} \rightarrow 50 \text{ cm/min}$. At each rate, 15 specimens of various thicknesses (1.5 mm , 3 mm , 6 mm) and containing a wide spread of notch length were tested to failure. Points of crack initiation, at rates up to 2 cm/min , were measured using a microscope and load/displacement 'blipper'. (At rates $> 2 \text{ cm/min}$ the points of initiation could not be measured with meaningful precision.) Average $K_{(I)c}$ values at crack initiation and final fracture were calculated. These are shown plotted versus cross-head rate in figure 4.19. The results at each rate were very consistent (scatter $\pm 8\%$) and showed no notch length dependence.

It can be seen from figure 4.19 that the points of crack initiation are very strongly dependent on cross-head speed whereas the K_{Ic} values are not. The

constant value of K at the onset of fast fracture was $K_{Ic} = 1.68 \text{ MN/m}^{3/2}$ - in close agreement with the constant load tests.

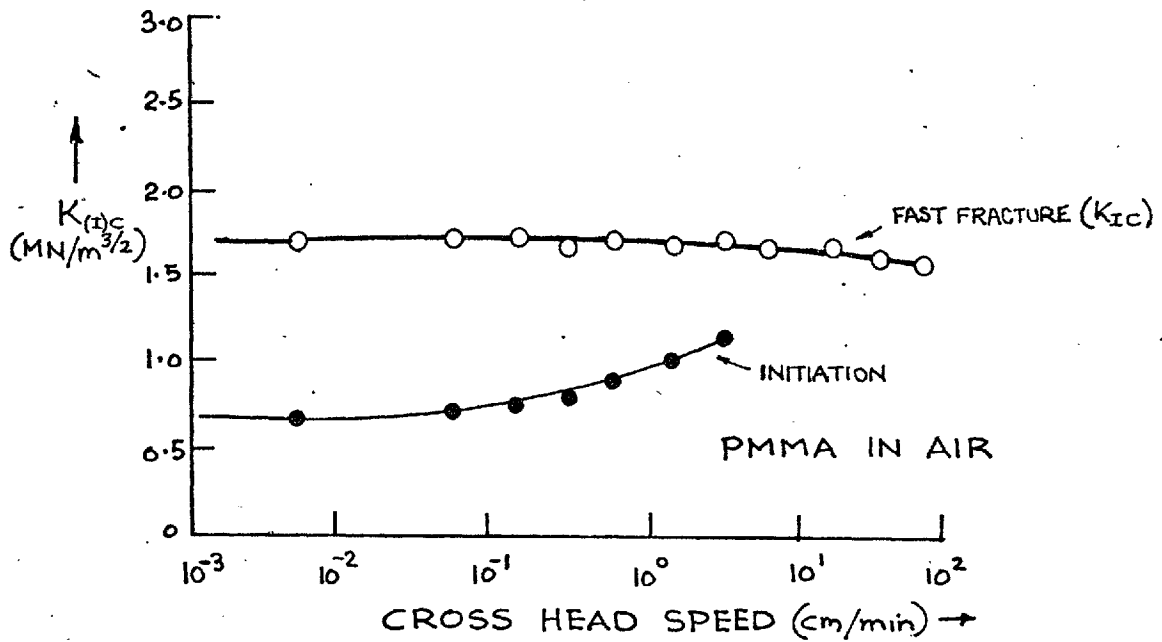


figure 4.19: Effect of Straining Rate on K_c Values - PMMA (SEN)

The transition in crack speed which occurs for $K > K_{Ic}$ was also measured in one or two of these tests. A conducting paint grid was painted onto the specimen surface immediately ahead of the point where slow crack propagation was expected to cease. When the crack propagated at high speed through the grid, the electrical resistance change was monitored on an oscilloscope and a crack length vs time curve obtained. The transition in speed of the crack was found to be very marked, the crack speed changing at instability from 50 mm/s to $1.8 \times 10^5 \text{ mm/s}$.

4.7 DISCUSSION OF K_c VS CRACK SPEED CURVE

From the results of this investigation it has been shown conclusively that the supposed constant K_c does, in fact, vary for PMMA - its value being strongly dependent on the speed of crack propagation. These measurements have only related to the 'slow' growth period of fracture, but others have shown that for high speed failure a K_c /crack speed relationship is again valid, GREEN [1971], COTTERELL [1965]. The full K_c /crack speed curve for PMMA is shown as figure 4.20, the results of Green being superimposed to illustrate the high speed regime. It can be seen that the curve is discontinuous after the slow growth although there are some results from impact tests - VINCENT and GOTHAM [1966] which seems to indicate that there is a falling curve for crack speed between 50 mm/s and 10^3 mm/sec (unpublished data of Broutman* also leads to this conclusion).

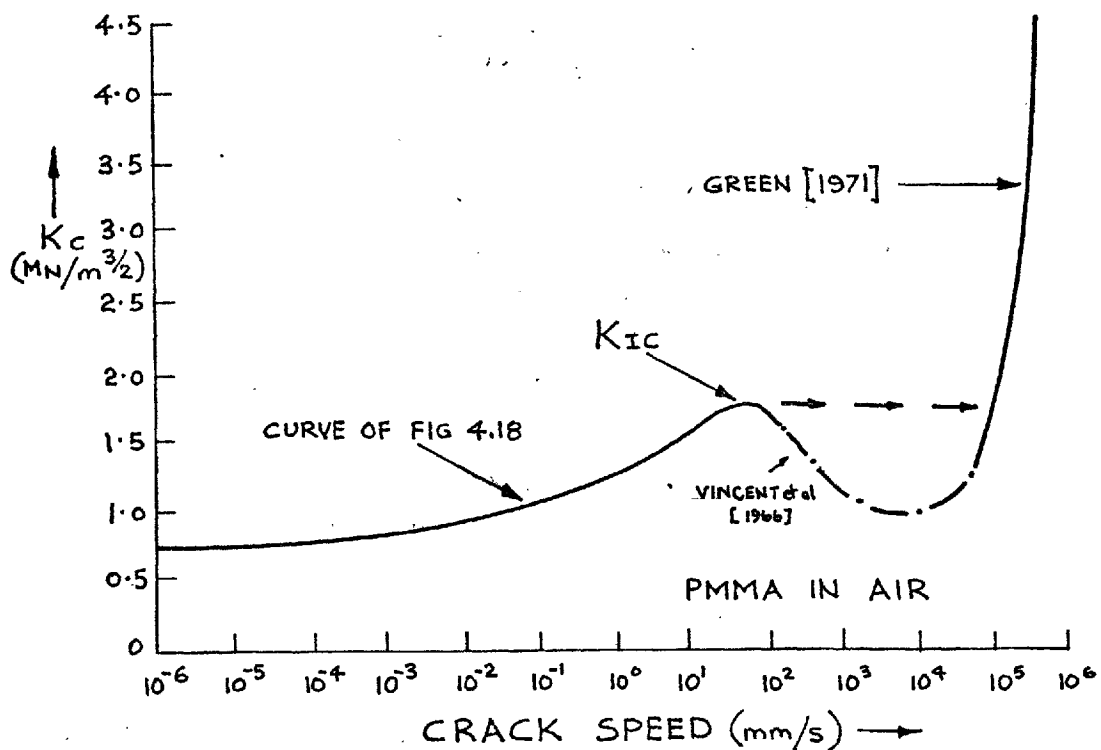


figure 4.20: Overall K_c vs. Crack Speed Curve - PMMA

* Private communication.

4.7.1 Viscoelastic effects

The K_c /crack speed curve for PMMA (figure 4.18) shows that the minimum extrapolated value of K_c for crack growth is $K_{CRIT} = 0.73 \text{ MN/m}^{3/2}$. Below this value, crack growth has not been observed in static loading tests on PMMA. Above this lower-bound value, the curve rises as shown until $K = K_{IC} \approx 1.70 \text{ MN/m}^{3/2}$ when there is the observed transition in crack speeds. It is proposed that the shape of the curve in between these values is a measure of the rate dependence of PMMA.

Although the material is often regarded as being one of the more 'elastic polymers', both the modulus and the yield stress are quite definitely time and rate dependent. Once a crack has started to propagate at $K > K_{CRIT}$ and as the crack speed increases, there is a corresponding increase in the modulus and yield stress of the material which is being strained at the tip of the crack. Thinking of the situation in terms of a critical strain criterion, the material has to be strained to the critical value for fracture, and the energy required to do this increases as the modulus of the material responds to the changing straining rate induced by the increasing crack speed. For a long time this rather glib and hypothetical explanation had to suffice, since there was difficulty in trying to predict the shape of the curve because the strain rate at the crack tip could not be assessed precisely.

WILLIAMS [1972] has recently overcome this problem and has derived an expression between the strain rate ($\dot{\epsilon}$) and the crack speed ($\dot{a}$) by examination of the strain distribution ahead of the crack tip. His expression is:

$$\dot{\epsilon} = \pi \epsilon^3 \{E(t)/K\}^2 \cdot \dot{a} \quad (4.4)$$

$E(t)$ being the time dependent modulus and ϵ the fracture strain.

Presuming the critical fracture strain (ϵ) to be the yield strain, he was able to develop equations to predict the strain energy release rate $G_c (\equiv \frac{2\gamma}{p})$

and the crack opening displacement (δ) in terms of the time dependent modulus.

By using measured values of the modulus obtained as a function of straining rate he predicted the shape of the K_c vs $\dot{a}$ curve of figure 4.13 in terms of G_c and δ , (using the conversion $K_c^2 = E(t) \cdot G_c$).

4.7.2 Thermal effects and instability

The continuing rise in the K_c vs $\dot{a}$ curve due to the increase in the time dependent material parameters will at some stage be counteracted by temperature effects at the crack tip. WILLIAMS [1965] proposed that the slow growth regime is essentially an isothermal condition, since the crack is moving sufficiently slowly for any heat generated at the crack tip to be dissipated. Plastics, however, have poor thermal conductivities and eventually at some critical speed a heat build up will start. If the crack speed is further increased, then so the thermal conditions will change from isothermal to adiabatic. As a consequence, the increase in temperature will cause the modulus and yield stress to fall; thereby counteracting the rise produced by the increased strain rate. Eventually, the consequences of increasing temperature will more than compensate for the strain rate effects and the K_c vs $\dot{a}$ curve will drop - as indicated by figure 4.20. In a later paper, WILLIAMS [1972] was able to show that a fall in the $K_c/\dot{a}$ curve at a velocity of $\sim 30 \text{ mm/s}$ was satisfactorily predicted by the thermal analysis.

The subsequent rise in the $K_c/\dot{a}$ curve at crack speeds $> 10^3 \text{ mm/s}$ is thought to be caused by the limitations of supplying energy to the crack tip. As the crack speed increases towards the velocity of the stress wave, extra energy is required to maintain crack propagation, and the curve once more starts to rise as shown.

The ramifications of high speed fracture are not pertinent to the present investigation and do not warrant further discussion here. For a more detailed discussion see GREEN [1971].

4.7.3 Complete K_c vs $\dot{a}$ curve

The complete K_c vs $\dot{a}$ curve of figure 4.20 is totally consistent with observations made in the present tests. The results of the slow growth regime have been found to agree with a viscoelastic analysis of crack growth, and the final instability occurring at 50 mm/s and $K_{IC} = 1.70 \text{ MN/m}^{3/2}$ is consistent with a thermal instability criterion.

The results of the SEN tests probably best illustrate what happens in a 'slow' loading situation in PMMA. The points of crack initiation were found to be strain rate dependent - as indeed would be expected from equation 4.2. Once the crack has started to grow, the crack speeds will be controlled by the K_c vs $\dot{a}$ curve and whatever the cross-head speed of the machine, the K_c value will be predetermined by the crack tip conditions - which will in turn be a function of the crack speed. Hence the crack runs according to the curve - eventually accelerating to 50 mm/s at $K = K_{IC}$ when the thermally induced transition in speed occurs. Having reached K_{IC} the curve falls, but in a test the load cannot be reduced quickly enough to accommodate this fall, and consequently the crack speed instantaneously increases to a value determined by the rising portion of the high speed K_c vs $\dot{a}$ curve, i.e. to approximately $2 \times 10^5 \text{ mm/s}$ - as found both here and by GREEN [1971].

The K_c -crack speed relationship thus explains the present results, but is it sufficient to account for the discrepancies encountered in the literature? A short comparative study is now given in the hope that the previous confusion can be finally explained.

4.8 COMPARISON OF RESULTS IN LITERATURE

A number of difficulties have to be overcome when attempting a comparison between the present results and those quoted in the literature. The biggest obstacle is that quoted results have usually been given in terms of the "Griffith" surface work, γ_p , and there are problems in assessing the appropriate modulus necessary for conversion of $\gamma_p \rightarrow K_c$ (or vice-versa) - via the relationship $K_c^2 = 2E\gamma_p$ (see page 26). In some cases the difficulty resolves itself, since many of the previous workers indirectly measured K_c in their tests when they obtained γ_p from the Griffith result viz:

$$\gamma_p = \frac{\pi \sigma_c^2 a}{2E}$$

i.e. They had to use E to obtain γ_p , and hence to find the corresponding K_c value it is only necessary to de-convert the result, using the quoted modulus. Where γ_p was measured directly by using experimental calibration techniques a modulus is needed and for present purposes K_c values have been obtained by using a modulus value appropriate to the crack speed at which γ_p was measured - via the results of WILLIAMS [1972]. If no speed was quoted, a value was assumed on the basis that the results at the quoted strain rates (which were all on cleavage specimens) would be close to the value of 10^{-3} mm/s obtained by BERRY [1963].

In all the above, care must be taken to ensure that the ' γ_p ' value quoted is really the surface work, and not the strain energy release rate G_c . The two are often confused since some forms of the Griffith equation omit the factor of 2 which accounts for the fact that two surfaces are produced at fracture - VINCENT and GOTHAM [1966] were the only culprits as far as PMMA was concerned.

Having taken these factors into account, a comparison of results is shown in tabular form in TABLE I (see page 62) and graphically on a K_c /crack speed basis in figure 4.21.

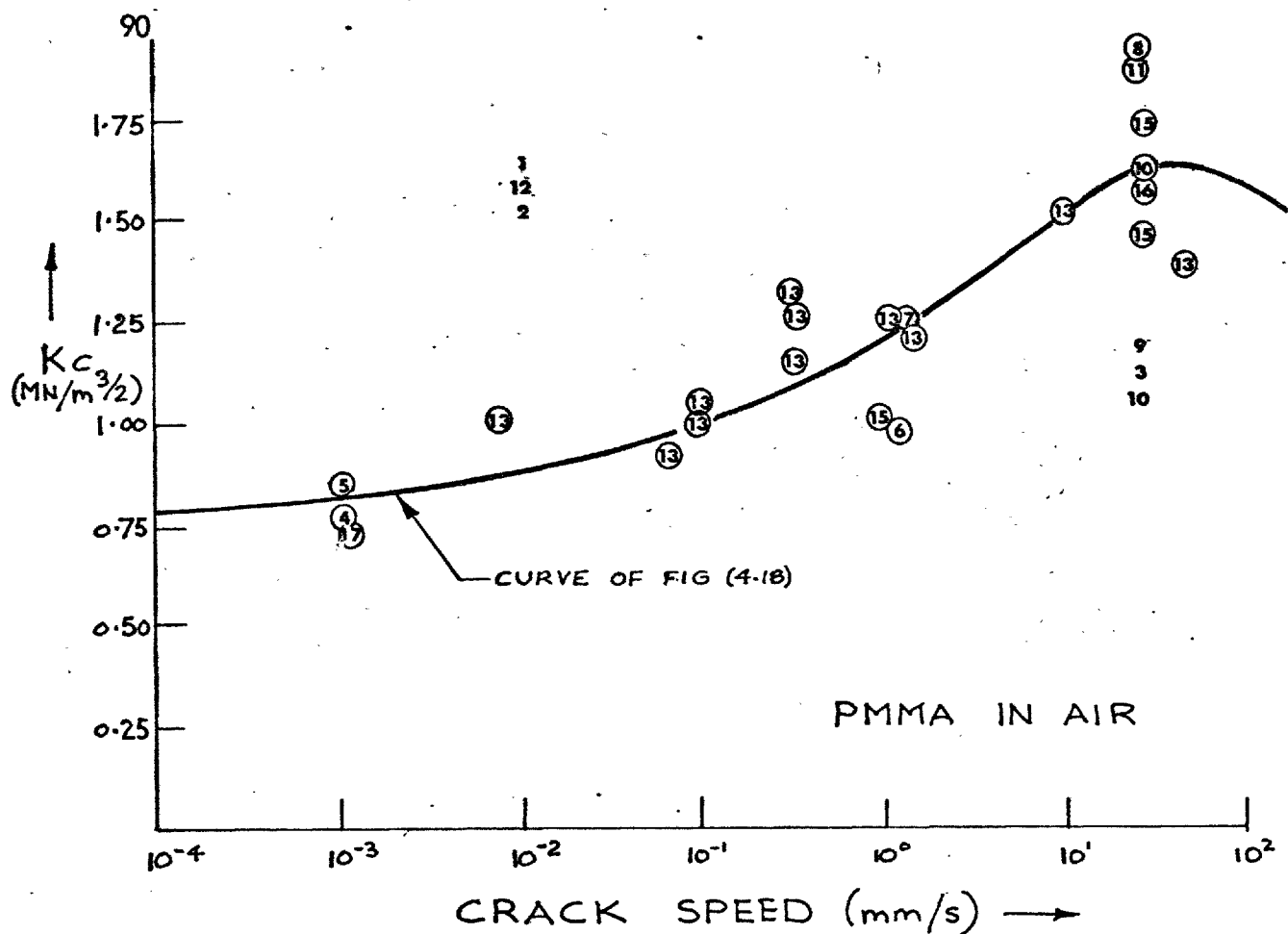


figure 4.21: Comparison of Quoted Results from Literature on $K_c/\dot{a}$ curve.

COMMENTS ON PREVIOUS RESULTS

(1) Instability

Nos. 3, 9, 10 - Ignored slow growth and their results would be correspondingly too low by a factor of $(a_f/a_0)^{1/2}$ where a_0 and a_f are the initial and final crack lengths.

Nos. 8, 11 - Doubtful notching techniques: 8 used a saw slit and 11 hammered in a 'sharp' crack with a screwdriver'. Both give blunt cracks and hence high $K_{(I)c}$ values.

(2) Slow Growth

Nos. 1, 2, 12 - Used compressive forces to control cracks in cleavage tests - unknown effect on the stress distribution - no experimental calibration.

No. 14 - Results quoted for crack initiation in rising load tests. They did not measure initiation stresses and hence results are too high by factor $\sigma_{instability}/\sigma_{initiation}$.

No. 6 - Authors quote 'updated' γ_p, K_c value in more recent paper shown on figure 4.21 as 7.

Circled numbers refer to references of TABLE I.

4.8.1 Experimental factors

It can now be seen that although there would appear to be wide disparity between the results in the literature when they are quoted as universal constants, they show a high degree of consistency when plotted on a K_{IC} vs $\dot{a}$ basis. Those results which are totally inconsistent are often explicable by reason of dubious experimentation and/or analysis of the results (- as indicated in the footnotes below figure 4.21) and they are shown as the uncircled points - their relevance being in some doubt.

The major errors in experimentation have arisen largely because various critical parameters were either ignored or not measured. For instance, BERRY [1961] used SEN specimens to measure γ_p (really K_{IC}) at crack instability and when evaluating his results he based K_{IC} on the original crack length (a_1). At instability the crack can have grown a considerable distance and so his results would be expected to be too low by a factor of $\{a_f/a_o\}^{\frac{1}{2}}$. If the K_{IC} values from the present series had been calculated in this way they would give exactly the same values as obtained by Berry. Similarly WILLIAMS et al. [1968] ignored the critical stress for crack initiation and their results would be too low by the factor $\sigma_{INSTABILITY}/\sigma_{INITIATION}$. Again, the present results would produce exactly the same numbers as those of Williams if the initiation stress was ignored. Both these errors are due to doubtful test procedure and the quoted results are really meaningless since they do not reflect any measure of a material property.

The offset slow growth results of SVENSSON [1962] and BENBOW et al. [1957, 1962] are more difficult to judge, since they used a cleavage system with compressive forces to control the cracks. The effects of the interactions of the compressive and crack tip stress fields are difficult to assess. Qualitatively, the results remain as anomalies although superficially it would appear that the testing method/analysis was at fault.

The remainder of the results are in close agreement with the present work and are sufficiently close as to confirm that crack speed variations are responsible for the observed differences in K_c and γ_p .

4.9 CLOSURE ON PMMA IN AIR

The K_{Ic} vs crack speed curve for PMMA in air has been shown to account for most of the variations in toughness values which are quoted in the literature. As such it is felt that the use of fracture mechanics to interpret the fracture data in this material has been completely vindicated.

The results from the present tests correlate well with a visco-elastic analysis and the observed variations of K_{Ic} with crack speed can be accounted for in terms of the time dependent properties of the material.

Also, the curve provides a rational basis for the comparison of fracture toughness data since if two materials are to be compared their single point values are essentially meaningless without the allied crack speeds. Results using different specimen geometries can also be effectively compared on a $K_{Ic}/\dot{a}$ basis since it should always be possible to measure crack speeds in a given cracking situation.

As a further exercise in analysing data in this way, it was felt that a study of the fracture of polystyrene would provide a more severe test of the fracture mechanics approach since the quoted results for this material show even more variations than those for PMMA. A report of the work on polystyrene follows - in Chapter 5.

TABLE II. Quoted 'Fracture Toughness' Values for Polystyrene.

Author(s)	Test Method	Crack Speed	γ_p	$K_{(I)c}$
		'Slow'/'Fast'	$\times 10^2$ Joules/m ²	MN/m ^{3/2}
BENBOW ('61') (1)		'Fast'	3.0	1.37
BENBOW ('61') (2)		'Slow'	19.0	3.45
BENBOW & ROESLER ('56')		'Fast'	25.5	3.95
BERRY ('62')		'Fast'	17.0	3.24
BERRY ('63')		'Slow'	7.1	2.09
van den BOOGAART & TURNER ('63')		'Fast'	5.5	1.8
BROUTMAN & Mc. GARRY ('65')		'Slow'	4.4	1.66
KEY, KATZ & PARKER ('69')		'Fast'	4.43	1.68
SVENNSON ('61') (1)		'Fast'	9.8	2.45
SVENNSON ('61') (2)		'Slow'	34.0	4.55
van den BOOGAART ('66')		'Slow'	6.5	1.99
TATTERSALL & TAPPIN ('66)		'Fast'	10.0	2.48
MURRAY & HULL ('71)		'Fast'	2.3-2.9	1.1-1.35

CHAPTER 5. FRACTURE OF POLYSTYRENE IN AIR AT 293°K

5.1 INTRODUCTION

'Crystal' polystyrene ("crystal-clear" as opposed to crystalline) is one of the most important thermoplastics and is widely used in many commercial applications. Although its optical properties are poorer than those of PMMA for example, it is a much cheaper plastic and is easier to process since it has good 'flow' characteristics (which make it suitable for injection moulding); it also has good dimensional stability and is easily pigmented.

Unfortunately, polystyrene has poor resistance to fracture in practice and components often craze and crack at very low stresses. Impact tests for example give strengths for polystyrene which are only half of those for PMMA.

Paradoxically, however, conventional notched tensile tests show entirely the reverse situation, since previous workers always quote 'strengths' (surface work values) for polystyrene which are often orders of magnitude greater than those for PMMA. The material has been studied with the same fervour as that lavished on PMMA but with somewhat less success - a summary of previous "estimations" of γ_p is shown as TABLE II.

The values of γ_p shown in TABLE II illustrate the almost total confusion, since not only are the values much greater than those for PMMA, but also they are exceedingly erratic - reproducibility of results being rather a weak point. The total inconsistency of this data and the erroneous predictions for practical strengths cast great doubts on the applicability of the Griffith criterion to plastics.

Although differences in material grade and molecular weight undoubtably account for some of the discrepancy they cannot provide a complete explanation for the observed variations in γ_p . BERRY [1964] pursued the molecular weight argument

in some depth - using PMMA as a 'model' material - and found that a change in M_v from 3×10^6 to 3×10^5 only produced a change in γ_p from 1.56 to 1.14×10^2 Joules/m². He also thought that the specimen configuration could have affected the result (an exceedingly dubious fracture mechanics argument!) and changed from using tensile to using cleavage specimens. Although he obtained a lower γ_p value (7.17×10^2 Joules/m²) the ratio of γ_p polystyrene $\approx 5\gamma_p$ PMMA was still maintained (for same geometries).

In almost all the tests on polystyrene it had been noted that the cracks which were induced and then grown to cause fracture were somehow different from those in PMMA. It was generally found that the crack tip in polystyrene is more 'diffuse' (to quote BERRY [1961b]) than in PMMA, because crazing "cracks" surround and obscure the main crack. Although no cogent argument was forthcoming as to the mechanism by which these crazes (then thought to be cracks) affected the results, it was generally held that their presence was somehow connected with the differences in the results - possibly by a mutual interference of stress fields, BERRY [1961b]. Since it is now known that crazes are not true cracks but are instead localized regions of plastically deformed material, a mechanism of toughening caused by the creation of a huge energy 'sink' at the crack tip is not hard to visualize and represents a viable argument for explaining the observed toughening effect.

The mechanism whereby the crazing occurs in the first place has, to date, remained unexplored; the presence of the crazes have instead been accepted as an unfortunate 'fact of life'. In practice, polystyrene fails at low stresses and the cracks which grow to failure are not thought to be accompanied by a large volume of crazing at the tips. Indeed, on the contrary, MURRAY and HULL [1970c] have shown conclusively that it is void coalescence within a craze which is often the cause of crack growth since crazes usually exist in a material as weak points in the structure.

At the start of the present project, it was felt that insufficient attention had been paid to the importance of the crack-tip crazing and that a study of velocity effects (as with PMMA) might go some way towards reducing the confusion which is apparent in TABLE II. BROUTMAN and McGARRY [1965], had made measurements from fracture surfaces in polystyrene which served to show that the amount of crazing was a function of crack velocity, there being much less crazing at high crack speeds.

Since the tapered cleavage specimen had proved to be successful with PMMA in maintaining stable running cracks, a preliminary series of tests using this specimen was made - using different loading conditions as before.

5.2 EXPERIMENTAL

The material which was used in all the tests was a compression moulded, general purpose grade of polystyrene having a viscosity average molecular weight of approximately 200,000.

5.2.1 Tapered cleavage tests - I

The notching technique used was exactly as before with PMMA, the crack being 'induced' to grow from a pre-weakened section by pre-loading the specimens. As expected, this technique produced cracks which were ill-defined and had large 'bunches' of crazes surrounding the main crack.

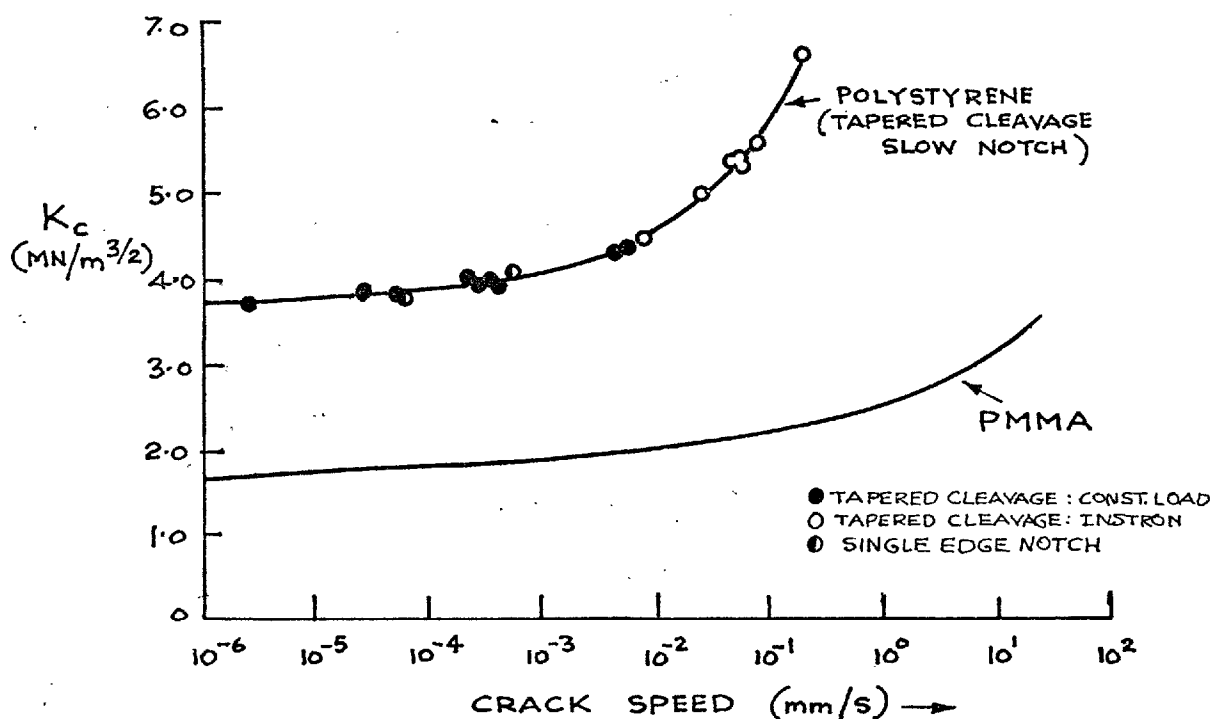


figure 5.1: K_c vs Crack Speed - PS - Highly Crazed Specimens

Tests on both the Instron and constant load machines showed that it was possible to grow this crack/craze system in a stable manner and a K_c versus crack speed was obtained - this is shown as figure 5.1. The corresponding curve for PMMA is shown on the same figure, and it can be seen that over the whole slow growth regime the highly crazed polystyrene gives much higher toughness values.

A sub series of SEN specimens pre-notched by forcing a wedge into a saw slit also gave the same type of result - see figure 5.1. On face value, it would therefore appear that crack velocity is totally unconnected with the crazing process in polystyrene. However, some of the tests which had been conducted on the constant load machines at the lowest K_{Ic} values had produced occasional fast fracture failures. This was seen to be caused by one of the crazes propagating ahead of the bunch (on a random basis), the crack eventually growing preferentially through this craze to cause unstable failure. Having grown ahead of the main craze bunch it would seem that the crack does not reproduce the macroscopic crazing at the tip but instead propagates through only localized regions of crazing - hence requiring less energy for propagation. (As found by BENBOW[1961] who noted that γ_p for 'fast' fracture $< \gamma_p$ -slow growth.)

On this basis it seemed likely that the large volume of crazing was purely an artefact of the notching technique and was not some intrinsic material property. Other methods of producing initial cracks were therefore examined.

5.3 NOTCHING METHODS

The cleavage test is unsuitable for an investigation of this nature and hence SEN specimens were used for all preliminary tests. Cracks were produced in three ways:-

- (i) A razor blade was forced slowly into the edge of a specimen using the Vickers jig attachment (see figure 4.4) - called Slow Razor Notches.
- (ii) A razor blade, mounted in a shaped weight was dropped on to the specimen edge using a small guillotine device - called Impact Razor Notches.
- (iii) Notches were inserted under various fatigue loading conditions - called Fatigued Notches.

5.3.1 Slow razor notching

This method is that previously used on PMMA to give 'natural' sharp cracks with only minute amounts of crazing. In polystyrene it gave less craze bunching than for wedge notching, but the cluster was still considerable.

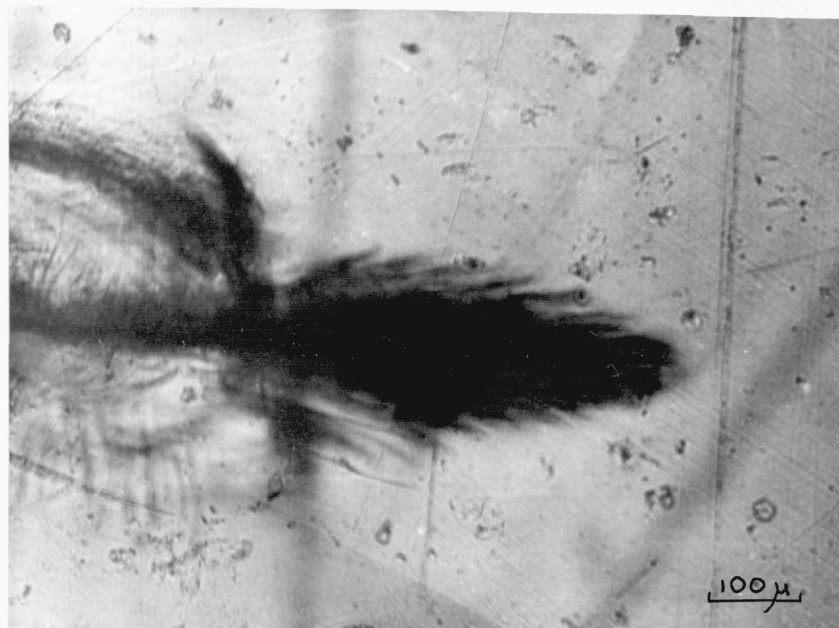


figure 5.2: Crack Tip Geometry - Razor Notching

Tests at 0.05 cm/min and 0.5 cm/min gave very rough fracture surfaces with considerable amounts of crack division (see fig 5.11 page 110) such features again being a consequence of craze bunches. In this situation, so much energy has been put into the specimen in propagating the craze bunch, that when the crack finally grows through one of the crazes the system finds itself with more than enough energy to propagate one crack. The excess energy is dissipated in many forms - heat, sound, etc. - but the most obvious sign is the propagation of additional cracks and hence the shatter type of failure.

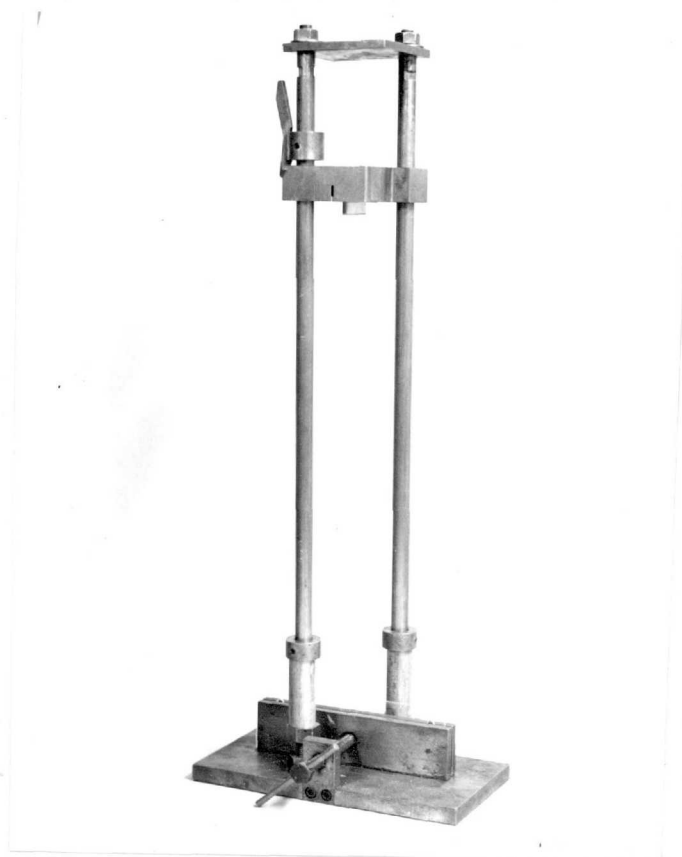


figure 5.3: Impact Notching Equipment



figure 5.4: Crazing Induced by Impact Notching

The K_{Ic} value at 0.5 cm/min was $1.87 \text{ MN/m}^{3/2}$ (with scatter of $\pm 12\%$).

This value is considerably below that obtained for wedge notched specimens which gave $K_{Ic} = 2.43 \text{ MN/m}^{3/2}$ at the same test speed. So, by reducing the volume of craze bunching the K_{Ic} value was reduced by 23%.

5.3.2 Impact notching

Notching with the special guillotine device (figure 5.3) had the great advantage of producing initial cracks which ran ahead of the razor blade and hence the condition of the inserted flaw was more consistent. Again craze clusters were present, though on a very much smaller scale than previously noticed - a typical example of an impact notch being shown as figure 5.4. A preliminary batch of specimens, tested at 0.5 cm/min gave a K_{Ic} value of $1.32 \text{ MN/m}^{3/2}$ with a scatter of $\pm 8\%$.

At the time of testing such values were deemed to be a more reasonable representation of the "true" behaviour of polystyrene and a full scale test series was carried out using impact notched specimens. Batches of twenty specimens containing cracks in the range $2 \text{ mm} \rightarrow 13 \text{ mm}$ were tested at every cross-head rate possible on the Instron machine. Each series contained three thickness ($1.5, 3.0, 6.0 \text{ mm}$) of specimens and two special series were tested at 0.5 cm/min to assess the effects of annealing specimens (both before and after notching).

When under load, the craze bunch starts to grow at some critical value of K , these values of K being plotted against cross-head rate in figure 5.5. The bunch continues to propagate until eventually instability occurs, by craze failure. In these tests the fractures in all cases resulted from the propagation of single cracks, there being no macroscopic signs of bifurcation. Figure 5.5 also shows the values of at instability as a function of cross-head rate. The corresponding results from similar tests on PMMA are superimposed in the same figure.

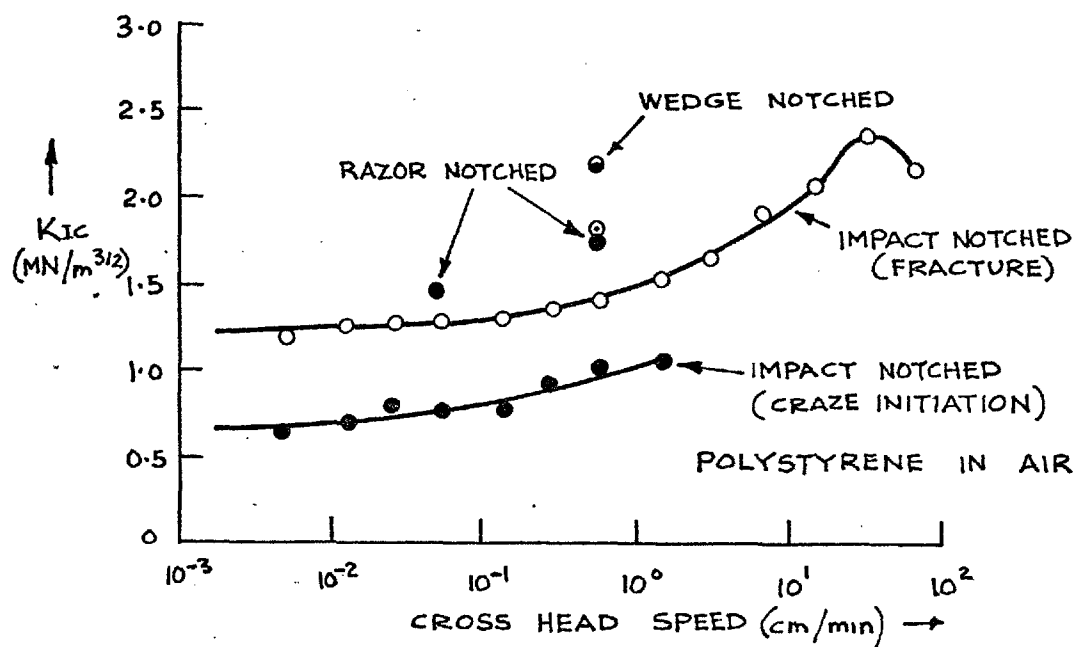


figure 5.5: Effect of Straining Rate on K_{IC} values - PS - Impact Notching

Figure 5.5 clearly shows that the impact notched specimens have much less crazing associated with the crack, since the K_{IC} values have again fallen - by a factor of 30%. Comparison with PMMA reveals that for cross-head rates below 5.0 cm/min , the K_{IC} values are less for polystyrene and hence the material's resistance to fracture is lower - as found in practice. The disturbing feature, however, is that the polystyrene results show a strong dependence on cross-head rate, whereas the PMMA values are essentially constant.

(a) Fracture surfaces: impact notched

A photograph of a fracture surface in the crack tip region is shown in figure 5.6. Several prominent features are indicated in the figure and correspond to:

- | | |
|------------------------|-----------------------------|
| A. Initial crack front | B. Initial craze front |
| C. Final craze front | D. "Fast" fracture surface. |

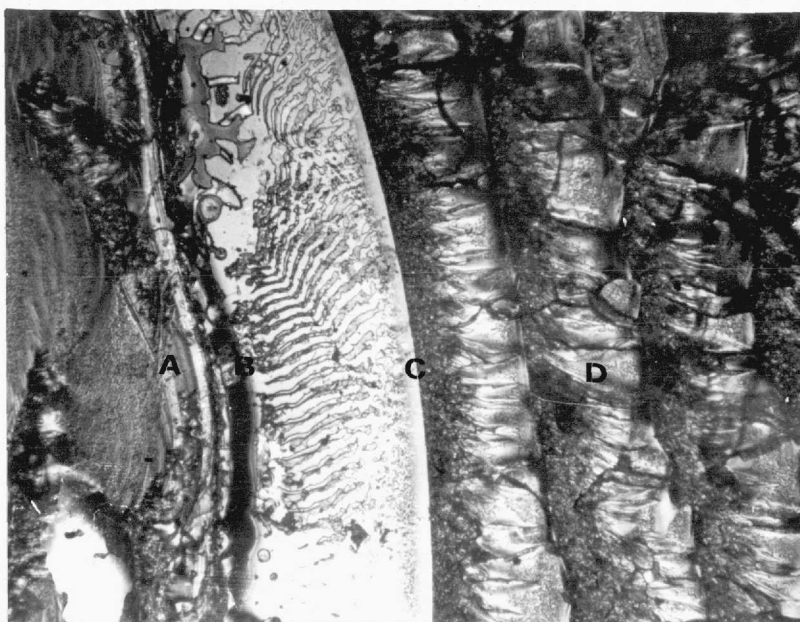


figure 5.6: Fracture Surface of Impact Notched Specimen

This type of fracture surface - from a pre-notched specimen - is commonly observed in polystyrene and HULL [1970] has provided a detailed description of the various micro-fracture processes which are involved in producing the various features. He proposed that the features produced in region BC are caused by irregular fracture within the craze in the manner shown schematically in figure 5.7.

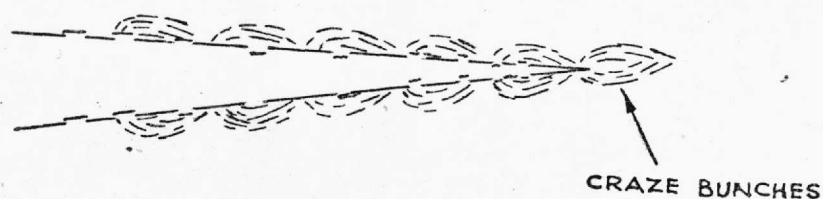


figure 5.7: Mode of Fast Fracture in Polystyrene - HULL[1970]

The crack propagates in a non-uniform manner fracturing along the craze matrix interfaces, thereby leaving the "islands" of material seen on the fracture surface. The banded structure which is shown in the fast fracture region is presumed by Hull to be caused by a stick-slip form of crack propagation. (The irregular nature of the surface is shown to good advantage in the photograph of figure 5.6.) He postulated that at the onset of fast fracture, the crack starts to propagate at high speed along one of the crazes at the crack tip. The propagation through the craze allows local stress relaxation and the crack slows down slightly thus allowing a new craze bunch to form at the crack tip. Whilst this bunch is forming, the energy build-up starts once more until eventually the crack starts to move through the new craze at high speed.

5.3.3 Fatigue notching

Early attempts at notching in fatigue by cycling in a conventional testing machine at approximately 2 Hz had shown little improvement over impact notching since crazed cracks were still produced. However, whilst drilling an improperly clamped plate specimen of polystyrene, it was noticed that cracks were slowly growing through the section. These cracks eventually caused total disintegration of the specimen, the fracture surface being mirror smooth as in PMMA - (see figure 4.8). Close inspection of the part through cracks revealed no sign of craze bunching - a situation on which much effort had been expended for a notching procedure! It was suspected that these "pure" cracks had been produced by high frequency vibrations and pilot fatigue tests on impact notched specimens at frequencies greater than 30 Hz showed that such mirror-smooth cracks could be induced in a controlled manner. For frequencies less than 30 Hz , craze bunching still occurred.

In order to produce such cracks on a large number of specimens, a high frequency electro-magnetic oscillator was adapted to accommodate a straining frame in which to hold the specimens; a half-wave rectifier being incorporated to ensure only tensile loading. Using this apparatus, mirror-cracks were induced from both razor and impact notches at a frequency of 30 Hz . At such a frequency, the crack motion was somewhat uneven and the crack front often irregular. In order to rectify this situation the frequency was increased to 300 Hz , when slow, steady crack growth ensued, the front being completely uniform. A load cell and oscilloscope which had been fitted to the apparatus indicated that typical K_{Ic} values for crack growth at such frequencies were in the range of $0.45 \rightarrow 0.55\text{ MN/m}^{3/2}$. Microscopic examination of the cracks produced in this way, showed that although a small single craze was discernible at the crack tip, there was no sign of any craze bunching. A photograph of such a craze is shown as figure 5.8 and it is to be compared with a similar craze at the tip of a "natural" crack in PMMA (figure 4.5).

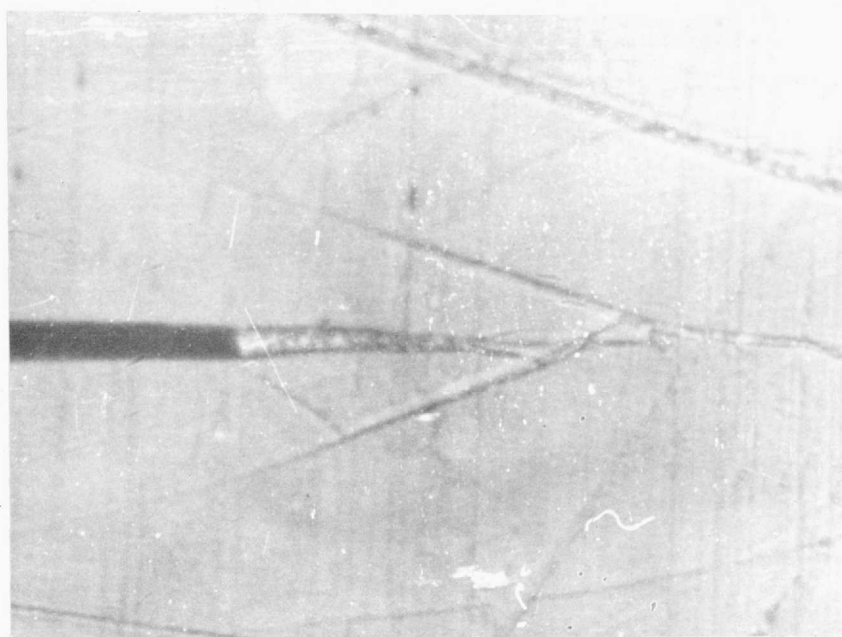


figure 5.8: Crack Tip - Fatigue Notched Specimen

It can be seen that the polystyrene craze is considerably longer than the craze in PMMA, the relative lengths being 40μ for polystyrene and 6.3μ for PMMA.

The fatigued notch, without the craze bundle, is obviously most realistic for testing to find a lower-limit K_c for crack propagation, and consequently both SEN and tapered cleavage specimens were notched using the vibrator - and then tested as before.

5.4 EXPERIMENTAL - FATIGUE NOTCHED SPECIMENS

5.4.1 Tapered cleavage tests - II

All tests using these specimens were conducted on the dead weight loading apparatus. When load was applied to a typical specimen, the mirror-smooth initial crack continued to propagate - providing a critical value of K had been exceeded. In some tests however, cracks started to wander out of the side slots (as in PMMA) due to irregularities in loading. In these cases the mirror surface became "pock-marked" by very fine craze bunches. These effects were particularly noticeable at the edges of the side grooves. The appearance of these crazes caused the crack growth rate to slow down and such tests had to be discarded. The ease with which crazing can take place illustrates the care which has to be taken when testing polystyrene; the "pure" crack is obviously very sensitive to loading conditions and it is necessary to maintain correct alignments in the loading system. The majority of the tests however, produced excellent crack growth histories, the crack speed being constant for any given load.

From the results of the constant load tests, including a series where the crack growth was filmed, a curve of K_c versus crack speed was obtained and is

shown as figure 5.9. The corresponding curve for PMMA (figure 4.18) is shown superimposed in the same graph.

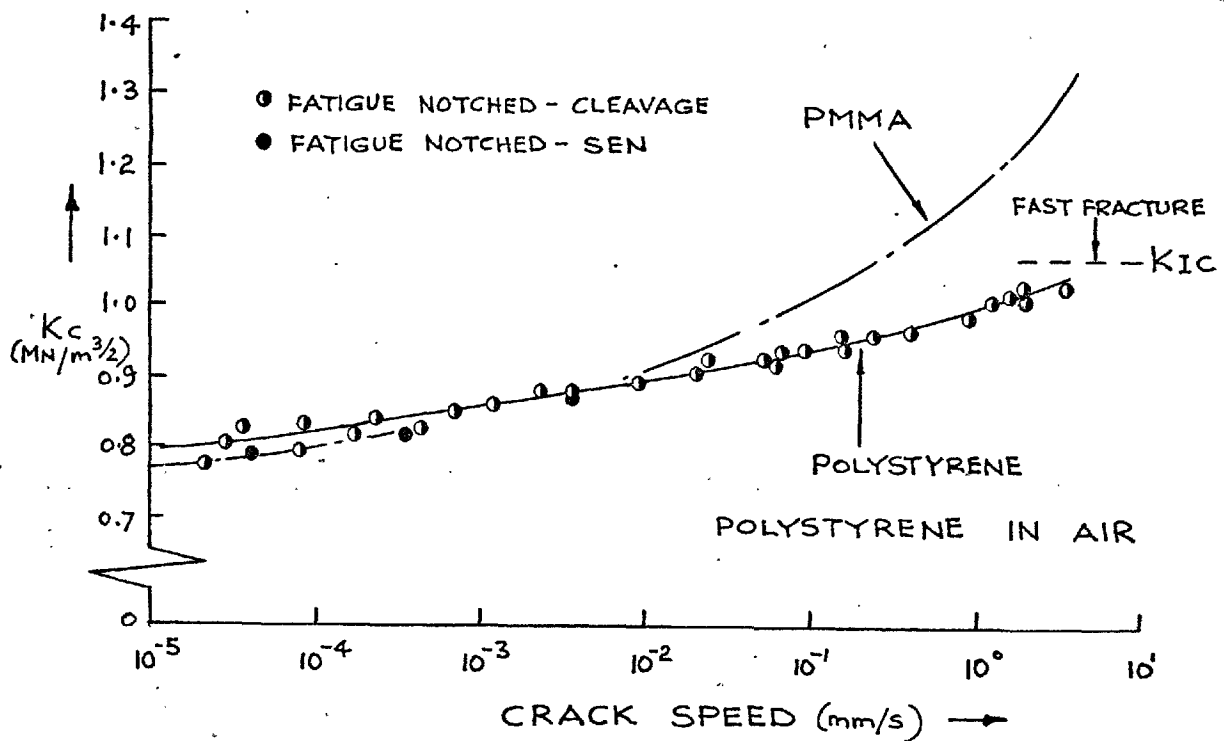


figure 5.9: K_c vs Crack Speed - PS - Fatigue Notched Specimens

It can be seen that the crack initiation value of $K_{critical} = 0.78 \text{ MN/m}^{3/2}$ is nearly equal for both materials. Indeed the two materials have almost identical growth characteristics for the slower crack speeds. As the growth rate increases, the curves increasingly diverge, the polystyrene crack becoming unstable at $K_{Ic} = 1.05 \rightarrow 1.10 \text{ MN/m}^{3/2}$ and PMMA at $1.68 \text{ MN/m}^{3/2}$. (The instability values for polystyrene were obtained by loading cleavage specimens continuously on the dead-weight loading rigs until fast fracture occurred.) As a check on these values - obtained using the cleavage specimens - a large number of SEN specimens were tested over a wide range of cross-head rates on the Instron.

5.4.2 SEN tests - fatigued notched specimens

The specimens used were of 1.5 mm and 3 mm thickness and had induced notches in the range $2.0\text{ mm} \rightarrow 20\text{ mm}$, the specimen width again being 50 mm .

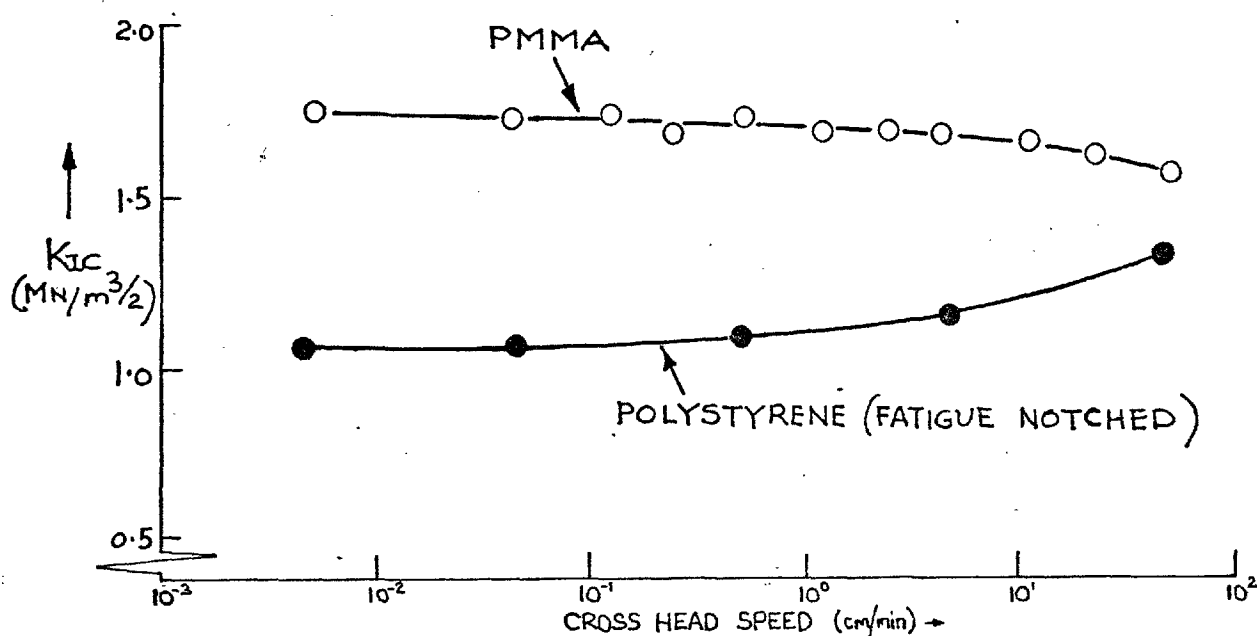


figure 5.10: Effect of Straining Rate on K_{Ic} Values - PS - Fatigue Notching

The K_{Ic} values at final fracture are shown plotted versus cross-head speed in figure 5.10. For values of cross-head speed below 0.5 cm/min there was a negligible dependence of K_{Ic} on testing rate, thickness effects being absent also - again the plastic zone size is very small compared with the specimen thickness and hence plane strain non-thickness dependent results would be expected. The fractures were all caused by single cracks with no sign of macroscopic crazing - a photograph of a typical fracture is shown in figure 5.11. The fracture is compared with previous fractures in razor and impact notched specimens in the same figure.



figure 5.11: Types of Fracture - SEN Specimens

- (a) Razor Notched
- (b) Impact Notched
- (c) Fatigue Notched

At the 50 cm/min cross-head speed however, K_{Ic} increased from $1.1 \text{ MN/m}^{3/2}$ to $1.37 \text{ MN/m}^{3/2}$. At this rate of testing, the loading was somewhat uneven, the specimen being subjected to a form of shock loading. It is suspected that this uneven loading produced small amounts of craze bunching at the crack tip (as in those cleavage tests which also had irregular loading), and hence excess energy was absorbed at the crack tip. This "bunching" thesis is further supported by the fact that in these tests, the fast fracture surfaces were much more irregular.

However, comparison of the fatigue crack results with the data obtained with other notching methods (figure 5.5), indicates that once more the values have fallen. The lower limit instability value of $K_{Ic} = 1.09 \text{ MN/m}^{3/2}$ obtained in the SEN tests is entirely consistent with the range of values

$K_{IC} = 1.05 \rightarrow 1.10 \text{ MN/m}^{3/2}$ obtained in the cleavage tests. These results at instability are an order of magnitude lower than the γ_p values obtained previously by BERRY [1961(b)] on polystyrene. A further check on the mutual consistency of values between the cleavage and SEN testing systems was made by invoking an analysis of IRWIN [1964] (see paper 2, MARSHALL et al. [1970] - in back cover) to calculate an "apparent" crack speed using the crack initiation values obtained on the Instron. The solution is:-

$$\dot{a} = \frac{1}{2\sqrt{2} \pi t^*} \left\{ \frac{K_c}{\sigma_y} \right\}^2$$

where t^* is the testing time to the onset of failure.

The results for the SEN tests are shown plotted in figure 5.9 and are seen to be in excellent agreement with the measured crack speed curve.

5.4.3 Fracture surfaces - fatigue notched specimens

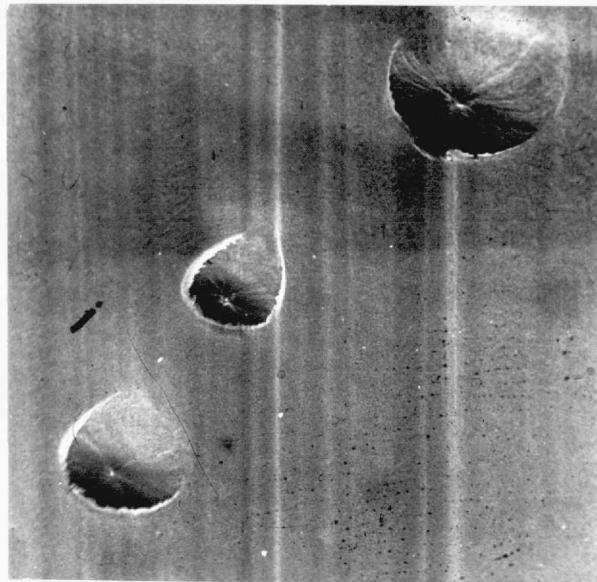


figure 5.12: Markings on 'Mirror' Fracture Surface

The mirror-smooth surfaces produced by high frequency fatigue notching exhibit many of the features normally seen when a crack has propagated through the centre of the crack tip craze. The colours produced by the oriented craze layers were evident on both fracture surfaces. Small surface features were evident all over the fracture surfaces - of both the initial cracks and those propagated under constant load. A stereoscan "close-up" of a region containing such markings is shown in figure 5.12.

Again, this type of surface has been described by MURRAY and HULL [1970c]. They postulated that the small secondary features are caused by cavitation within the craze - in the manner shown in the schematic diagram, figure 5.13. Such an explanation would seem to adequately explain the observed features in the present case - the essential features being that the crack grows via void coalescence through the middle of a single craze.

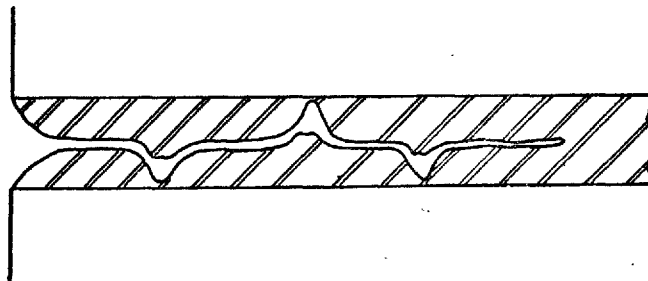


figure 5.13: Crack propagation through centre of a craze - MURRAY & HULL [1970d] .

More details on the various types of features which can be seen on fracture surfaces in polystyrene are discussed in many of Hull's paper and also by BIRD et al. [1971] .

5.5 DISCUSSION OF RESULTS

The results which have been presented in this chapter have illustrated (at some length) that polystyrene is not as inherently 'tough' as previous experiments would suggest. The lower bound K_c /crack speed curve which has been achieved by using the fatigued initial cracks is thought to represent the 'true' nature of the lower-limit fracture condition in polystyrene. The results are self consistent since it has been shown that different geometries and loading conditions produce the same numbers for K_c - as 'demanded' by the fracture mechanics theory.

5.5.1 Validity of results

In the preceding sections, it has been implicitly assumed that the notches which are produced by the high frequency fatigue method used are in fact comparable to those which occur in the material under service conditions. The results of figure 5.9 show that cracks generated in this way start to grow at the same loading level as those in PMMA and that instability occurs at $K_{Ic} \approx 2/3 K_{Ic} \text{ PMMA}$. There is no comparable practical situation against which to check the initiation value - since this is the first time such low K values have been produced for polystyrene - but the instability ratio between polystyrene and PMMA compares well with the ratio of relative material performances under impact loading conditions. In an attempt to check on the lower-limit K_c value, a number of specimens containing small razor notches were left under constant loads at $K \sim 0.78 \text{ MN/m}^{3/2}$ to see if 'mirror' cracks could be induced by some form of void coalescence process. In all cases the specimens eventually fractured - although similar tests loaded to give $K_{INITIAL} = 0.65 \text{ MN/m}^{3/2}$ did not. (This method is not to be recommended as a notching technique since in most cases the re-initiation process lasted for

a number of days.) From these two pieces of indirect evidence it would seem that the results are indeed valid and that the K_{IC} /crack speed of figure 5.9 represents the minimum fracture toughness condition for failure in air.

The reasons for the production of 'pure' cracks by the fatigue notching technique is still open to speculation. The processes at work in the fatigue situation are numerous, but it does not seem likely that localised temperature rises would play a large part in enhancing the propensity for causing low-energy cracking. In the case of a polystyrene specimen with a 'bunch' of crazes at the crack tip, such localised heating would be greatest at the central section of the crack/craze system due to the higher stress concentration. The heating would cause preferential craze growth along this plane and the central craze would grow more quickly than the rest. Because of the cyclic loading, unstable failure would not occur and the craze would continue to grow until eventually a crack would be started within the craze, due to void coalescence. Such a crack/craze system would then have a low energy requirement for propagation and if the loading were maintained this apparently 'pure' crack would grow clear of the original craze bunch.

The only evidence which is available to support the localised heating argument is that when testing tapered cleavage specimens with highly crazed notches at temperatures greater than 310°K, mirror cracks could be produced and at high temperature these cracks grow at low K levels - as in the present tests. (The use of higher macroscopic temperature to pre-notch has not yet proved to be successful for more temperature testing, however, since higher K_{IC} values are produced - probably due to a blunting effect induced by the gross temperature rise - a finding which endorses CESSNA et al.'s [1965] results on high temperature notching in PMMA.)

5.5.2 Comparison of results

A summary of the values obtained by previous investigations for the 'surface energy' of polystyrene is shown as TABLE II. Since no rate dependent modulus is available, as yet, the results have been converted to K values by either de-converting the γ 's using quoted values of E or by using a 'standard' modulus, $E = 3.1 \times 10^3 \text{ MN/m}^{3/2}$. The errors involved in this procedure will be negligible for polystyrene since most of the numbers shown are rendered irrelevant by virtue of the use of specimens containing highly crazed initial cracks. Although differences in molecular weight can be critical with polystyrene, the huge discrepancy between the quoted numbers is thought to be largely due to variations in pre-notching and other testing variables. The K_{Ic} values obtained with the fatigued notches in the present investigation are in some cases lower than the quoted values by a factor of 10. The results of MURRAY and HULL [1971] (published after completion of the present work) are the nearest equivalents to the K_{Ic} values obtained here. They used a wedge notching technique to induce their cracks and although they had a large craze at the crack tip (300μ cf. 40μ here) the K_{Ic} values are similar to those obtained with fatigued notches. That they were able to obtain single-craze cracks by wedge notching would seem to indicate that there is a considerable difference between the two materials used in our respective tests. It is interesting to note that Murray et al. found that their notching technique only worked with a polystyrene containing a mineral oil lubricant (incorporated to improve the processability of the material). This coupled with their low K_{Ic} values with large craze cracks suggest that there is a possibility of the lubricant oil being a stress cracking agent which thereby promotes cracking. A small amount of oil is known to be incorporated in the material used in the present tests but the type/grade is unknown. The effects of mineral oil lubricants on the fracture toughness of unadulterated polystyrene obviously require further study.

5.5.3 Craze stress

One of the most important factors which must be considered in a discussion of the speed effects on K_{Ic} is the effect which an increasing speed has on the yield stress and modulus of the crazed material. It is strongly suspected that the increase in K_{Ic} due to the increase in speed is explicable in terms of the modulus and yield stress increases - as is the case for PMMA - WILLIAMS [1972]. Certainly the very flat shape of the K_{Ic} /crack speed curve is consistent with known evidence that the modulus and yield stress are very much less rate dependent in polystyrene than in PMMA. Sufficient data is, as yet, not available from creep tests to be able to predict the nature of the crack speed results, but the argument can be partially evaluated by making use of the Dugdale model for plastic zones at crack tips (see p. 28). Unfortunately no measured values of craze lengths ahead of propagating fatigued notches are available, but other measurements made on the impact notched results may be used. Using these results at both craze initiation and final fracture gives a general idea as to:-

- a) the applicability of Dugdale's solution to a craze system and
- b) the relevance of the stress so calculated as the fracture pattern, in that a strong dependence of K_{Ic} on straining rate was observed in these tests (see figure 5.5). The appropriate analysis is made by using the equilibrium equation derived from Dugdale's model as follows:-

The craze length, X , is given by equation 2.11.

$$\text{i.e.} \quad \frac{a_o}{a_o + X} = \cos \left\{ \frac{\pi}{2} \frac{\sigma}{\sigma_c} \right\}$$

where a_o is the crack length, σ is the applied stress and σ_c the stress carried by the craze.

For $\sigma \ll \sigma_c$ we have:-

$$X = \frac{\pi}{8} \frac{a_f}{a_o} \cdot \frac{K_{Ic}^2}{\sigma_c^2} \quad (5.1)$$

where a_f is the crack plus craze length (i.e. $a_o + X$).

This equation can be applied at either craze initiation or final fracture as all the lengths can be measured from the fracture surfaces (see figure 5.6) and all loads were monitored constantly.

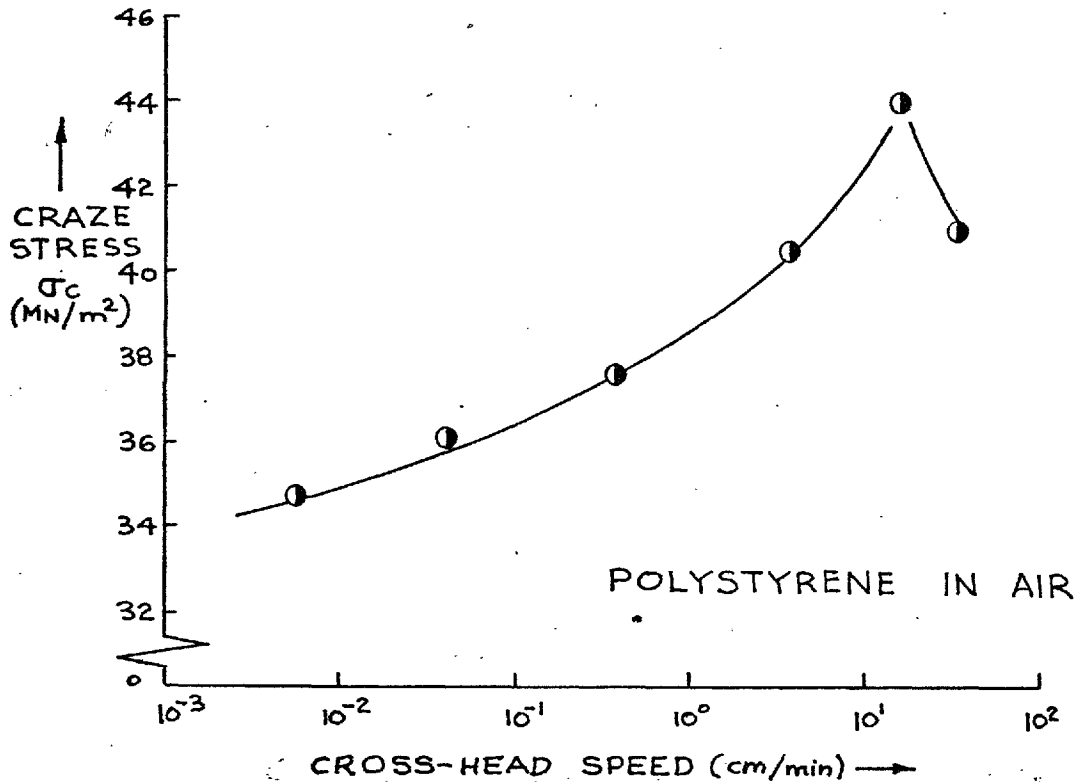


figure 5.14: Effect of Straining Rate on Craze Stress

Using equation 5.1 it was found that a value for σ_c could be calculated for each specimen at each cross-head rate, scatter on results being of the order $\pm 10\%$ - a reasonable figure for such an analysis. The values of σ_c at initiation and final fracture were very similar on all specimens (at any given cross-head speed) thus indicating that there had only been small changes in craze structure during the growth period. The average values of σ_c at each cross-head rate are shown in figure 5.14. There is clearly a rate dependence effect of the same form as the K_{Ic} dependence illustrated in figure 5.5, both graphs showing a clear peak at a cross-head rate of approximately 25 cm/min .

Thus it can be seen that the rate effects on K_{Ic} values and a corresponding increase in craze stress go hand-in-hand and that such a process could go some way

towards explaining the crack speed effects of figure 5.9 - using fatigued notches. Before any firm conclusions can be drawn a great deal of further work needs to be done on this problem, in particular more information is required about the crack tip craze.

It is however, possible to use the values of craze stress derived by the Dugdale model to correlate results obtained on unnotched specimens.

5.5.4 Fracture Mechanism for Polystyrene

In a series of tests (at 0.5 cm/min) using very carefully prepared 'dumbell' specimens, it was found that tensile failure occurred at a stress (σ_f) of $38.6 (\pm 7\%) \text{ MN/m}^2$ - in close agreement with the value obtained by MURRAY and HULL [1970(a)] using similar material. It was also noticed that at $(0.8 \rightarrow 0.9) \sigma_f$ the whole specimen surface became covered with crazes growing from 'inherent flaws' in the material. At no stage were the specimens touched by hand and so environmental effects due to hand oil etc. can be ignored.

The traditional method of interpreting these results is to use the fracture stress in conjunction with the critical value of γ_p or K_c to compute the size of the inherent flaw which is deemed to be responsible for the final specimen fracture.

For the present results, using $\sigma_f = 38.6 \text{ MN/m}^2$ and $K_c = 0.78 \text{ MN/m}^{3/2}$ gives the inherent flaw size (a_I) as 0.1 mm . This compares with a value of 0.35 mm obtained by MURRAY and HULL [1971] and 1 mm obtained by BERRY [1962] using higher K_c values. Since such flaw sizes are not observable on the fracture surfaces (or internally, prior to testing) there is an obvious contradiction. The procedure of calculation is disputable in terms of practical

reality, since it is intrinsically assumed that the 'inherent' flaw in the unnotched test is a through thickness edge notch and this is most unlikely to be the case.

MURRAY and HULL [1971] tried to overcome this difficulty by using measured 'inherent' flaws from fracture surfaces in conjunction with a solution for K for a penny shaped crack embodied in the centre of an infinite plate. The γ_p values so calculated were subject to excessive scatter and on average were only half the values calculated from notched specimens. They gave an intuitive explanation of the discrepancies, which presumed that a given crack with a large craze has a low fracture energy requirement than one with a small craze. Since this seems to contradict the results presented here, the agreement would seem to be in error. The most likely explanation of their results would appear to be the use of an invalid solution for γ_p , since not only were the flaws non-central (some were more akin to edge notches) but the specimen width was only 6 mm - hardly an infinite plate!

On the basis of the present results it would seem that the search for inherent flaws is only part of the story since slow crack propagation is not the only fracture mechanism which can operate.

P.T.O.

The Dugdale solution which was used to calculate the craze stress σ_c (immediately prior to fracture) is valid for equilibrium conditions and the analysis implies an instability when the gross applied stress exceeds σ_c . In the present case σ_c , although strain rate sensitive, was found to have values in the range $34.5 \rightarrow 44.1 \text{ MN/m}^2$. These values are in such good agreement with the failure stresses in unnotched tests that it would seem likely that these failures are caused by craze rather than crack instability - providing the 'equivalent inherent flaw' size is less than 0.1 mm . For such specimens, the lower bound failure criterion is satisfied by the given stress exceeding the 'craze 'tensile strength' (σ_c) and not by attainment of a critical value of γ_p or K being achieved since if flaws are less than 0.1 mm it would need $\sigma > \sigma_c$ for $K = K_c$. Conversely if flaws are greater than 0.1 mm then the K_c/γ_p criterion would operate as critical conditions are achieved for $\sigma < \sigma_c$.

The most significant factor which emerges from this discussion is that it is always necessary to minimise the size of inherent material flaws. Although no large inherent flaws were observed in the present unnotched tests, it must be remembered that there was very careful specimen preparation and material handling was minimised. In practice such care would not be taken and the effects of environments cannot be neglected. Polystyrene is known to be susceptible to attack by many kinds of common environments - oils being particularly pernicious - and in tests using minute quantities of vegetable oil and white spirits applied to the surface of unnotched specimens

it has been observed that cracks of 3.4 cm length can be grown under stresses $\sim 0.04 \text{ MN/m}^2$ *. The possibility of cracks growing by a few hundredths of a millimetre by the action of environment and applied or residual stresses is by no means a remote possibility and hence there is always the danger of fracture occurring due to critical crack length/stress conditions being achieved - this being borne out by the failures which so often occur in practice.

* R.J. FERGUSON (private communication).

5.6 CLOSURE ON POLYSTYRENE

By using fracture mechanics concepts to analyse the results of fracture tests on polystyrene, it has been demonstrated that it is possible to obtain different values for the supposed unique parameter K_{Ic} . This has been shown to be attributable to the presence of craze bunches at the tips of artificially induced flaws, the quantity of crazing being a function of the notching technique used. A procedure using high frequency oscillations which has been developed allows a 'pure' crack to propagate and leads to a lower limit instability value of $K_{Ic} = 1.05 \text{ MN/m}^{3/2}$ and a lower limit value for slow crack propagation of $K_{Ic} = 0.78 \text{ MN/m}^{3/2}$. The $K_{Ic}/\dot{a}$ curve which has been obtained using cleavage and SEN specimens has been shown to be a unique curve, independent of both loading technique and specimen geometry. The comparatively shallow form of the curve, cf. that obtained for PMMA, has been attributed to the relative insensitivity of the modulus of yield stress to viscoelastic effects.

By use of the Dugdale model to evaluate craze stresses ahead of the cracks it has been possible to account for the nature of failure in unnotched tension tests.

CHAPTER 6. ENVIRONMENTAL STRESS CRACKING OF POLYETHYLENE

6.1 INTRODUCTION

During the late 1950's and early 1960's there was an intense amount of interest in the environmental stress cracking of polyolefins and in particular of polyethylene. The interest had arisen largely because polyethylene was being widely used as an insulation coating for undersea telephone cable and for underground pipework and in both applications there was naturally a fear that cracking might occur. However, in spite of the large volume of time and effort expended on the problem there is, as yet, no convincing explanation as to the cause of E S C

The main stumbling block impeding progress has been that to date, there is no test method which is able to provide satisfactory data for predicting the service performance of polyethylene. Numerous types of test have been proposed and found wanting because of irreproducibility of data and also because there is still dispute as to the most critical parameters by which to measure the material's resistance to ESC.

6.1.1 Test methods for E S C

LANDER [1960] has used un-notched tensile strips - subjected to constant loads to measure a limiting stress below which failure did not occur within a finite time (at a given temperature). In a more exotic test, McFEDRIES et al. [1962] used specimens shaped in the form of a Maltese Cross to measure critical stresses under biaxial tension. In both these reports the experimental data appears to be very good, but critics of the methods dispute the validity of the numbers, pointing out that not only do the critical values vary between one material

and another but also vary if the loading conditions are changed or if the specimen dimensions are altered, DOLL and PLAHER [1961] . They proposed instead that it is better to use a critical strain criterion, obtained from results of tensile tests where the strain was maintained constant until cracking occurred.

Whatever the criterion of failure, be it critical stress or strain it is arguable that in this type of test there are bound to be built-in error factors, because with both methods the results will be highly dependent on the surface condition of the material and the care with which samples are made. (Hence inter-laboratory discrepancies!)

One test which has tried to overcome this by using a razor notched specimen, is the 'bent strip' or 'Bell Telephone' test which was originally devised by DE COSTE et al. [1951] to give data on low density cable sheathing material. The slit is made down the longitudinal axis of a $12.5 \text{ mm} \times 37.5 \text{ mm} \times 3.1 \text{ mm}$ specimen which is then bent to fit inside a brass channel jig which is, in turn, immersed in a test tube of detergent solution at a temperature of 320°K . The specimens are usually tested in batches of ten and the time at which 50% of the specimens have failed is taken as the stress-cracking time. (Failure is normally indicated by the development of cracks perpendicular to the slit and near the peak of the bend.) The bent strip test is now the current ASTM standard test for evaluating E S C resistance in polyethylene although the results of the tests are by no means universally accepted. Indeed the ASTM themselves admitted that the test is "not capable of giving precise, universally reproducible values" and CLEGG et al. [1959] report that a round robin of ASTM numbers confirmed that data from different laboratories on exactly the same grades of material did not agree.

6.1.2 Paradoxes in testing

Not only is data hard to reproduce in any of the above tests, but also there is at least one major area in which the tests give completely different results. In the constant loading tests, increasing the density of polyethylene increases the life of the specimen in any given environment - LANDER [1960], McFEDRIES et al. [1962]. However, in constant strain tests and the bent strip experiment, increasing the density results in a shorter life and lower critical strains for cracking. HOWARD [1964] claims that the latter two tests give the most "accurate" result because they best represent service conditions (although here he is only really talking about cable applications). McFEDRIES et al. [1962] fundamentally disagree because they point out that much of the scatter in times to fail in the 'bent strip' test is due to variations in modulus and related stress rather than true variations in failure behaviour. When a more rigid (high density) sample is bent to the same radius as a sample of low rigidity, the stress developed is proportional to the modulus and this produces a pronounced difference in the failure time. They also quote a number of practical cases where indeed high density material is found to have superior stress-crack resistance. From a commercial point of view, the confusion is particularly undesirable because imprecise data and tests can lead to much wastage.

In all the tests, the very inconsistency of the results is a sure sign that no real understanding of the ESC phenomenon exists and that the test results are little more than educated guesses. Plastics manufacturers are left with little alternative at present, but to follow the "standard" test procedures in order to provide some guide as to ESC resistance, on the basis that any number is better than none. The unfortunate fact is that articles made from polyethylene still break because of environmental stress cracking. The manufacturers themselves

can produce grades of polyethylene which have virtually total resistance to cracking, but only at a price, since the cost of making and re-processing these grades is often prohibitive to end users. In a harsh commercial world, the end users of the polymer resins want to use the cheapest material possible and hence they need precise data to enable them to make a realistic assessment of the service performance of any given grade.

6.2 SCOPE OF PROJECT

Because of the present unsatisfactory situation with regard to the testing of ESC behaviour it was thought at the outset of this project that it would be worthwhile attempting a fracture mechanics approach, similar to that used on PMMA and polystyrene. The field seemed ripe for exploitation, because macroscopically the fractures produced by ESC appear to be brittle and there are certainly no signs of extended plastic flow. It was thought that by using pre-notched specimens, many of the difficulties attributable to variations in material condition could be overcome. By using a K_{IC} approach there is also no need to worry about variations in modulus especially if the results are plotted versus crack speed which is a sensitive measure of rate dependent processes.

The project now reported is an investigation of the potential of fracture mechanics as a future tool for the correlation of ESC data. The tests are confined to an analysis of the behaviour of two low density materials.

6.3 TEST PROGRAMME

In the tests on PMMA and polystyrene it has been shown that the value of the fracture toughness K_{Ic} depends on the crack speed. Because the environmental stress cracking of polyethylene is a slow crack situation all results are correlated on a K_{Ic} /crack speed basis in this investigation.

6.3.1 Experimental details

The tests were made on two low density grades ($\rho = 0.912$) of polyethylene, both of which had relatively high MFI's (7 and 20) and which would therefore be expected to crack in relatively short times in alcohol environments. Ethanol and methanol were used to promote the cracking. It was found that cleavage specimens are not really suitable for use with polyethylene since the low modulus of the material allows the arms of the specimens to twist and/or buckle, and so only SEN specimens were tested.

The main test series was carried out under constant loading conditions, the specimens being totally immersed in environmental baths of alcohol. Other tests involving the measurement of crack initiation as a function of straining rate were also conducted on the Instron, which was fitted with appropriate immersion testing equipment.

The specimen dimensions were $150 \text{ mm} \times 50 \text{ mm} \times 1.5 \text{ mm}$ in general, although a sub-series of tests was made on 3 mm and 4.5 mm thick material to evaluate thickness effects. Finally, to investigate the effects of pre-soaking polyethylene, two batches of specimens from the MFI 20 grade were left to soak in ethanol for periods of up to 300 h before testing.

6.3.2 Constant load tests

In these tests the crack growth under load was measured and crack length versus time curves plotted for each specimen - an example is shown in figure 6.1.

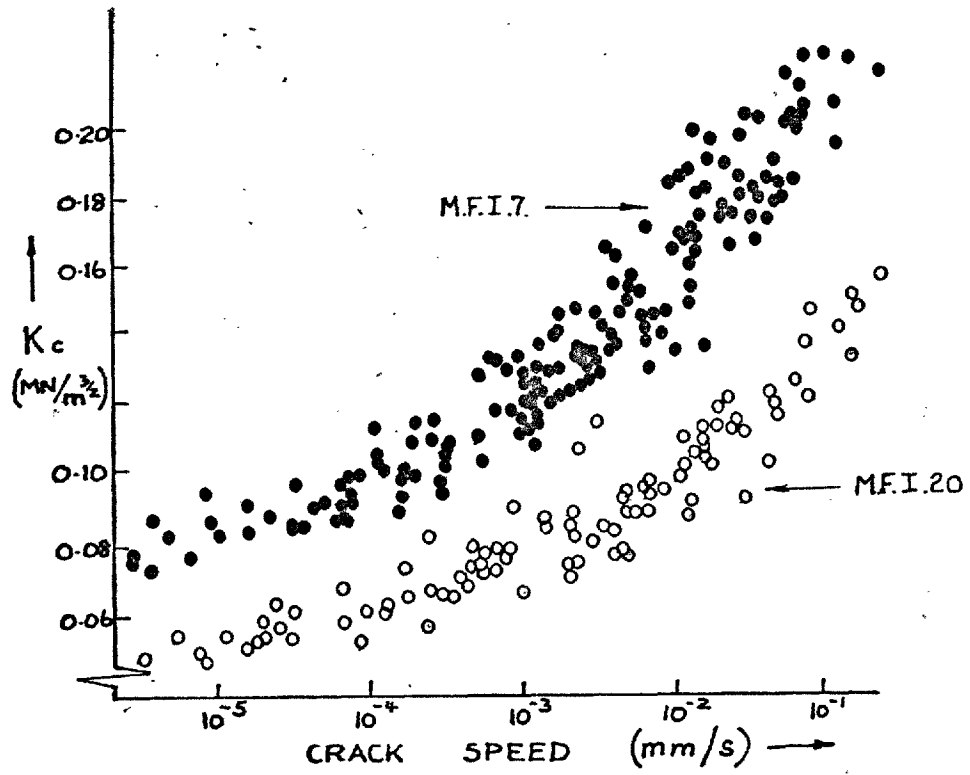


figure 6.2: K_c versus Crack Speed Curve - Polyethylene in Methanol

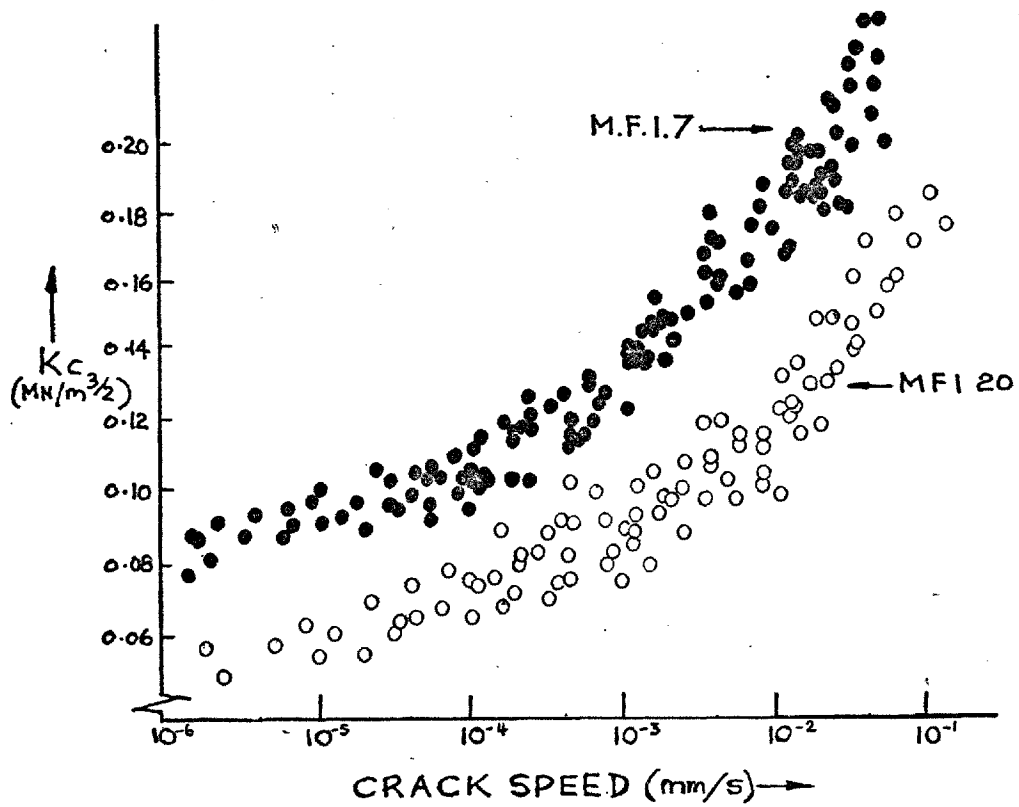


figure 6.3: K_c versus Crack Speed Curve - Polyethylene in Ethanol

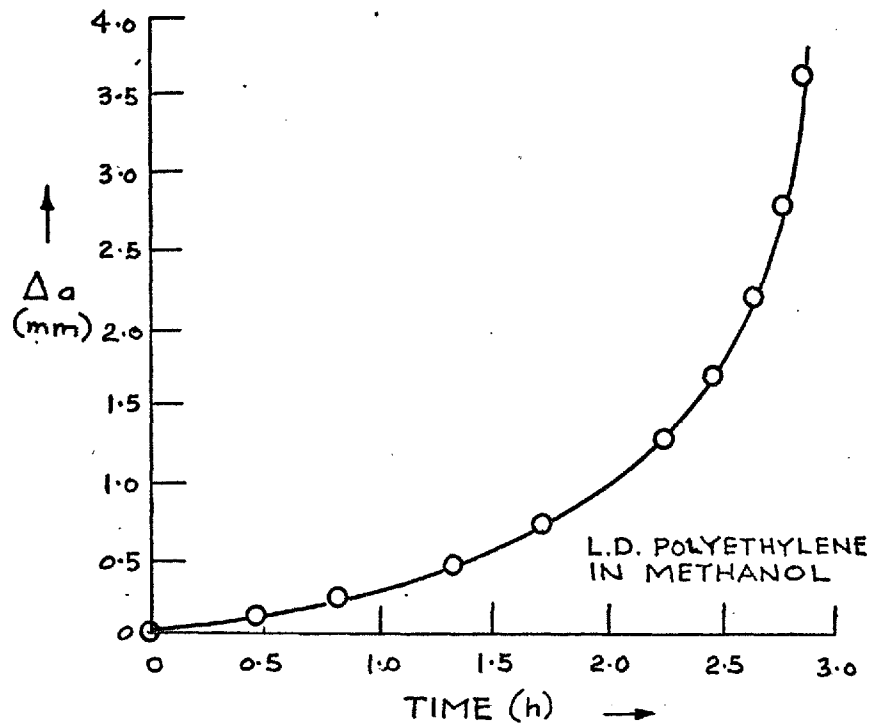


figure 6.1: Crack Length vs Time Curve - SEN

It can be seen that the growth rate increases throughout the test - in a manner very reminiscent of PMMA and polystyrene. These materials, however, exhibited a sudden transition in growth behaviour at the point of crack instability, whereas cracks in polyethylene in alcohol behaved in a very stable manner and allowed careful measurements to be made over long periods of slow growth. On the other hand, a disadvantage of using this polymer was the difficulty encountered in clearly defining the cracks because of its low translucence, and good lighting conditions were found to be essential.

From these results, plots of K_{Ic} versus crack speed were made for each of the material/environment combinations - as shown in figures 6.2 and 6.3. The large number of results obtained from these tests show that within the test limits there is a unique relationship between K_{Ic} and crack speed. The scatter on results is of the order of $\pm 10\%$ which is considered acceptable for this type of test - it is certainly far better than the precision of any other type of stress crack-ing test. It should be noted that in principle, a complete curve as in figures

6.2 and 6.3 would be obtained from each specimen. This is not practicable, however, but figure 6.4 shows that each specimen does form a part of the general curve.

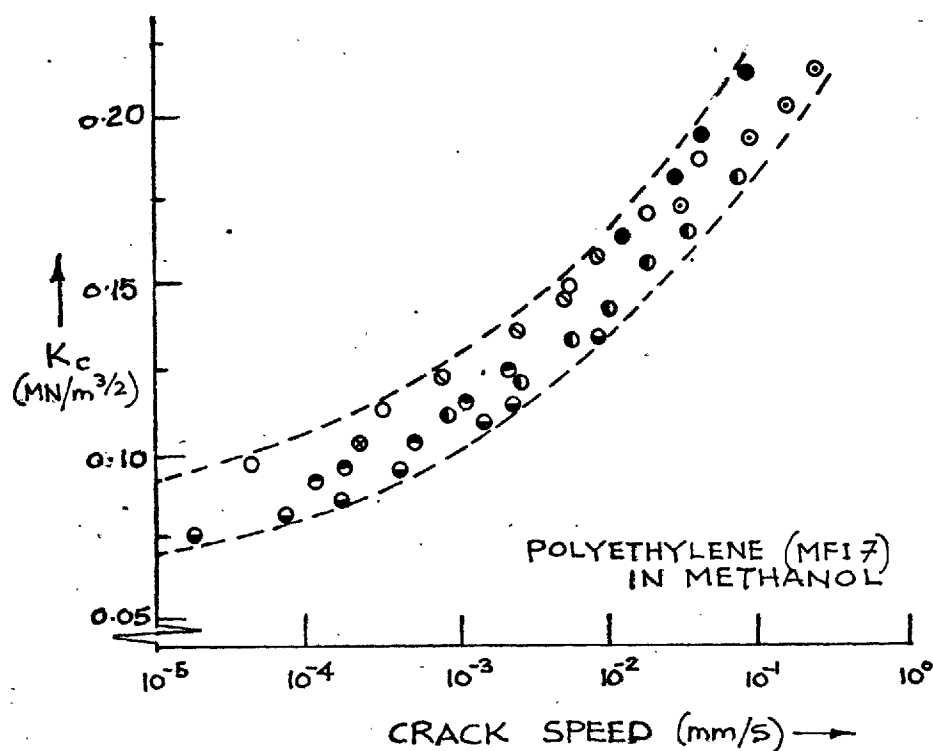


figure 6.4: K_c vs Crack Speed - Results of Individual Specimens

There are, however, certain limitations on the "uniqueness" of the K_c / crack speed curves. In other tests, not reported here, it became apparent that the relationship breaks down when comparatively large gross stresses are applied to specimens having crack length : width (a/W) ratios > 0.4 . This phenomenon would appear to be a result of a large net section stress leading to the eventual breakdown of basic equations as plasticity and finite plate effects become pre-dominant.

For a/W ratios below 0.4, the results shown in figures 6.2 and 6.3 are all valid and indeed appear to indicate that the ESC failure mode is totally brittle.

Casual examination of the fracture surfaces produced in these tests would also lead to the same conclusions, since there was no sign of any ductility on the

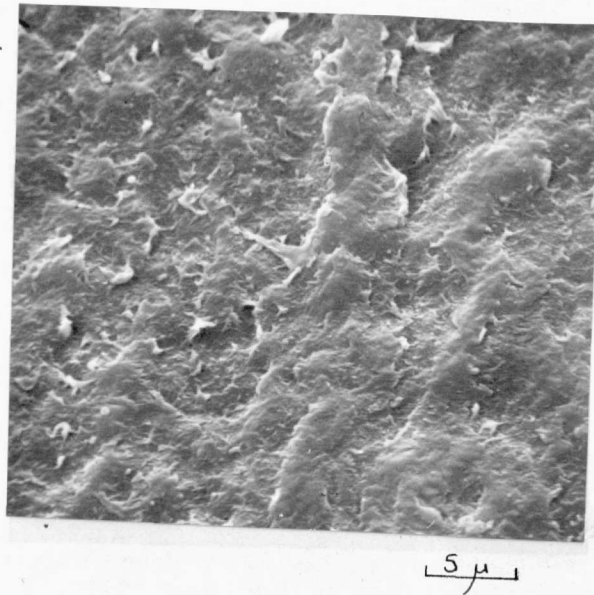


figure 6.5: Fracture Surface - 'Brittle' Failure

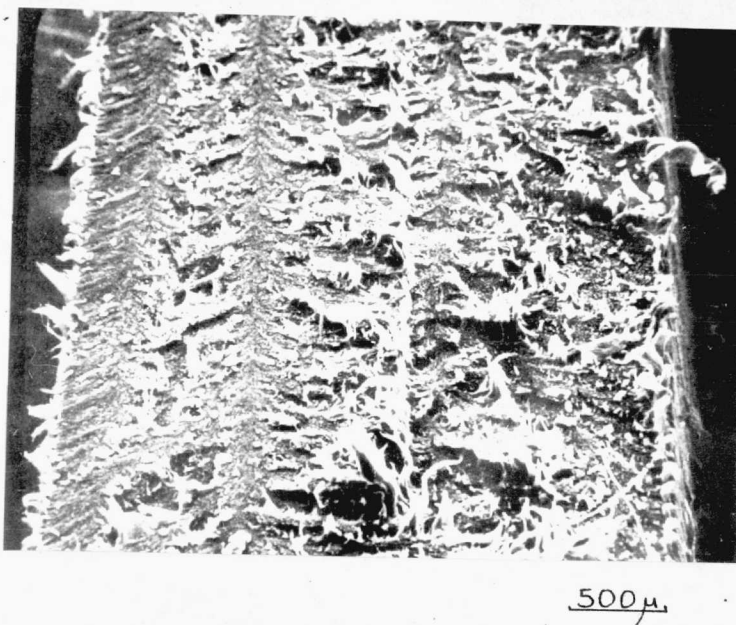


figure 6.6: Ductility Induced by Finite Plate Effects

macro scale - as there is for failure in air! Figure 6.5 shows a stereoscan micrograph of a typical fracture surface in MFI 20 grade polyethylene (cracked in methanol) and even at high magnification it can be seen that there is only a marginal amount of micro-ductility. For those tests which had been invalidated by high net section stresses and finite plate effects, the amount of ductility increased markedly and was readily apparent at low magnifications - see figure 6.6.

The results obtained with the 3 mm and 4.5 mm thick materials are shown plotted on the MFI 7 in methanol curve in figure 6.7 and it is clear that there is no thickness effect on the results - thus indicating that plane strain conditions are operative. This is a somewhat surprising result with polyethylene which is not normally renowned for its lack of plasticity and serves to illustrate the complete transition in behaviour produced by the environmental stress cracking.

The results from the pre-soak tests, figure 6.8, also clearly indicate that soaking the polymer for up to 300 h in alcohol has no effect on the crack propagation properties. This was to be expected since alcohol is a precipitant for polyethylene and is not therefore likely to be absorbed into the unstressed bulk material.

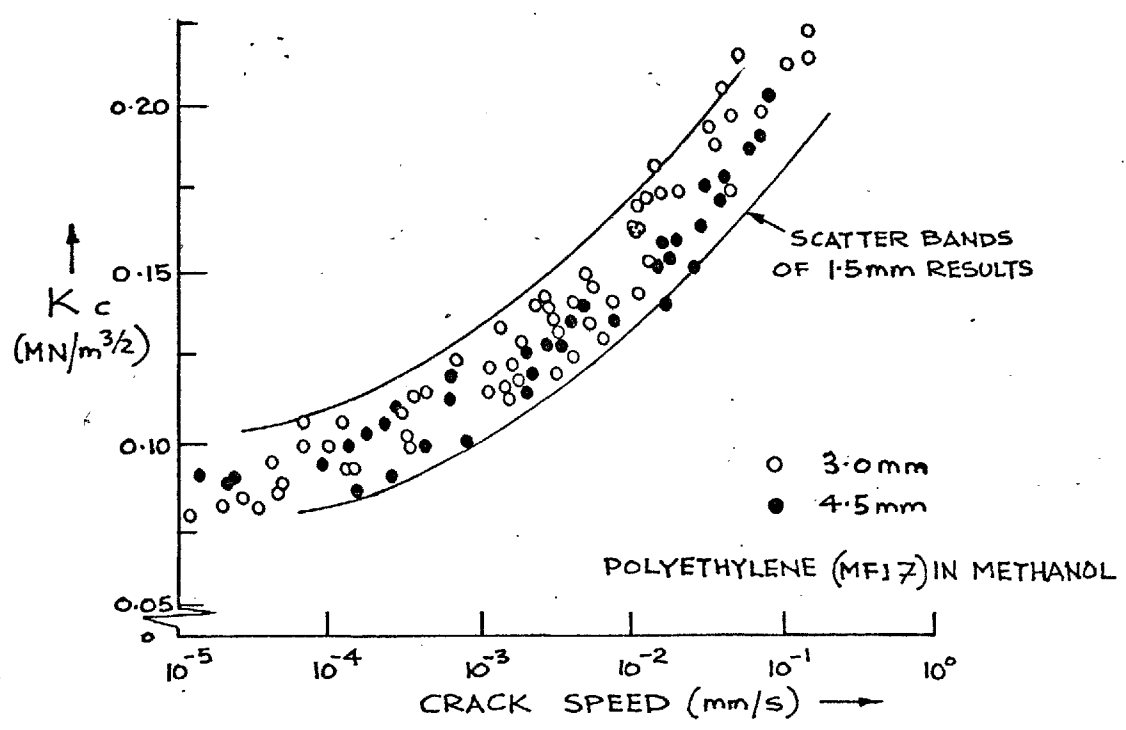


figure 6.7: Effect of Specimen Thickness on Crack Propagation

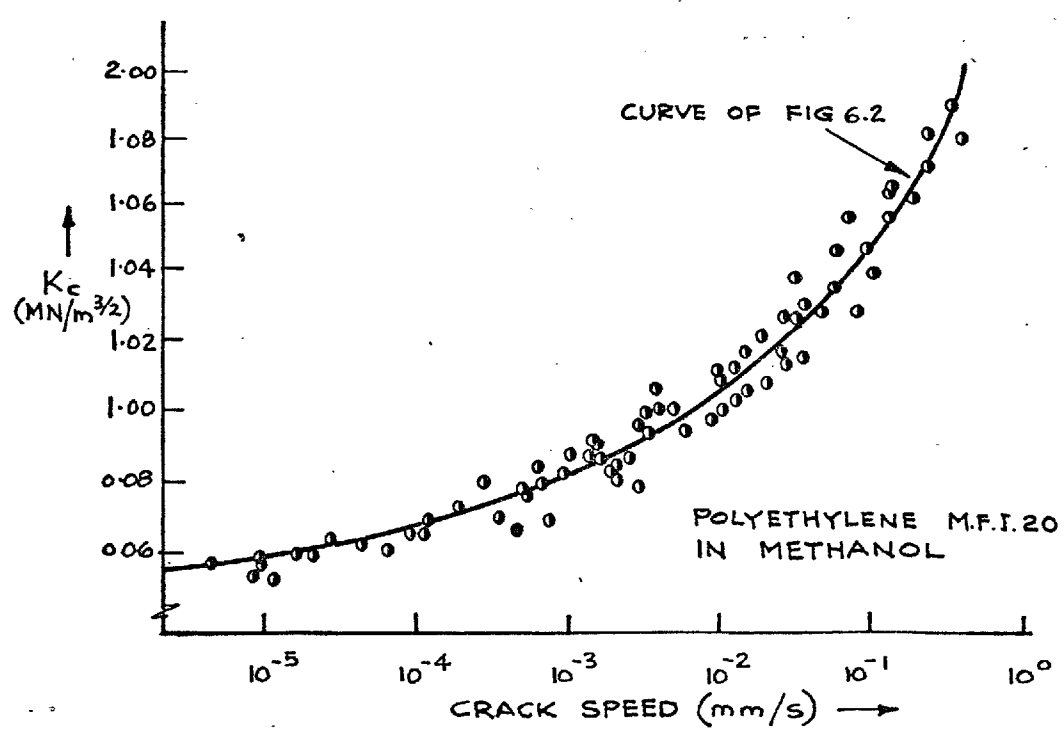


figure 6.8: Effect of Pre-soaking on Crack Propagation

6.3.3 Strain rate tests

Polyethylene is known to be a very strain-rate-sensitive material and it was thought desirable to investigate its fracture behaviour at various rates of straining.

Test batches of twenty specimens having notch lengths varying from 1.2 mm to 20 mm were tested in methanol on the Instron at various cross-head rates. The specimens were clamped (rather than pin-loaded) with a 50 mm gauge length between the grips. Points of crack initiation were observed via a microscope and the load/displacement chart marked accordingly.

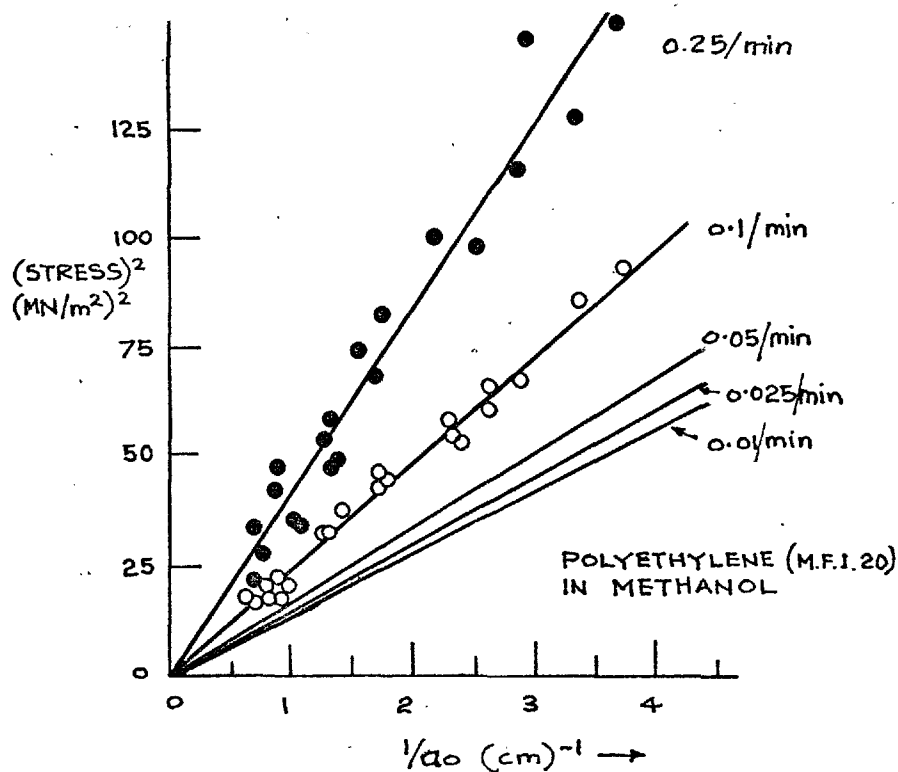


figure 6.9: Effect of Straining Rate on K_{Ic} Values

In all some 300 tests were performed and a typical set of $(stress)^2$ vs $(crack\ length)^{-1}$ curves - used to calculate K_{Ic} from equation 2.6, (p. 25) is shown as figure 6.9. The observation of the initiation of crack growth was difficult, and at high straining rates - where the growth was particularly fast - this led to consistently higher degree of scatter in the results as can be seen in the graph. The data for straining rates of 0.25/min and 0.1/min only are

shown - for the sake of clarity. However, the scatter of $\pm 11\%$ was thought to be acceptable in view of the difficulties in actually seeing the cracks.

The equipment used in these tests required the ends of each specimen to be clamped and hence produced a uniform stress field across the specimen. This allowed the infinite plate solution to be used to calculate K_c values, i.e.

$$K = \sigma\sqrt{\pi a}$$

This is in contrast to the constant load tests which were pin-loaded, carried a non-uniform stress and required the use of the finite plate correction factor (Y^2) of equation 2.7, page 25.

The slopes of figure 6.9 were used to calculate K_c which was in turn used to calculate an "apparent" crack initiation speed via the analytical solution proposed by IRWIN [1964] (for derivation see p. 96 in paper 2 at end of thesis).

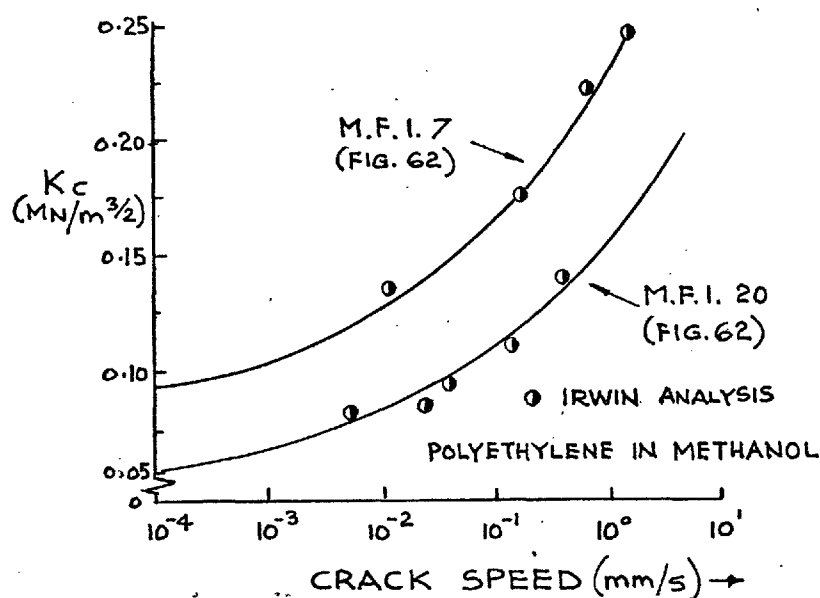


figure 6.10: Comparison of Constant Load and Constant Straining Rate Results

The K_c and "apparent" crack speed values obtained in this way are shown superimposed on the experimental K_c / crack speed curves in figure 6.10. The agreement between the two sets of results is excellent thus lending confidence to both the analysis and the present experimental work.

6.4 DISCUSSION OF RESULTS

6.4.1 K_c vs crack speed curve

The most pleasing aspect of the tests which have been reported in this section, is that they are consistent in all cases and show that the K_c /crack speed curve provides a sensitive measure of the ways in which environmentally induced cracks grow in polyethylene. The results clearly show that the lower MFI material has superior resistance to environmental attack over all the speed ranges and that ethanol is the more hostile of the two environments - in both cases. It is particularly pleasing to note also that the results are consistent for the different types of loading systems used.

By using the stress intensity factor, K , as the controlling parameter rather than adopting the traditional "surface work" approach, the difficulties involved in assessing the values of modulus, E , over the long terms have been avoided, since all the material parameters are accommodated in K . The rate at which the material creeps will obviously affect the results; but in the present case, the viscoelastic responses are shown up in the rates of crack growth and the general shape of the K_c /crack speed curves. It is hoped that a viscoelastic analysis (similar to that used by WILLIAMS[1972] on PMMA) will satisfactorily explain the shapes of the curves - when sufficient data is available.

6.4.2 Relevance of fracture mechanics

The main practical conclusion which can be drawn from the results is that K_c is a sensitive measure of the resistance of polyethylene to environmental stress cracking. The use of this fracture toughness measure and other allied parameters to explain and describe fracture processes is now standard practice in the metals field, and it is hoped that when further results are obtained on most commercial grades of polyethylene, similar advances can be made in the stress cracking of

polyolefins. Indeed a project on high density polyethylene has been started in the fracture laboratory at Imperial College as a result of the present work and the results on even the most crack resistant materials are very encouraging (for a preliminary report see LINKINS et al. [1972]).

Using notched specimens in the way described here, is seen to work very well, since there is no discrepancy introduced by the materials having a different degree of surface finish. In those tests which use unnotched specimens, the tests will necessarily depend to a large extent on surface conditions and will therefore be liable to huge scatter on results, especially where different moulds or dies etc. are used to make test samples. By the very nature of the present tests it is always assumed that flaws exist in the material and that it is from these inhomogeneities that cracks grow to produce eventual failure. It is arguable that different materials may have in-built differences in structure which make crack initiation less likely, but it is still maintained that even in these cases, the K_{IC} /crack speed curve is a much more sensitive measure of material performance since any structural characteristics which produce toughening would still be manifested in the crack propagation data, i.e. those materials having greatest resistance to crack propagation are likely to be the ones with the greatest resistance to crack initiation.

Given a critical stress below which cracking does not occur in an unnotched test (LANDER [1960]) and the minimum K_{IC} value obtained from the K_{IC} /crack speed curve, it is also possible to calculate the sizes of the critical crack lengths from which fracture initiates in practice - by feeding the stress and K_{IC} value into equation 2.6. Any changes in the production process could affect this quantity and by careful tests it should be possible to identify sources of flaw generation.

The precision of the present tests also means that there is now a reliable test procedure for evaluating the effects of material structure in environmental cracking situations. By careful future testing it should be possible to resolve the confusion over the effects of material density and also to examine the nature of the effects of temperature and other testing variables.

PART III

ENVIRONMENTAL STRESS CRAZING MECHANICS

CHAPTER 7: CRAZE GROWTH IN PMMA IN METHANOL

CHAPTER 8: PMMA IN METHANOL - EFFECT OF CYCLIC LOAD

CHAPTER 7. PMMA IN METHANOL

7.1 INTRODUCTION

The problems associated with the behaviour of stressed glassy plastics in 'hostile' environments has not received the same amount of attention as the ESC problem in polyethylene. The environments which cause cracking or crazing in glassy plastics are known to react with the materials (cf. ESC where there is no chemical reaction) and consequently sudden, unexpected failures are not quite so prevalent.

The previous work on the subject has concentrated, in general, on relating the chemical factors which cause environments to crack or craze, e.g. BERNIER et al. [1968] , (see section 3.9.1). There are however, two rather superficial reports by ANDREWS and BEVAN[1966] and STERNSTEIN and SIMS [1964] who both conducted a number of notched plate tests on PMMA in various alcoholic mixtures. Andrews et al. tested in methylated spirits and reported that an 'energy' criterion (essentially - G_c) was operative for 'crack' initiation. The results were subject to considerable scatter and their 'cracking' concept seems to be at variance with reported effects of alcohols on glassy plastics since BERNIER et al. [1968] classify both methanol and ethanol as crazing environments. Sternstein et al. on the other hand reported that a 50-50 mixture of water and ethanol caused PMMA to craze and they gave a number of results of craze propagation tests. They found that there was a correlation between notch length and craze speed - although they placed no significance on the result. Their tests again are a little difficult to assess since they had allowed the specimens to pre-soak for 24 hours before testing and this must assuredly have influenced their result in some way, since ethanol is a swelling environment for PMMA.

Because none of these authors chose to comment in any constructive manner on the significance (or otherwise) of their results it was felt that a more detailed investigation was necessary to try to resolve the cracking/crazing controversy and also to identify the role played by the environment. The success of the previous work on PMMA, polystyrene and polyethylene seemed to indicate at the outset, that a fracture mechanics approach via the testing of pre-notched specimens could provide useful information and parameters concerning the nature of environmental attack in glassy plastics.

7.2 TEST PROGRAMME

7.2.1 Preliminary tests

At the start of this investigation no clear test programme could be finalised, as there was some doubt as to what kind of "fracture" behaviour would ensue when pre-notched specimens of PMMA were stressed in mild solvent environments.

Hence, a pilot series of tests was conducted using both SEN and cleavage specimens - tested in ethanol, methanol and methylated spirits (the "Andrews mixture"). The most important finding to come out of these tests was that all the environments caused crazes to grow from the tips of the induced notches. This was clearly illustrated with the cleavage experiments where the crazes grew into the arms of the specimens, due to the high bending stresses induced with this geometry:- the crazes growing perpendicular to the principal stress directions. The SEN specimens have a more uniform stress distribution and crazes grew uniformly along a line perpendicular to the loading axis - figure 7.1 - and hence this geometry was used for all the tests now reported.



figure 7.1: Linear Craze Growth in a SEN Specimen

Methanol was chosen as the most "suitable" environment because ethanol and methylated spirits were far more hostile and had a tendency to cause general surface crazing of the specimen, thereby obscuring and interfering with the growth of the main craze. Although methanol does have the disadvantage of being hygroscopic, it was found that with controlled atmospheric conditions it quickly reaches its equilibrium content of 1.07% water.

7.2.2 Craze growth tests

It has previously been maintained that the process of craze growth is controlled by a critical stress, STUART et al. [1964]. To test the validity of this criterion, a number of specimens - containing a variety of induced notch lengths - were tested at a selected range of applied stresses. The variation of craze length with time was measured with a travelling microscope (apparatus is shown in figure 7.2).

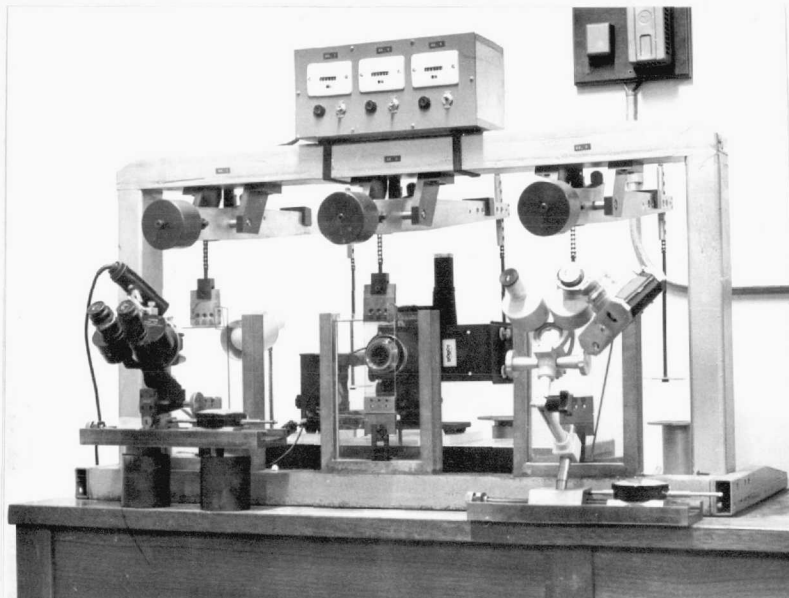


figure 7.2: Dead-Weight Loading Apparatus

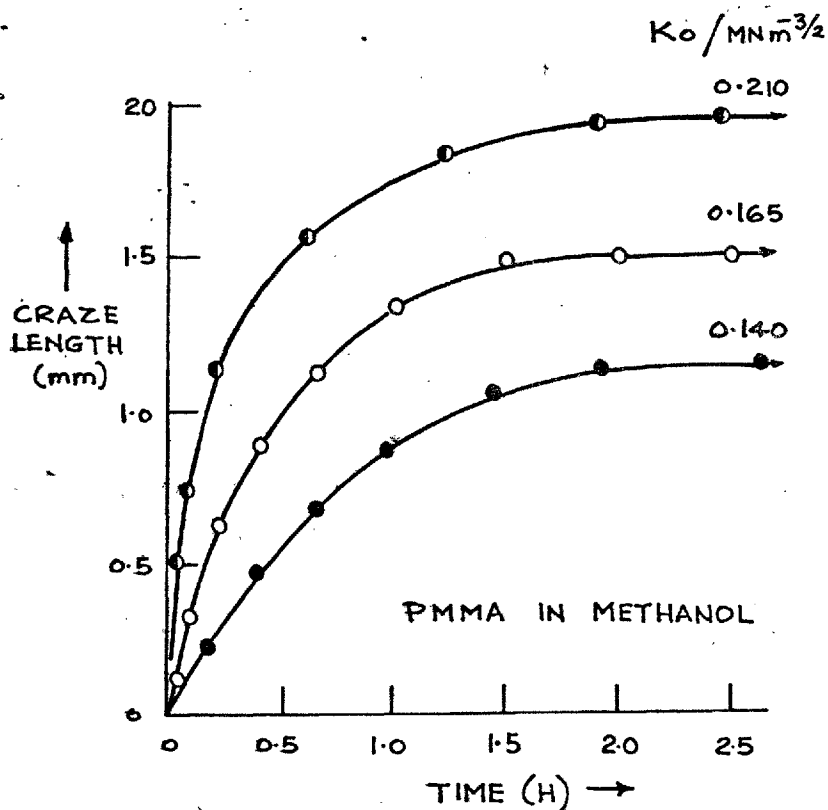


figure 7.3: Craze Length vs Time - craze arrest.

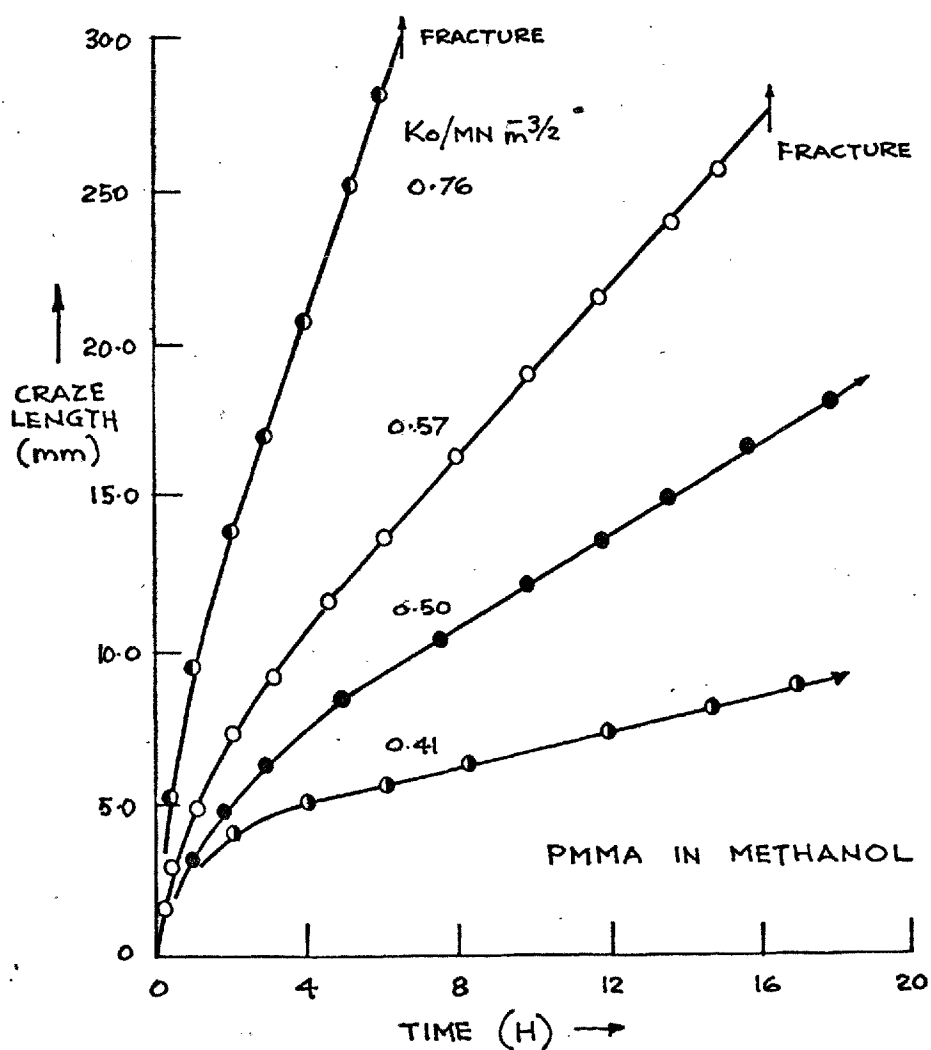


figure 7.4: Craze Length vs Time - leading to fracture

It was found that two distinct types of growth behaviour could be produced - these are illustrated in figures 7.3 and 7.4 showing the variation of craze length with time. In the first type, figure 7.3, a craze grew from the tip of the induced crack with a relatively high initial speed - typically $3 \times 10^{-2} \text{ mm/s}$ - which fell continuously until eventually no further craze growth could be observed. For the other type, figure 7.4, the initial craze growth rate was again high ($3 \times 10^{-2} \text{ mm/s}$) but, although the growth slowed during the early period, it eventually settled to a constant rate which was maintained until craze failure occurred (for discussion of failure modes see page 182). The rates of craze growth and stopping lengths varied test to test depending on the loading condition.

It was immediately obvious that the gross stress was not the controlling parameter since specimens tested at the same stress level could produce markedly different craze growth histories when the induced notches were of different lengths. After attempts to correlate the results using K_o (calculated using the current crack plus crack length) and net section stress had also proved to be fruitless, it was eventually found that the stress intensity factor, K_o - (calculated using the applied stress and initial crack length - which had not grown!) - proved to be the governing parameter. For increasing values of K_o , the craze growth rate and final lengths increased together as shown in the craze length vs time graphs.

To check on the validity of K_o control, a further series of tests were made. Five or six specimens containing a range of flaw sizes were tested at each of a number of K_o levels (viz. $K_o = 0.3, 0.4, 0.5, 0.6, 0.8 \text{ MN/m}^{3/2}$). The results obtained at $K_o = 0.4 \text{ MN/m}^{3/2}$ are shown as figure 7.5.

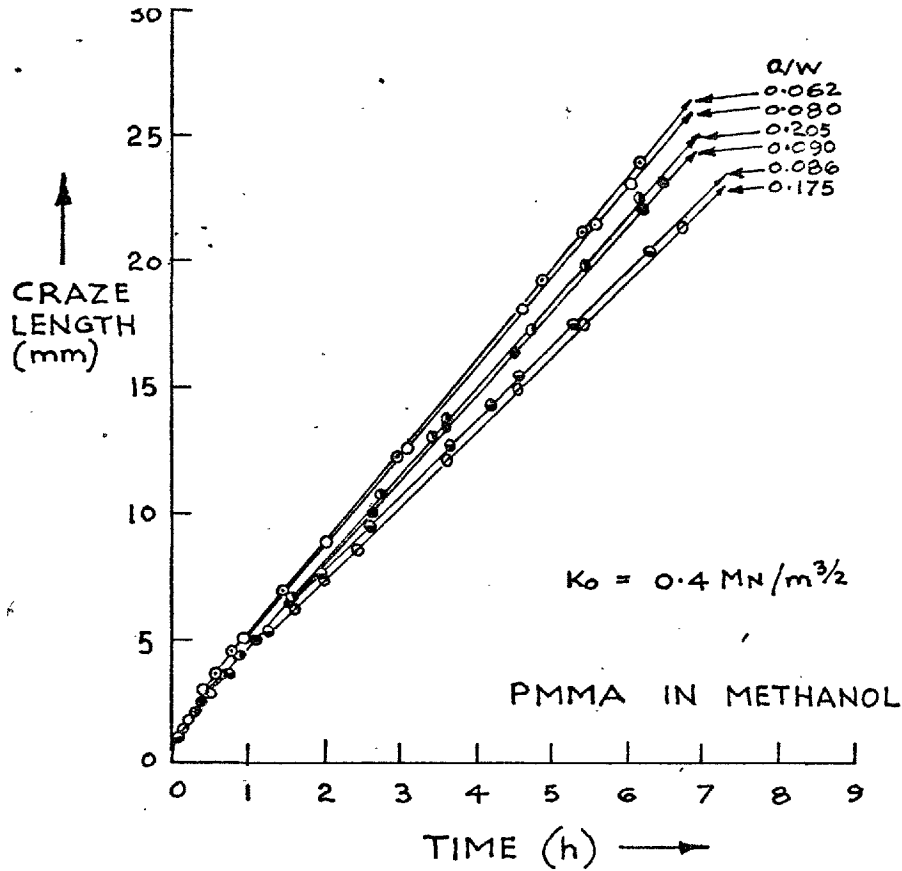


figure 7.5: Effect of Crack Length on Craze Propagation - ($K_0 = \text{constant}$)

It can be seen that the parameter K_0 provides a good basis for the correlation of data for specimens with different crack lengths. The slight variations specimen to specimen are not thought to be a function of flaw size, rather they are a measure of the degree of uniformity of the craze. If the loading was even slightly asymmetric the craze would tend to twist out of alignment and slow down. The results from such tests were not considered to be representative of any material property and are not included in subsequent discussion and presentations.

Temperature variations could also cause growth rate fluctuations. WEBBER [1971] has shown that at temperatures close to 293°K , a $\pm 5^\circ\text{K}$ variation can produce $\pm 30\%$ variation in any given craze speed - (a similar sensitivity of 'craze' initiation to temperature in this region has also been noted by ANDREWS and BEVAN [1966]).

Allowing for such variations it was considered that the K_0 control was sufficiently good to warrant further investigation and more tests were conducted using 3 mm and 6 mm thickness materials.

7.3 CRITICAL K_o VALUES

7.3.1 Craze initiation

From the tests which have been performed, it was found that two important values of K_o emerged. The first was a value, now designated K_m , below which no craze growth would occur. The dead weight loading technique could only give a very approximate value of $K_m = 0.05 \text{ MN/m}^{3/2}$ and so a number of supplementary tests were made. In these tests, the load was applied at a constant rate by controlling the flow of water into a loading tank attached to the end of one of the lever arms on the dead-weight machine. The results for two different rates of loading are shown plotted on a $(\sigma^2 Y^2) \text{ vs } (a_o)^{-1}$ basis in figure 7.6 (the slope yielding K_m from equation 2.7).

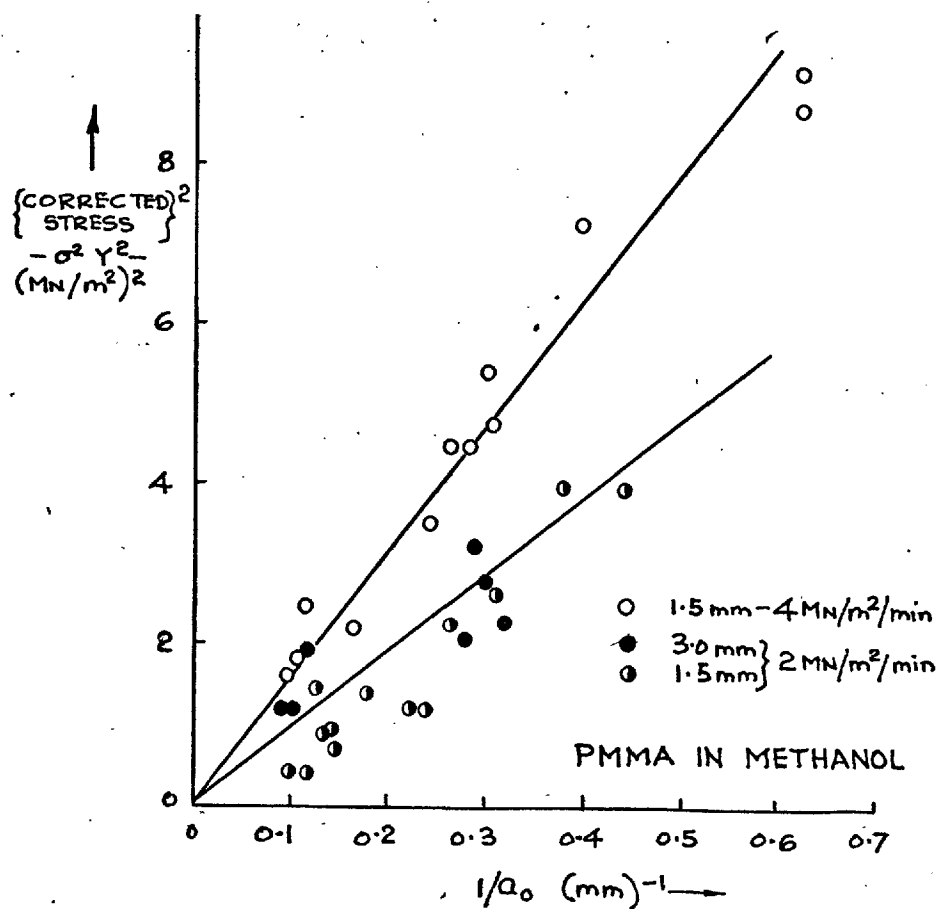


figure 7.6: ('corrected' stress)² vs (crack length)⁻¹ - Craze Initiation

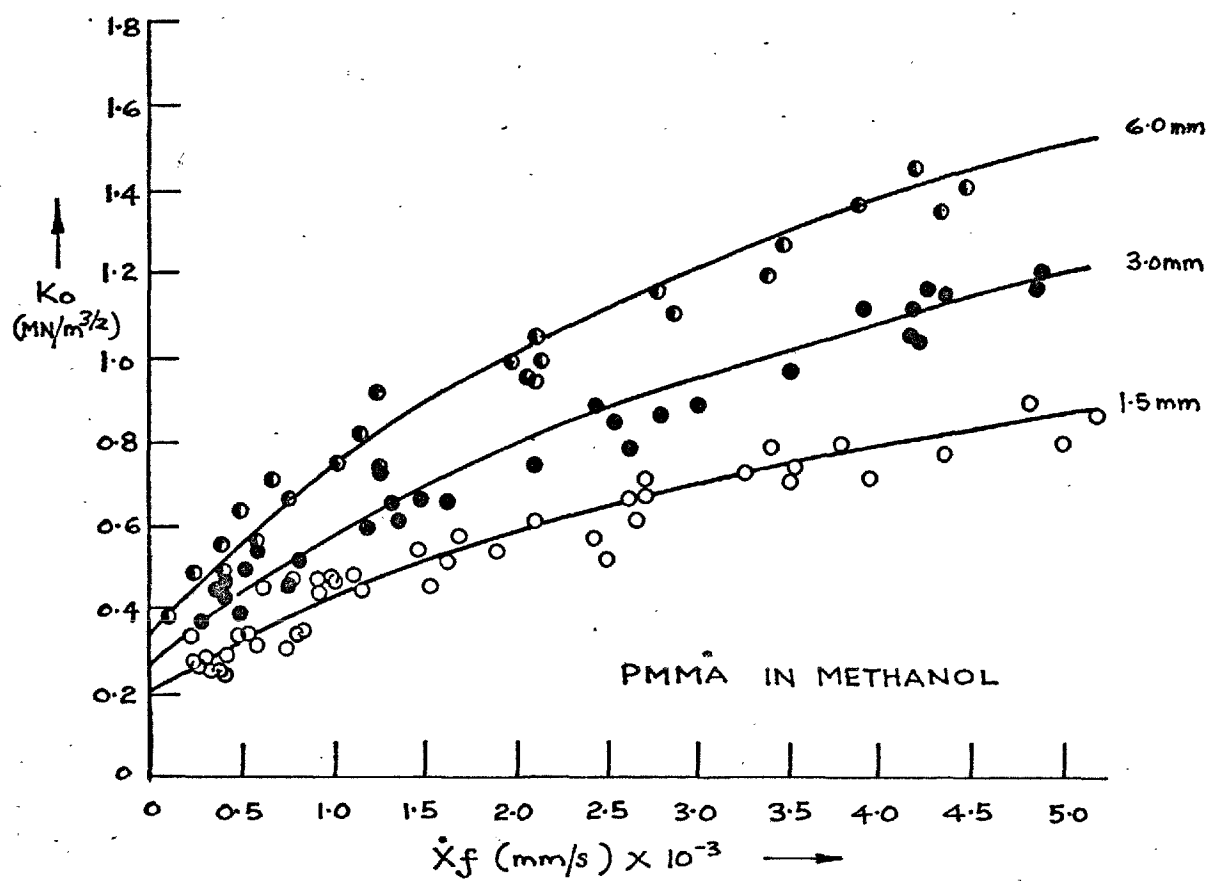


figure 7.7 Variation of Craze Speed with Initial SIF, K_0

The scatter on the results reflects the difficulty in establishing the exact point of craze initiation due to the similarity of appearance between cracks and crazes. The results however, do show that K_m is independent of specimen thickness - but is dependent on the rate of loading. Two values for K_m of $0.061 \text{ MN/m}^{3/2}$ and $0.043 \text{ MN/m}^{3/2}$ were obtained, these numbers comparing well with the approximate value from the previous tests.

7.3.2 Craze propagation

The second significant value of K_o - now designated K_n - was found to control the craze growth pattern. When $K_m < K_o < K_n$, the growth behaviour was always of the form shown in figure 7.3. For tests in this range, fracture never occurred; instead the rate slowed at a rate which was dependent on the K_o value until a final craze length was reached, this also being a function of K_o - as shown in the figure. However for $K_o > K_n$, the growth followed the pattern shown in figure 7.4, the final craze speed being a function of K_o as shown in figure 7.7. It can be seen from this graph that the final craze speeds also appeared to depend on the specimen thickness, as indeed did K_n - the limiting value for this type of growth. Mean values of K_n were $0.21 \text{ MN/m}^{3/2}$ for 1.5 mm thick sheet, $0.25 \text{ MN/m}^{3/2}$ for 3 mm sheet and $0.30 \text{ MN/m}^{3/2}$ for 6 mm thick sheet.

Although the results were generally consistent there was some individual specimen variation on these numbers. At values of K_o just greater than K_n (+ ~10%) crazes, which would have been expected to grow to eventual failure, occasionally started at a constant rate and then stopped after a few (~10) millimetres of growth. In these cases the crazes which may have started out as being "perfectly square" appeared to gradually twist over - especially where the stress levels were low ($< 1.5 \text{ MN/m}^2$). Again, this behaviour was probably caused by irregularities in the loading system and the effect is not thought to be of any great significance.

7.4 CRAZE APPEARANCE

7.4.1 General

It has already been noted in the crazing survey (page 33) that crazes in glassy plastics appear as highly reflective bodies and are easily confused with cracks. In the present tests, although the crazes have the macroscopic appearance of a crack (e.g. see figure 7.1) - differences can be observed through a microscope. Cracks usually have the "river" markings - noted previously (page 80) whereas the crazes were generally completely featureless. The exceptions occurred at slow growth rates, when it was noticed that the craze front had a distinctive 'granular' appearance - see figure 7.8.

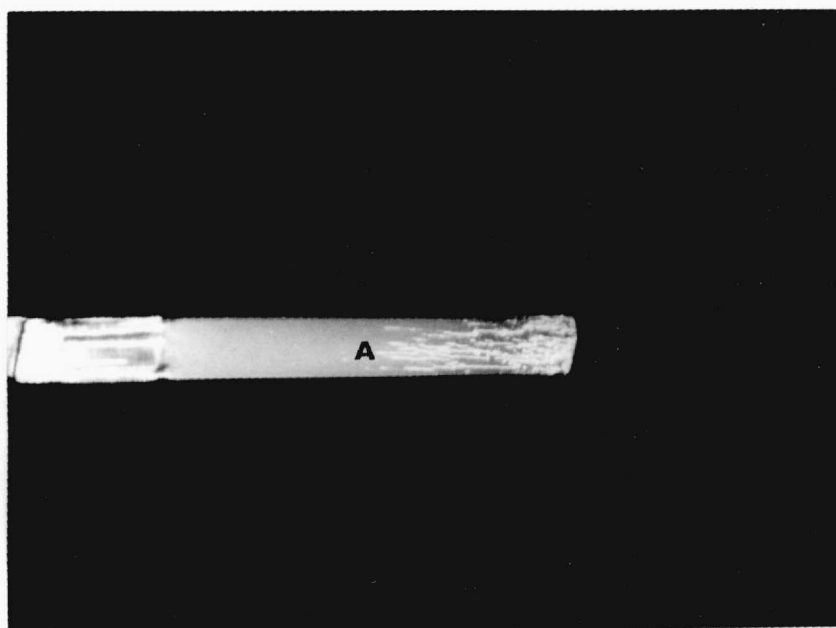


figure 7.8: Markings at Slow Craze Speeds

As growth continued, a portion of craze which had exhibited this type of 'grainy' surface, would gradually become smoother until eventually no sign of the 'grain' could be observed ((A) in figure 7.8 is such a region). In these cases, the craze is very 'thin' and the grain is probably a reflection of a heterogeneous struc-

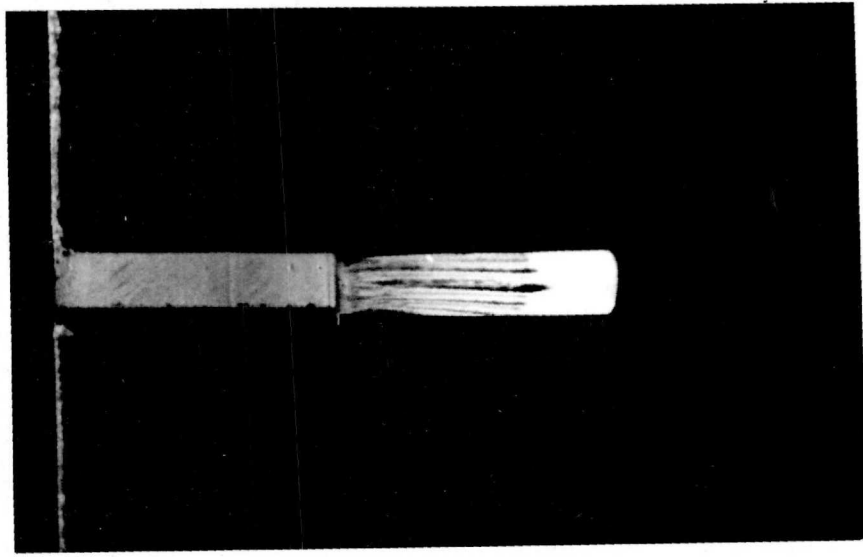


figure 7.9: Craze Front Geometry - craze arrest tests

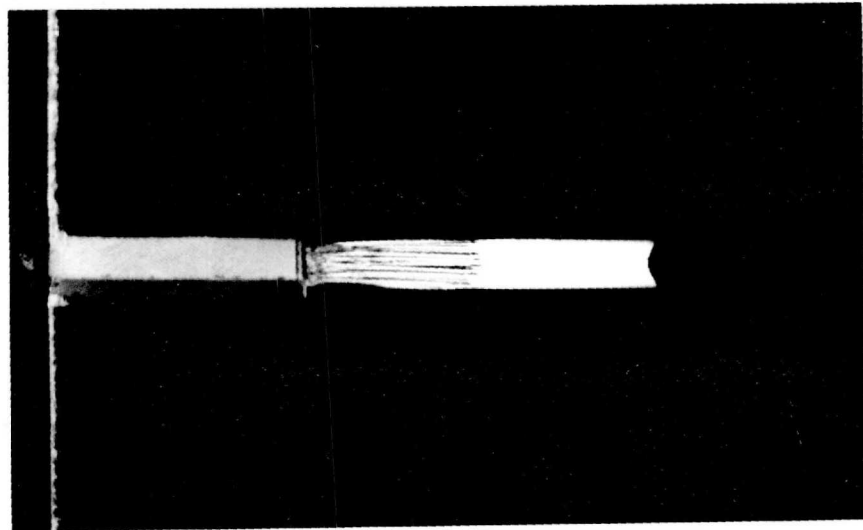


figure 7.10: Craze Front Geometry - tests leading to fracture

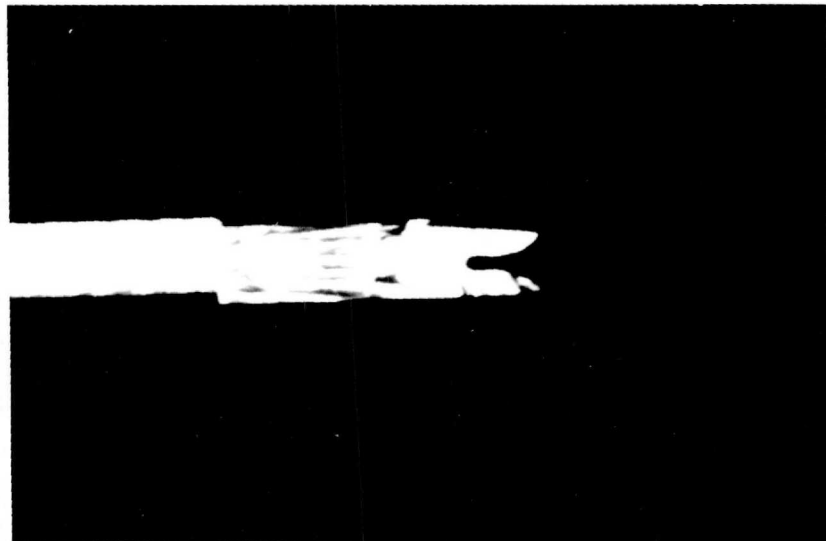


figure 7.11: Craze Growth from Specimen Surfaces

ture in the newly formed craze. As the craze gets longer - and 'thicker' the constituent material will tend to become more perfectly oriented and hence the graininess becomes less distinct.

7.4.2 Craze front geometries

The craze front itself was also a variable quantity. In tests where the craze stopped ($K_o < K_n$), the craze front was a mirror image of the original crack front - as shown in figure 7.9. For crazes which eventually grew at a constant rate to fracture ($K_o > K_n$) the craze front gradually changed from that shown in figure 7.9 to that shown in figure 7.10. For very high K_o values, the transition period was minimal and the craze developed initially as shown in figure 7.11. At these high loadings, the craze appeared to start at the specimen surfaces and gradually to propagate inwards into the thickness as well as across the specimen width. Eventually both sides met in the middle to form a uniform craze as in figure 7.10.

It can be seen from figure 7.11, that there was considerable secondary craze growth at the original crack tip at the high K_o levels. These secondary crazes appeared in 1.5 mm material at $K_o \approx 0.45 \text{ MN/m}^{3/2}$ - though they seldom interrupted the craze growth behaviour - since they stopped growing after a millimetre or so. For $K_o > 0.8$ the secondary crazes could be very troublesome and often grew along with the main craze, thereby distorting the whole craze growth pattern. Results on such tests were discounted.

7.4.3 Craze geometry

In a published paper on this work - MARSHALL et al. [1970 (b)] - it was assumed that the craze had a uniform thickness down its length. Subsequent improvement of the glass in the environmental tanks and the use of a higher powered microscope (see figure 7.2) has allowed the craze to be viewed in much closer detail, and it is now known that the craze shape is very much more triangular - as shown in figure 7.12.

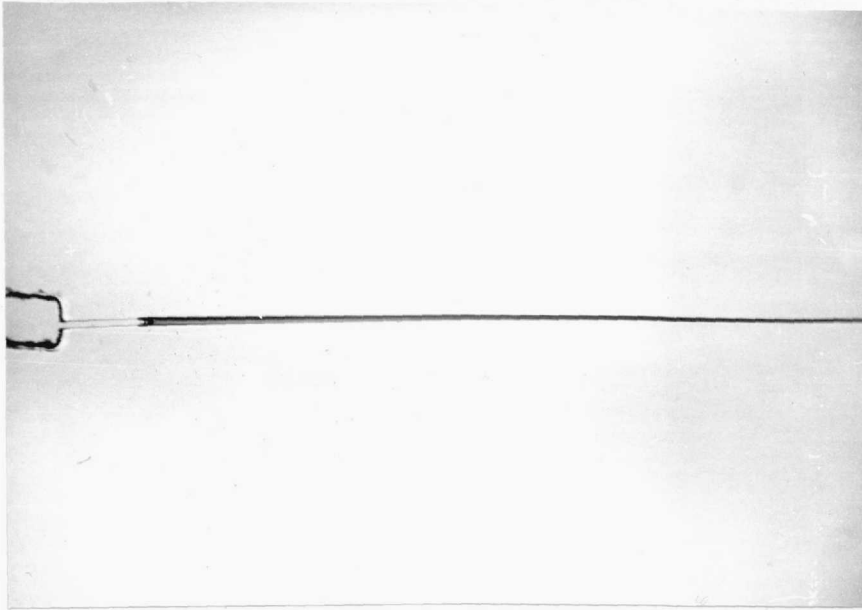


figure 7.12: A Growing Craze Viewed from the Side

It is impossible to view the tip of the craze itself and there is a possibility that the macroscopically triangular shape which is readily apparent in the crack tip region is not maintained all the way down the craze, since extrapolation of the truncated sides which can be seen, does not give the craze tip as the apex of the triangle - the tip is considerably ahead of this point.

The deflections within the craze increase as the craze becomes longer and measurements of the crack tip show that the deflection in this region is proportional to the craze length - as shown in the graph of deflection vs length for a craze grown at $K_O = 0.4 \text{ MN/m}^{3/2}$ - figure 7.13.

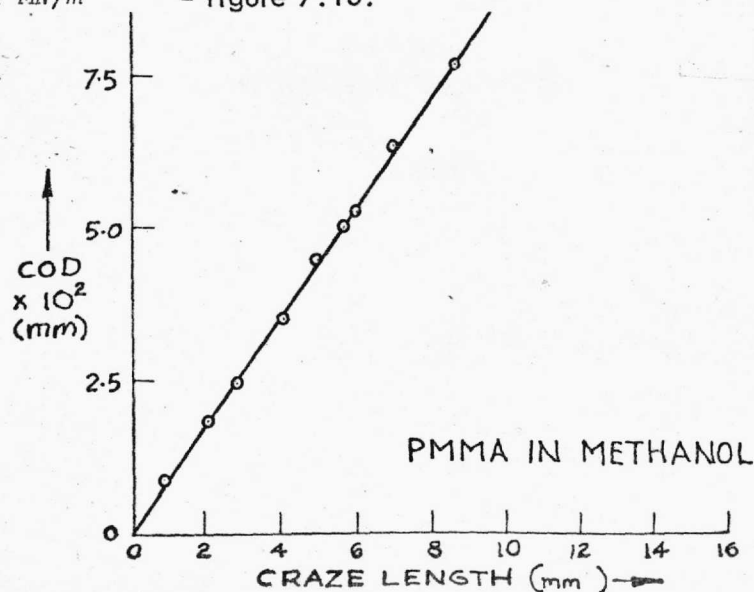


figure 7.13: Crack Opening Displacement vs Craze Length for $K_O = 0.4 \text{ MN/m}^{3/2}$

Since the deflections are increasing throughout the life of the growing craze then, presuming that no new craze is created from the bulk material outside the zone, it would seem to follow that the void content must increase. However, not only are the deflections increasing but also there is some contraction of the craze which would also appear to increase as the craze grows. KAMBOUR [1964b] has argued that this lateral contraction is sufficient to compensate for the extension of the craze (- analogous to cold drawing) - hence maintaining a constant void content. (A line representing the apex of such an indentation can be seen running down the craze shown in figure 7.12). Although equipment to measure the indentations on a growing craze is not yet available, some measurements were made using a Talysurf profilometer on crazes which had been removed from the methanol. The deflections increased from $\sim 0.5\mu$ at the craze tip to $\sim 30\mu$ at the crack tip and although there was a trend for large deflections in the crack tip region no consistent pattern of indent depth with craze length was observed because of the relaxation of the craze. Confirmation of Kambour's supposition will obviously therefore require more precise measurements on growing crazes and such a project is actively under consideration at the moment. However, it would seem reasonable to accept his postulate as a working hypothesis since he has effectively shown that variations in void content are small for crazes of different thicknesses in different materials.

7.5 ANALYSIS OF CRAZING MECHANISM

That the craze speed at large distances from the original crack should seem to be controlled by the prevailing conditions at the crack tip is somewhat unexpected. It might be thought that control of such growth should depend upon the applied or net section stress. This is not so, however, and suggests that a detailed examination of the local stress system around the crack is necessary. Also, the photographs of figure 7.9 to 7.11 indicate that the mode and direction of environmental attack is crucial to a solution, and hence the role of alcohol mobility within a craze must be considered.

On the basis of the experimental results, a model for craze formation and growth is now presented, in an attempt to provide an avenue of approach which may usefully serve as the foundation for future detailed studies.

7.5.1 Model for craze formation and growth

The only previous analysis which has attempted to describe craze growth behaviour is that by KNIGHT [1965] who derived a two-dimensional model for the stresses around a craze in an infinite elastic medium. He proposed that the craze is essentially of constant thickness and by using a finite stress condition, he derived expressions for predicting the stress distribution within the craze. The expressions showed that the craze stress would be essentially constant when the total length exceeded ten times the length of the newly formed craze tip. However, the stress distribution which was predicted for the craze tip region itself was rather unexpected - as shown in figure 7.14.

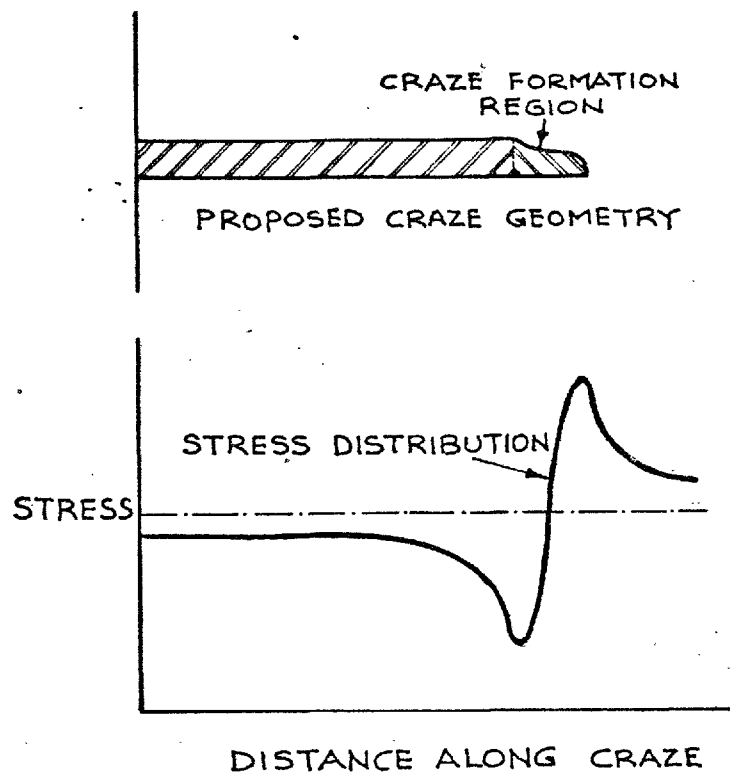


figure 7.14: Stress Distribution Around a Craze - KNIGHT [1965]

Knight had to make a number of "adjustments" to the mathematics in order to avoid discontinuities in the stress distribution and it seems probable that the eventual result is due to uncontrollable variations in the mathematics since the real stress distribution is unlikely to vary in the manner shown. Also, the analysis was couched in terms of a constant craze thickness and the parameters are inconvenient for measurement in craze propagation studies. The use of fracture mechanics concepts allows the problem to be discussed in terms of the conditions prevailing at the end of the original crack.

For present purposes, it is proposed that there are three main stages involved in craze propagation.

(a) Stage 1 - Craze formation

For the case of a specimen containing an infinitely sharp crack and subjected to an applied stress σ at a distant boundary, a plastic zone, in which the material is at the bulk yield σ_y , is immediately formed at the tip of the crack. In reality,

the original crack front will have a finite height - since no notching technique can hope to produce an infinitely sharp crack - and the material at the tip must first be deformed in an elastic manner before yield conditions can be achieved and a plastic zone formed.

A schematic view of the situation at the crack tip is shown in figure 7.15.

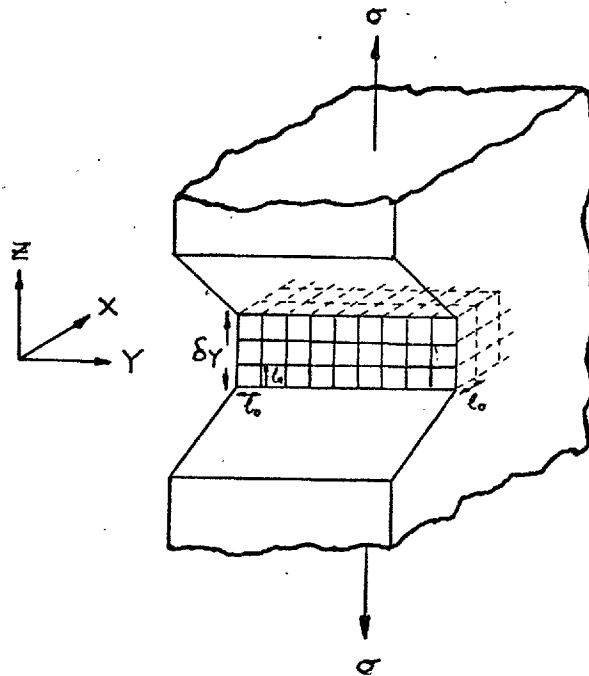


figure 7.15: Schematic View of Crack Front

As shown in the diagram, application of the stress has caused a plastic zone to form at the crack tip and the material has yielded and hence extended to produce a C.O.D. δ_y . The width of the crack tip is considered to be divided into small "process zones" of side l_o . It is this material which is now attacked by the crazing environment and starts Stage 2 in the process.

(b) Stage 2 - Void formation

Because the yielding has produced a high degree of ordering of the molecular chains in the material within the plastic zone, some of the environment is absorbed by the yielded material almost instantaneously. The material becomes plasticized

and hence suffers a drop in yield stress and continues to extend under the action of the applied stress to a new value of C.O.D. δ_o . Assuming that the section is under plane strain conditions - a not unreasonable assumption in that only a very thin surface layer approximates to plane stress - the lateral contraction of the extending material is restrained by material outside the zone and voids are subsequently formed in an area adjacent to the crack tip. The voids originate at sites of inhomogeneities in the molecular structure and for present purposes, the average distance between the sites is assumed to be the process zone size, l_o . The formation of the voids in the plastic zone allows the liquid environment to flow into the zone and to soften the next region. Although a small craze already exists at the tip of any artificial flaw in PMMA its presence may be ignored for present purposes, since the environment will be able to flow easily through this craze to begin the attack on the unvoided plastic zone. (From the appearance of the craze when viewed through a high powered microscope, it would appear that this small original craze does not become plasticized but breaks because of the subsequent extension of the material beyond it.)

(c) Stage 3 - Craze growth

The process of void formation and growth continues through stage three of the initiation process until a stable zone of oriented material separated by voids is formed. From the measurements of KAMBOUR [1969] it would then appear that on reaching a 50% void content no further void expansion takes place. The subsequent deformation behaviour of the 'wet' craze thus formed is still a matter for conjecture, but it would appear that there is a period of stabilisation when no further deformation takes place. When craze extension does subsequently occur, it is accompanied by lateral contraction and it is proposed that these two processes go hand-in-hand and maintain the constant 50% void content measured by KAMBOUR et al. [1969].

A consequence of the formation of the softened craze zone ahead of the crack is that the plastic zone (carrying a stress σ_y) must grow in length ahead of the liquid front so as to maintain equilibrium. This material is then attacked as before, thereby producing the long "environmental craze" observed in the experiments.

The mechanism which has been described above, requires the liquid to be absorbed at the craze tip faster than it travels through the voids. Such a condition is reasonable because the solid diffusion, causing plasticization of the craze tip plastic zone is over a very small length l_o , and has a high concentration gradient which is maintained by the flow through the voids.

7.5.2 Void area

The spacing of void initiation sites is designated l_o , and it is assumed that each "process zone" forms a single void. The zone arrangement shown in figure 7.15 is taken to be of a regular nature, although in practice the voids would be randomly distributed throughout the section.

If the plastic zone height δ_y is composed of 'n' zones ($n=3$ is shown) each of side l_o , then:-

$$\sigma_y = n l_o \quad (7.1)$$

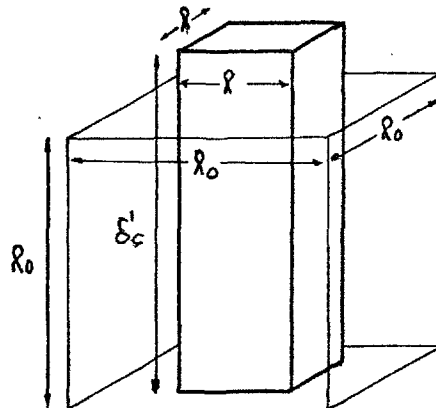


figure 7.16: Process Zone Model

Considering one of the small process zones at the tip of the crack, figure 7.16, the extension associated with the softening action causes the zone height to increase to δ_c' and the width to decrease to ' l '.

As the total extension is δ_c then:-

$$\delta_c = n\delta_c' \quad (7.2)$$

Assuming constant volume of the extending material:-

$$\delta_c' l^2 = l_o^3$$

and substituting for l_o and δ_c' from equations 7.1 and 7.2 gives:-

$$l^2 = \frac{\delta_y}{\delta_c} l_o^2 \quad (7.3)$$

The area of voiding (ψ) given by the change in zone geometry, is:-

$$\psi = n\delta_c' (l_o - l) = \delta_c (l_o - l)$$

and substituting for l from equation 7.3 gives:-

$$\psi = l_o \delta_c \left\{ 1 - \left(\frac{\delta_c}{\delta_y} \right)^{-\frac{1}{2}} \right\} \quad (7.4)$$

7.5.3 Void area in terms of COD

In the introductory section on fracture mechanics concepts (page 29) the expression for COD was given as:-

$$\delta = \frac{K^2}{\sigma_y E}$$

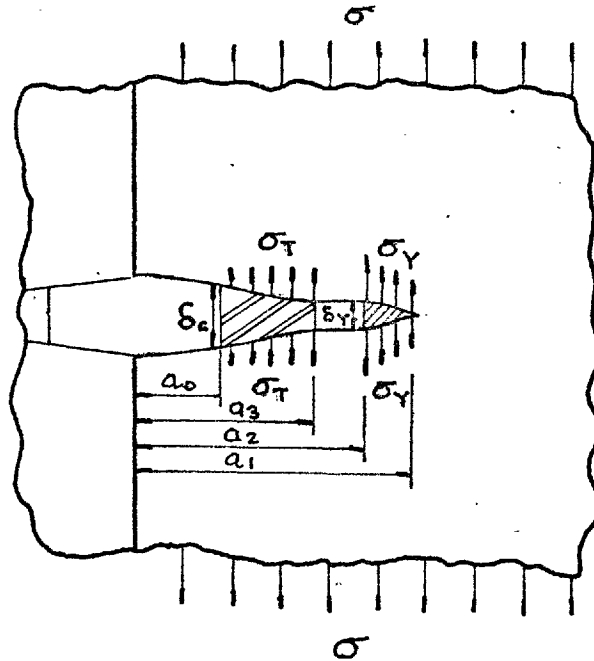


figure 7.17: Co-linear Plastic Zones for a Propagating Craze

A craze propagating from a crack may be represented by the co-linear plastic zones illustrated in figure 7.17. The original crack of length $2a_0$ in an infinite plate, subjected to a uniform stress, σ , has three zones at each end of the crack. One zone represents the craze ($a_3 - a_0$), one the craze formation region ($a_2 - a_3$) and the third, a zone of length ($a_1 - a_2$), represents the plastic zone at the tip of the craze.

The material within the crazed section is at the craze yield stress σ_c , but because of the extension and voiding, the material within each "process zone" will reduce to a section of side ' l '. Hence the stress across the craze will have fallen to a value σ_T where:-

$$\sigma_T = \sigma_c l^2 / l_o^2 \quad (7.5)$$

The plastic zone at the craze tip will carry the bulk yield stress σ_y .

Knight's analysis of the stresses within the craze in a similar situation showed that for a craze of constant thickness, the stress within the craze ($\sigma_{\overline{I}}$) remains essentially constant. (Although his analysis for the tip zone is debatable, his conclusions on the main craze stress distribution are thought to be valid.) In the present case, although the craze is not of constant thickness all the way down the length, the void content is constant, KAMBOUR [1967]. This being so, then l^2/l_o^2 will be constant and for a uniform displacement (δ_c) in the region surrounding the base of the newly formed craze, the plastic zone displacement will be equal to the initiation value, viz:-

$$\delta_y = \frac{K_o^2}{\sigma_y E} \quad (7.6)$$

and the plastic zone size will be unchanged.

The void content of crazes has been exhaustively measured by Kambour who obtained values between 40% and 60%. As explained in detail elsewhere (page 35) he finally adopted a value of 50% as being the most precise figure - KAMBOUR [1969]. Using this value, an estimate of the value of δ_c may be made.

$$\text{void content} = 1 - \frac{l^2}{l_o^2} = 1 - \frac{\delta_y}{\delta_c} = 0.5$$

$$\text{i.e.} \quad \delta_c = 2\delta_y$$

Also, using equation 7.4, the void area (ψ) is given by:

$$\psi = 0.6 l_o \delta_y \quad (7.7)$$

Whence:

$$\psi = \left\{ \frac{0.6 l_o K_o^2}{\sigma_y E} \right\} \quad (7.8)$$

7.5.4 Flow of the environment into a craze

It is now necessary to consider the means by which the environment can be absorbed into the crack/craze tip plastic zone. KAMBOUR [1964] has shown that the voids within a craze are interconnected and that there is evidence to suggest that a diffusion process controls the flow of the liquid within the craze. He found that the silvery boundary retracted as $(time)^{\frac{1}{2}}$ when a craze was unloaded and removed from the crazing environment. Since in this case the boundary represents the limit of fluid penetration in the craze it can be presumed that the flow of the environment within the craze follows this typical diffusion relationship.

For modelling purposes, the present analysis considers the craze to be a homogeneous porous medium so that the equations of motion of the environment can be derived. Liquid will be presumed to move within the pores of a craze because of the pressures upon it, the motion being resisted by viscosity and the effects of surface roughness within the pores.

A model based on capillarity as being the main reason for liquid adsorption was rejected since in this case the driving force would be constant - for a given pore size - and would certainly not be expected to follow a $x/t^{\frac{1}{2}}$ relationship as indicated by Kambour's results. Also the rate of flow would increase for small pore diameters - which would in turn mean that "thin" crazes (i.e. low K_o values) ought to grow faster than "thick" ones (high K_o 's) - in contradiction with the experimental results.

An exact analysis of the modelled situation is not possible and consequently the medium will be regarded as consisting of long filaments and modifications of the usual Navier-Stokes channel flow will be employed. Using this approach, the uniform velocity, V , through a channel of uniform cross-section is given by:-

$$V = \frac{D^2}{12\mu} \cdot \frac{d\bar{p}}{dx} \quad (7.9)$$

where D is the channel height, μ is the liquid viscosity, and $\frac{dp}{dx}$ the pressure gradient.

In a craze the channels will vary in size and spacing, and (D^2) in the above equation should be considered as the mean effective area. This is a form of D'Arcy's law which is widely used for flow in porous media.

A schematic diagram of the ways in which the environment could possibly attack a specimen with a through-thickness edge crack and the types of expected craze geometries, is shown below as Figure 7.18 (a) and (b).

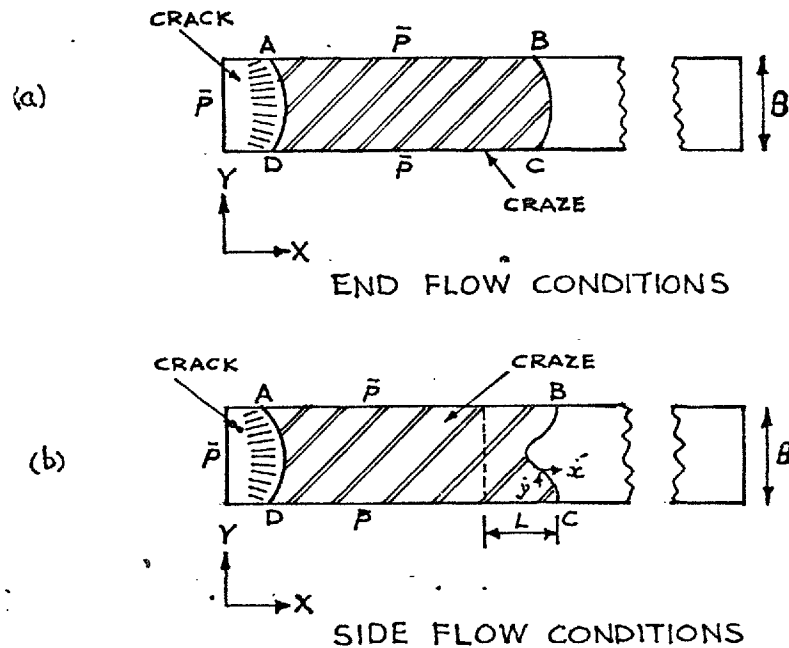


figure 7.18: Flow Conditions in a Craze

Inducing a crack into a specimen, produces a plastic zone in which the larger central area is under plane strain conditions, and the outer surface layers under plane stress. A liquid environment could attack the plastic zone in two ways:-

- (i) by softening the material in the mid-section of the plastic zone and then flowing down the craze via the end of the crack tip (AD in figure 7.18a) - producing a craze as shown.

Such crazes were observed during the craze propagation experiments (see figure 7.9).

- (ii) By softening the surface regions of the plastic zone and then flowing through the sides of the specimen (AB and CD in figure (7.18b)). Again an equivalent process was observed experimentally - see figure 7.10.

These two forms of flow will be considered separately:-

7.5.5 'End' flow of environment

Consider first, that the flow of the liquid takes place through the end of the crack AD only (figure 7.18a). It is presumed that the pressure in a newly formed void is zero and if the pressure of the liquid is $\bar{p}$ (atmospheric pressure for shallow immersion of the notch) then the pressure gradient along the craze is:-

$$\frac{d\bar{p}}{dx} = \frac{\bar{p}}{X}$$

where X is the craze length. Substitution for $d\bar{p}/dx$ in equation 7.9 gives:-

$$V = \frac{dX}{dt} = \frac{D^2}{12} \cdot \frac{\bar{p}}{X} \quad (7.10)$$

where t is the time.

Although the pressure in this case is atmospheric, it is of interest to note that it has been shown that the application of very high hydrostatic pressures can suppress crazing, BIGLIONE et al. [1969]. They found that crazing in polystyrene could be stopped when the surrounding pressure was greater than $2 K_b$. At these pressures, flaws are closed and hence no crazes are formed.

Taking the void area as being proportional to the COD, δ , from equation 7.7

$$\psi = D^2 = 0.6 l_o \delta_y = 0.6 \left\{ \frac{l_o K_o^2}{\sigma_y E} \right\} \quad (7.11)$$

whence, by integrating equation 7.10, substituting for D^2 from equation 7.11 and using the condition that $x=0$ at $t=0$,

$$x = \left\{ \frac{l_o \bar{p}}{10 \sigma_y E} \right\}^{\frac{1}{2}} \cdot K_o \cdot t^{\frac{1}{2}} \quad (7.12)$$

This expression is of the form typical for such a flow process, namely:-

$$x = \text{constant} \times t^{\frac{1}{2}} \quad (\text{for any given } K_o)$$

and shows that the craze length should depend on the parameter K_o .

7.5.6 Side flow of environment

In this case all the flow is deemed to be through the sides AB and CD of figure 7.18b, which also shows a typical resulting craze front pattern which would be expected from this type of process.

The inverted "vee" of the craze boundary is taken to represent the zero pressure condition. The pressure gradient is maintained by the side flow of the environment, but the situation is more complex than for end flow because the flow of the liquid inwards from the sides, causes the craze to spread in the 'x' direction and this spread is not uniform through the thickness. The problem thus involves a Laplace equation with moving boundaries and as such does not yield a simple solution. The present intention, however, is to establish the major variables involved in the process, and to that end simplifying approximations are made.

As the stress intensity factor, K_o , increases, the area of voiding produced and hence the axial craze velocity, dx/dt , also increases. It is reasonable to assume that a corresponding increase in the velocity, dy/dt - (see figure 7.18b)

would result, as both velocities are governed by the rate at which the environment is able to move into the voided material. This being so, the length (L) over which the pressure drops will be independent of K_o , depending instead on the ratio of $\dot{x} : \dot{y}$ and the material half thickness ($B/2$) - since flow will occur through both sides of the zone:-

$$\text{i.e.} \quad L \propto \frac{\dot{x}}{\dot{y}} \cdot \frac{B}{2} \quad (7.13)$$

This relationship is modified to:-

$$L = \phi \cdot B$$

where $\phi = \text{constant}$.

Substituting for X in equation 7.10 gives:-

$$\frac{dx}{dt} = \frac{D^2}{12} \cdot \frac{\bar{p}}{\phi \cdot B}$$

i.e.

$$\frac{dx}{dt} = \frac{1}{2\phi B} \cdot \left\{ \frac{l_o \bar{p}}{10\sigma_y E} \right\} \cdot K_o^2 \quad (7.14)$$

The flow model thus provides two relationships, equations 7.11 and 7.14 which may be used to examine the observed craze behaviour. The tests which had been performed so far, however, allowed both types of flow process to occur and specific conclusions could not be inferred from the results. A further series of tests was therefore conducted in which all side flow was prevented, in an attempt to identify the roles of the two modes of flow in the general crazing process.

7.6 SIDE AND END FLOW EFFECTS

7.6.1 'No side flow' tests

The separation of the side flow process was achieved by coating the side of the specimens - along the expected craze paths - with a silicone grease which is resistant to methanol. This grease was in turn covered by small glass plates to provide both a seal and also a uniform interface through which the craze could be viewed.

During this preparation, care was taken to ensure that no grease entered the crack, as this could have reduced the contribution of the end flow of the environment.

A large number of such specimens, containing a variety of initial crack lengths, were tested over a wide range of K_O values - the craze growth histories being measured for each specimen. In these tests no specimens fractured; all the crazes grew to a final length with a reducing propagation rate and the initial crack did not grow. The craze front geometries were similar to those in the previous tests in which the craze growth also stopped (figure 7.9). At very high K_O values (approx. $K_O > 0.6-0.7 \text{ MN/m}^{3/2}$) the bifurcations produced at the original crack became very troublesome and often obscured the craze fronts.

7.6.2 No side flow $K_m < K_O < K_n$

The results showed that for tests in the range $K_m < K_O < K_n$, the growth patterns were of exactly the same type as previously found for completely unprotected specimens. At any given K_O value, the craze growth histories were the same (within the limits of experimentation) - see figure 7.3. It is therefore inferred that for K_O values in this range, all the flow is through the end of the crack, irrespective of whether the environment is excluded from attacking the sides of the specimens. The appearance of the craze front geometries also lend support to this argument since they were of the form which the flow model predicts for an end flow process (figure 7.18a).

7.6.3 No side flow $K_o > K_n$

For values of $K_o > K_n$, no change was found in the general craze growth characteristics, a behaviour in marked contrast to that of the unprotected specimens. The rates of craze propagation and final craze lengths continued to increase with K_o until another critical value, designated K_z , was reached. For values of $K_o > K_n$ the curves of craze length versus time were all virtually identical, the rates of craze growth, dx/dt , and the final craze lengths having attained their maximum values. The value of K_z was thickness dependent being $K_z = 0.475 \text{ MN/m}^{3/2}$ for 1.5 mm thick sheet, $0.6 \text{ MN/m}^{3/2}$ for 3 mm sheet and $0.7 \text{ MN/m}^{3/2}$ for 6 mm sheet.

7.7 DISCUSSION OF RESULTS

The experimental results just presented should be capable of a rational physical explanation and one is postulated in terms of void formation. It is suggested that crazing occurs when the material at the crack tip reaches a critical strain, ϵ_c or crack opening displacement, δ_y , - a measure of δ_y being given through equation 7.6 for $K_O = K_m$.

For $K_O < K_n$ there is evidently no flow of the environment through the sides of the specimens and it is postulated that for loadings where $K_O < K_n$ the surface regions do not form the voids necessary for environmental transport. The shape of the plastic zone at the crack/craze tip allows the surface layers, which are under plane stress conditions, to move inwards without forming voids for $K_O < K_n$. The large central area, however, is under plane strain conditions and resists this inward movement, causing a triaxial stress system to exist in this region and thereby allowing voids to form.

As the K_O value is increased, the material which is collapsing inwards will eventually attain critical conditions and either break or form voids. It is thought that the voiding is more likely since the close-up photographs of the crack growth through the craze showed that a surface "skin" still persists even for very long crazes - see figure 7.25. The exact point at which the surface region becomes voided or collapses is very difficult to predict since there is a complex situation due to the voiding within the plane strain region.

When the plane stress region has eventually collapsed and/or voided, the environment is able to flow through the sides of the zone and so promote further void formation and craze growth. It is reasonable to presume that such a process would depend on specimen thickness in that as the thickness increases the plane strain region becomes proportionally larger and is able to constrain the lateral

contraction more successfully. Hence a larger value of K_o would be needed to promote voiding in the surface regions and K_n would be thickness dependent as observed.

7.7.1 Application of model

(a) End flow results

So that the experimental results may be interpreted in terms of the flow model, the predicted relationships for the flow processes must be modified to include the craze initiation value, K_m . Hence K_o must be replaced by $(K_o - K_m)$ which gives, for an end flow process (via equation 7.12):-

$$x = \left\{ \frac{l_o \bar{p}}{10 \sigma_y E_{II}} \right\}^{\frac{1}{2}} \cdot \{ K_o - K_m \} \cdot t^{\frac{1}{2}} \quad (7.15)$$

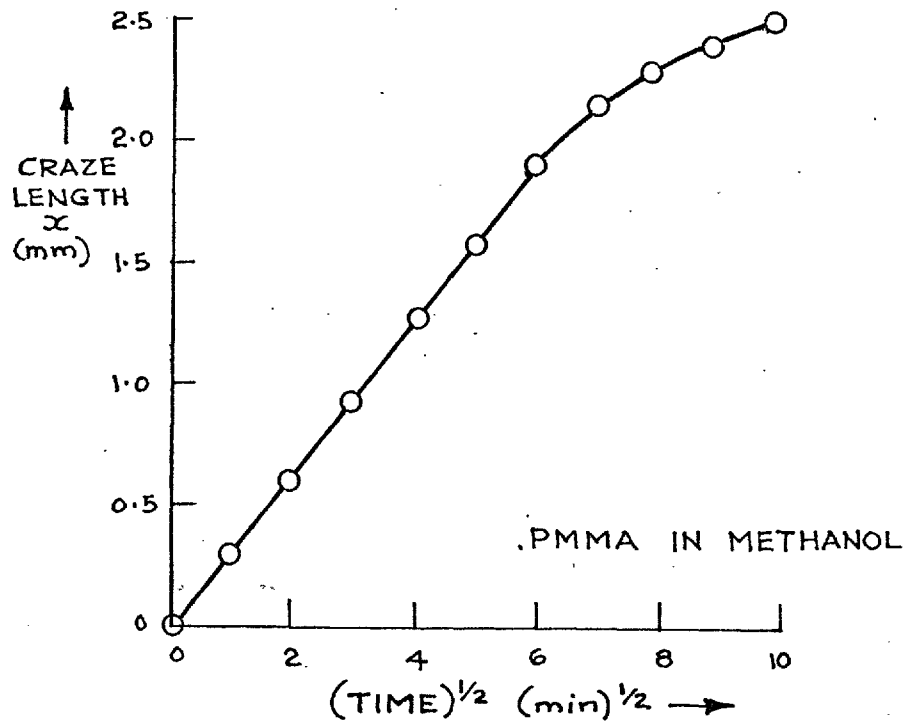


figure 7.19: Craze Length vs $(\text{Time})^{\frac{1}{2}}$ - Craze Arrest

As a check on the relationship given by equation 7.15 the results of the "end flow" tests were re-plotted on a basis of craze length (x) versus $(\text{time})^{\frac{1}{2}} (t)^{\frac{1}{2}}$.

A typical example of such curves is shown as figure 7.19. It can be seen that the relationship holds good for a large part of the growth history and only breaks down in the latter period of growth. These findings are consistent with the results of KAMBOUR [1964b] for alcohol evaporating out of a craze. The breakdown in the relationship in the present results can be explained by the fact that as the craze becomes longer, it becomes more difficult to maintain a sufficient pressure gradient and also the voids through which the alcohol has to flow will be changing in shape as the craze thickens and the surface regions collapse - both factors tending to produce craze arrest. For tests at low K_{Ic} values the stopping will be dependent on the gross stress/crack length relationship, since equilibrium conditions (see p 28) would cause the plastic zone to eventually disappear. The "no-side flow" tests however were under loadings in excess of K_{Ic} and the zone was consequently there, waiting to be converted to craze. In these cases, the pressure drop and craze structure changes are the most likely sources of explanation of the craze arrest.

A comparison between the rates of craze growth in the two major test series, i.e. when side flow is/is not prevented, is shown in figure 7.20 where the slope of the $x/t^{\frac{1}{2}}$ curves (as in figure 7.19) are plotted for all specimen thicknesses. The $x/t^{\frac{1}{2}}$ parameter (through equation 7.15) is a measure of the rate of end flow into the craze, and the results show how well the data from the two test series agree.

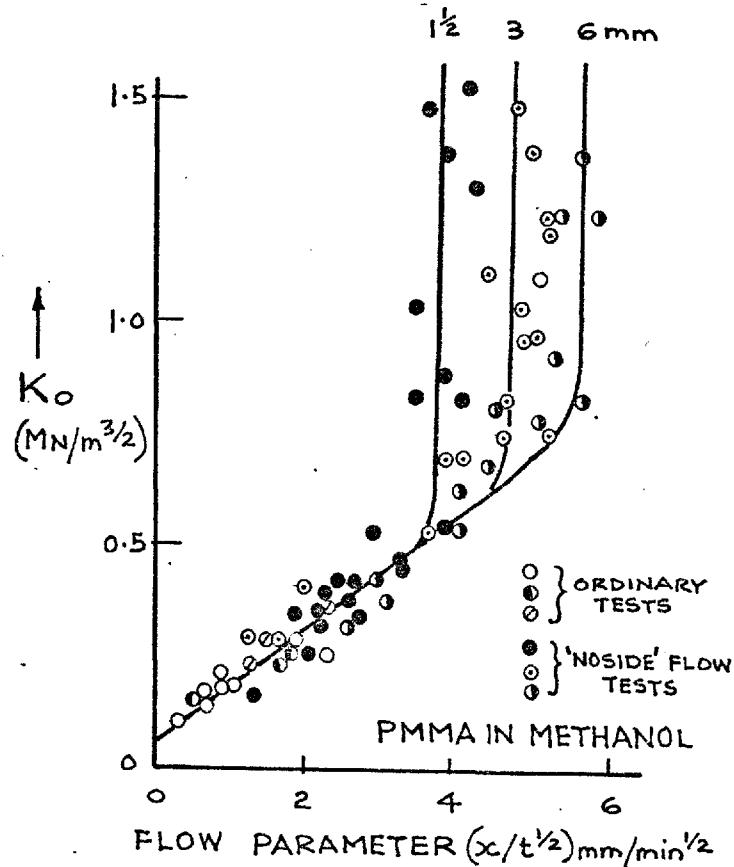


figure 7.20: Variation of Flow Parameter ($x/t^{1/2}$) with K_o - experimental values

The experimental results of figure 7.20 satisfy equation 7.15 and tend to the same lower limit value of K_m as previously obtained in the water loading tests. The K_o vs $x/t^{1/2}$ results are also independent of specimen thickness - again as expected, since at these load levels and craze lengths the lateral contractions are too small to affect the results.

The transition for $K_o > K_z$, caused by the end flow achieving a maximum speed, is clearly indicated. It is believed that this transition occurs because at this loading level, the lateral contraction and thickening of the craze have a pronounced effect on the shape of the voids through which the alcohol has to flow. It was noticeable that at any point on a given craze the Talysurf profilometer

records showed that the side indentations became markedly greater as K_o exceeded K_z . Although these records were taken from dried-out crazes and would therefore be numerically incorrect, the trends should still be valid.

The fact that there are changes in void sizes and/or shape down the craze would not affect the side flow results since this mode of environmental attack is solely concerned with the voids being produced in the region adjacent to the craze/plastic zone front. The lateral contractions in this region will be minimal and hence side flow will continue unabated. Also, one would expect the $x/t^{1/2}$ relationship to remain valid for the whole of this process since the environment has only to travel through the material half thickness (flow occurring from both surfaces).

TABLE III

Thickness (H) (mm)	K_n MN/m ^{3/2}	K_z MN/m ^{3/2}	K_n/K_z	ϕ	L (mm)
1.5	0.21	0.475	0.44	0.79	1.24
3.0	0.25	0.60	0.42	0.76	3.70
6.0	0.30	0.70	0.43	0.73	7.10

It is interesting to note that if it is presumed that the thickness variation of K_z values is caused by the same factors of constraint which caused the thickness variation of K_n , then one might expect the $K_{n,z}$ values to be in the same proportion irrespective of thickness. The ratios of K_n to K_z are shown in TABLE III and it can be seen that this ratio is, indeed, essentially constant for all thicknesses.

In addition, in all tests for $K_o > K_z$, craze bifurcations occurred at the original crack tip (see figure 7.11) - these crazes presumably initiating from the

ancillary crazes which surround the tip of a crack in PMMA (see figure 4.5).

Although these crazes did not usually grow across the whole section, energy must be absorbed in their propagation - as in polystyrene (see page 100) . Hence for $K_O > K_g$ there is the possibility of an extra source of craze propagation and the presence of such an energy sink would tend to limit the propagation of the main craze - especially where the main craze length is comparatively small. For long crazes the ancillary crazes would tend to have a much reduced effect and would not be expected to affect the side flow process.

(b) Side flow results

It has been demonstrated that for $K_o < K_n$ the environmental flow occurs solely through the end of the crack or craze. Consequently, the growth curve obtained for any K_o value $> K_n$ (figure 7.7) must presumably be the result of some combination of side and end flow effects. Equation 7.14 shows side flow to be a constant speed process for any value of K_o and it seemed likely that the constant growth rate portions of the curve for $K_o > K_n$, could be due to side flow alone.

To test this hypothesis, a craze length corresponding to the final craze speed (assumed applied uniformly throughout each test) was deduced from each craze growth history and this produced curves of the form previously found for end flow only, - figure 7.9.

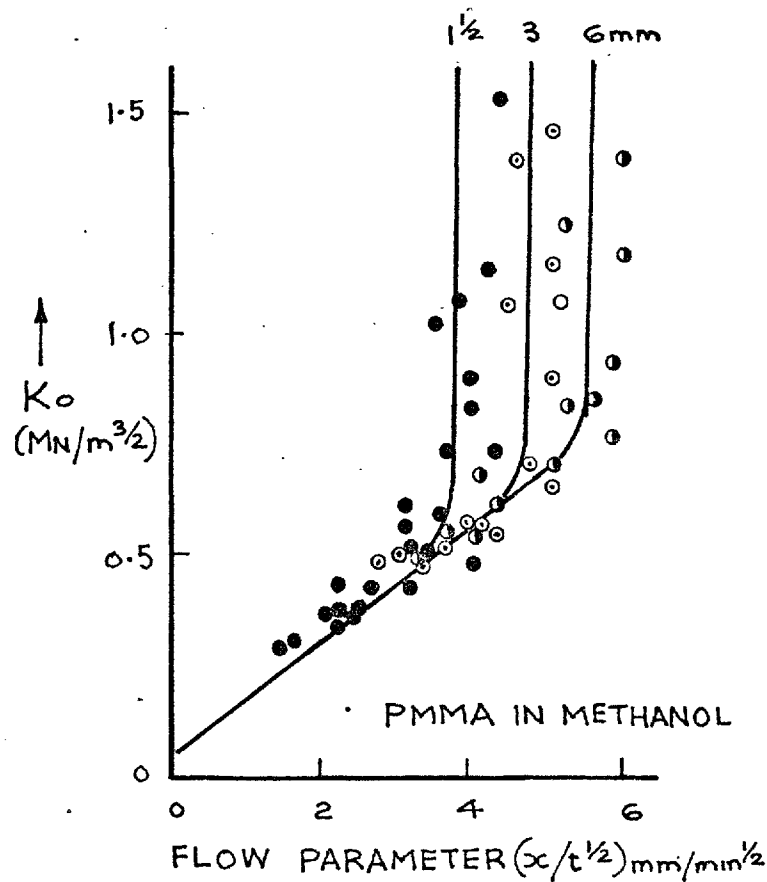


figure 7.21: Variation of Flow Parameter $(x/t^{1/2})$ with K_o - 'deduced' values

Values of the flow parameter $x/t^{\frac{1}{2}}$ from these curves, plotted as a function of K_o in figure 7.21, showed good agreement (for all specimen thicknesses) with the corresponding results involving end flow alone. It is therefore concluded that for $K_o > K_n$, the constant growth-rate part of the craze growth history is a result of side flow alone, whereas the initial part of the curve is the result of a combination of both side and end flow. The craze front geometry produced whilst the craze runs at constant speed (figure 7.10) is also commensurate with that expected for a side flow process.

Because of the limiting values K_m and K_n the predicted relationship for side flow - equation 7.14 must be modified to:

$$\dot{x}_f = \left\{ \frac{1}{2\phi B} \left(\frac{l_o \bar{p}}{10\sigma_y E_u} \right) \right\} \left\{ (K_o - K_m)^2 - (K_n - K_m)^2 \right\} \quad (7.16)$$

The constant ϕ is unknown, but can be found indirectly by predetermining an arbitrary point on each of the K_o versus $\dot{x}_f$ curves (figure 7.7). The slope (α) of the K_o vs $x/t^{\frac{1}{2}}$ graph Figure 7.20 is:-

$$\alpha = \left\{ \frac{l_o \bar{p}}{10\sigma_y E_u} \right\}^{-\frac{1}{2}} \quad (7.17)$$

- from equation 7.15

and so ϕ can be found by combining the two values. The values of ϕ were found for each thickness and are shown in TABLE III (page 174).

Comparison of these values at each thickness shows that the length, L ($= \phi B$), over which the pressure drops in side flow is indeed proportional to the specimen thickness as was presumed earlier in the analysis (page 167).

7.8 ESTIMATION OF CRAZING PARAMETERS

The equations which have been derived for predicting the craze lengths and speeds (equations 7.15 and 7.16) are couched in terms of l_o - the void site spacing.

Using the fit to the experimental results, it is possible to make an estimate of this value and also of the void size ($l_o - l$) - presuming a 50% void content. These values may then be compared with measured values of both quantities.

7.8.1 Void spacing

The void spacing, l_o , is representative of the spacing between the sites of the micro-inhomogeneities which produce voids and is presumed a constant for the material. There is good evidence from the results of X-ray scattering patterns on stressed film that this is a valid assumption - ZHURKOV [1969].

The value of l_o for PMMA can be estimated as follows:-

From equation 7.17, the slope (α) of the graph of K_o vs $x/t^{1/2}$ (figure 7.20) is:-

$$\alpha = \left\{ \frac{l_o \bar{p}}{10 \sigma_y E \mu} \right\}^{-1/2} = 6135 \text{ MN}^{1/2} / \text{m}^{5/2}$$

Using $\bar{p} = 0.1 \text{ MN/m}^2$, μ for methanol = $2.3 \times 10^{-7} \text{ MN.s/m}$

$$\sigma_y = 100 \text{ MN/m}^2 \quad E = 2000 \text{ MN/m}^2$$

(The values of σ_y and E being those appropriate to the range of craze speeds concerned - obtained via WILLIAMS [1972].)

we have:-

$$l_o = 0.122 \mu$$

In their X-ray diffraction work, ZHURKOV et al. [1969] have studied various polymers (not PMMA unfortunately) and found that when voids are produced

the spacings are typically in the range $0.1 \rightarrow 0.2\mu$.

Considering the approximations made in the present analysis, such agreement is really quite excellent.

7.8.2 Void size

Studies of void shapes in crazes have shown that they are typically spherical cavities the sizes of which range in general from $20 \text{ \AA} \rightarrow 200 \text{ \AA}$ - KAMBOUR et al. [1969].

In the present analysis, the voids have been presumed to be more rectangular in shape, but nevertheless some idea as to the likely sizes can be made by taking the average void size (β) on any transverse plane as being:

$$\beta = (l_o - l)$$

For a constant void content of 50%

$$l^2/l_o^2 = 0.5$$

and for $l_o = 122\mu$

$$l = 0.086\mu$$

hence

$$\beta = 0.036\mu = 360 \text{ \AA}$$

Considering the assumptions made in the model, this value compares well with the average main craze void size of $200 \text{ \AA}$ obtained by KAMBOUR et al. [1969] from his tests based on direct measuring techniques.

7.8.3 Craze yield stress

The crazes grown under end flow conditions may be used to calculate an approximate value for the craze section stress, σ_T , in that at craze arrest, the stresses are in equilibrium and even though there may still be an unconverted yield zone at the craze tip of the craze, the length of this craze is negligible

compared to the craze itself. (In those tests involving side flow, there was no difficulty in maintaining the pressure gradient and consequently the craze growth continued in a stable manner until eventual failure.)

Using a modified DUGDALE [1960] model, an equilibrium analysis can be derived for a two-stage plastic zone ahead of a crack tip - as shown in figure 7.15.

The solution is:-

$$\sigma = 2/\pi (\sigma_y - \sigma_T) \cos^{-1}(a_2/a_1) + 2/\pi \sigma_T \cos^{-1}(a_0/a_1) \quad (7.18)$$

For $(a_2 - a_1) \ll (a_1 - a_0)$ this solution tends to that for a single zone viz:

$$\sigma = 2/\pi \sigma_T \cos^{-1}(a_0/a_1) \quad (7.19)$$

where $(a_1 - a_0) = x$ - the craze length at equilibrium.

A graph of σ versus $\cos^{-1}(a_0/a_1)$ is shown as figure 7.22 and σ_T calculated from the slope is:

$$\sigma_T = 3.5 \text{ MN/m}^2$$

Hence from equation 7.5:

$$\sigma_T = \sigma_c \cdot \frac{l^2}{l_0^2}$$

whence $\sigma_c = 7.0 \text{ MN/m}^2$

Such values for σ_T and σ_c are by no means negligible and serve to explain why attempts to analyse craze growth in the same way as crack growth were unsuccessful.

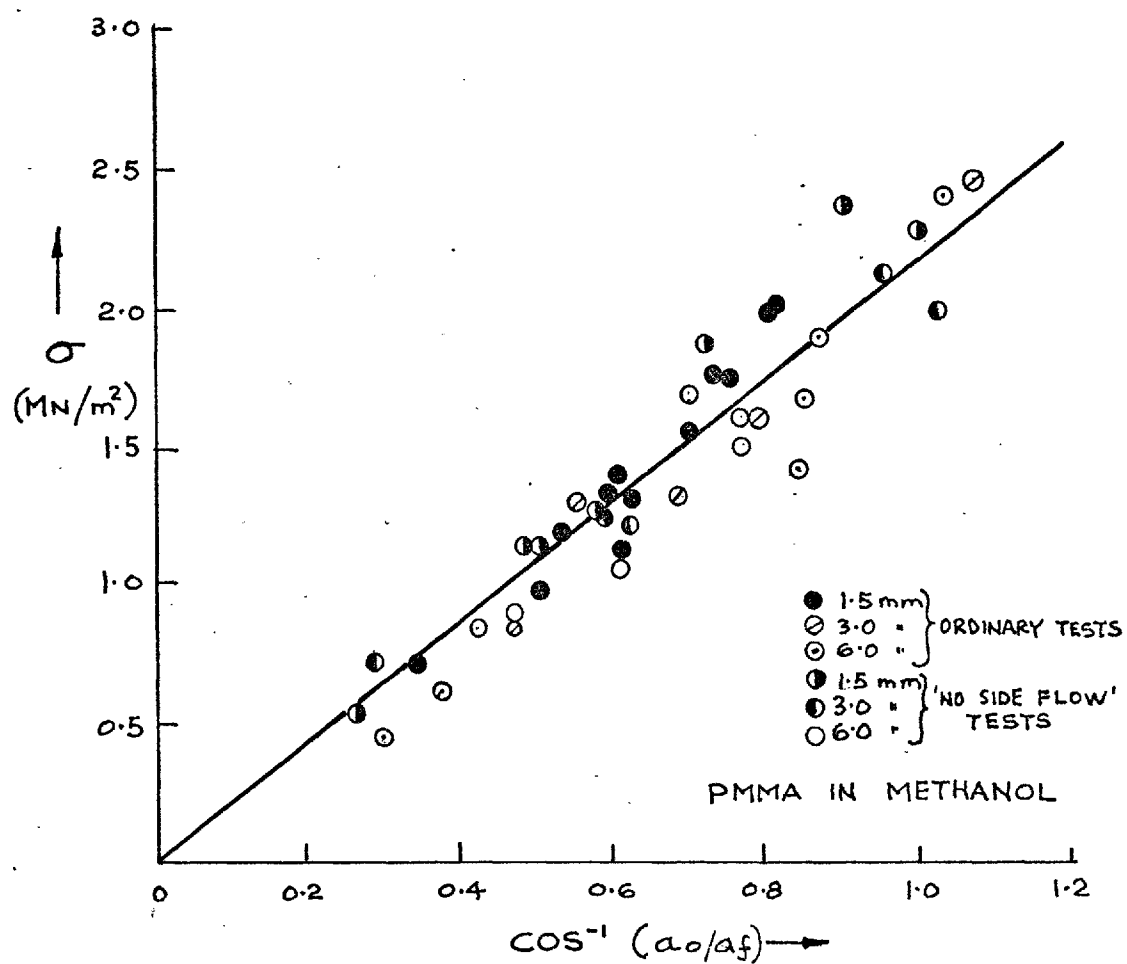


figure 7.22: Determination of Craze Stress,

7.9 FRACTURE PROCESSES IN PMMA IN METHANOL

The fracture surface patterns produced by the final crack propagation along a long "wet" craze in PMMA were totally unlike any previously observed in the notched tests on either PMMA or polystyrene in air.

Three distinct zones could be identified on the fracture surfaces, depending on the position along the craze, as indicated on the schematic diagram of figure 7.23 (the relative lengths of each region being approximately as indicated).

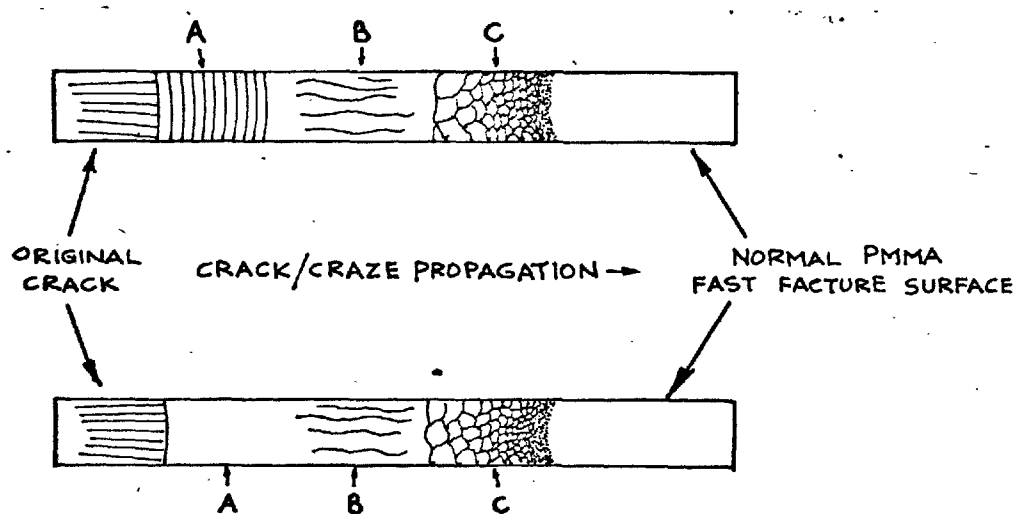


figure 7.23: Schematic View of Fracture Surface Patterns

Regions *B* and *C* were of the same type in virtually all cases, whereas there were two quite distinct patterns observable in region *A*. Each region will be dealt with separately - explanations for the observable features being purposefully brief since it is not the present intention to embark on a highly detailed micro-graphic study.

7.9.1 Region A - 'mirror' surface

In the region immediately ahead of the initial crack front, one of two distinctly different surfaces was always observed. Either the surface would appear

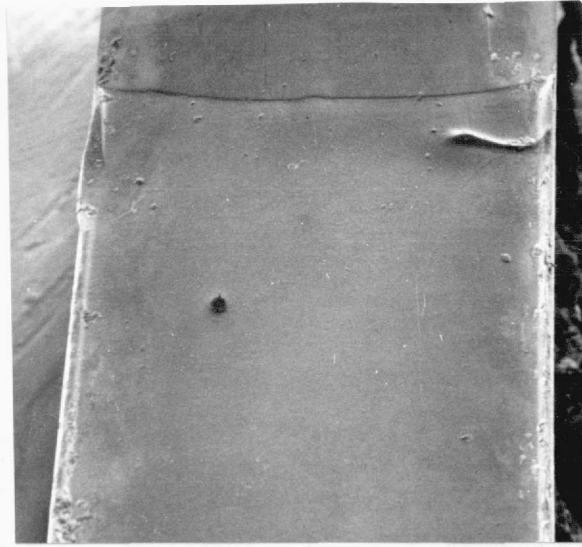


figure 7.24: 'Mirror' Fracture Surface

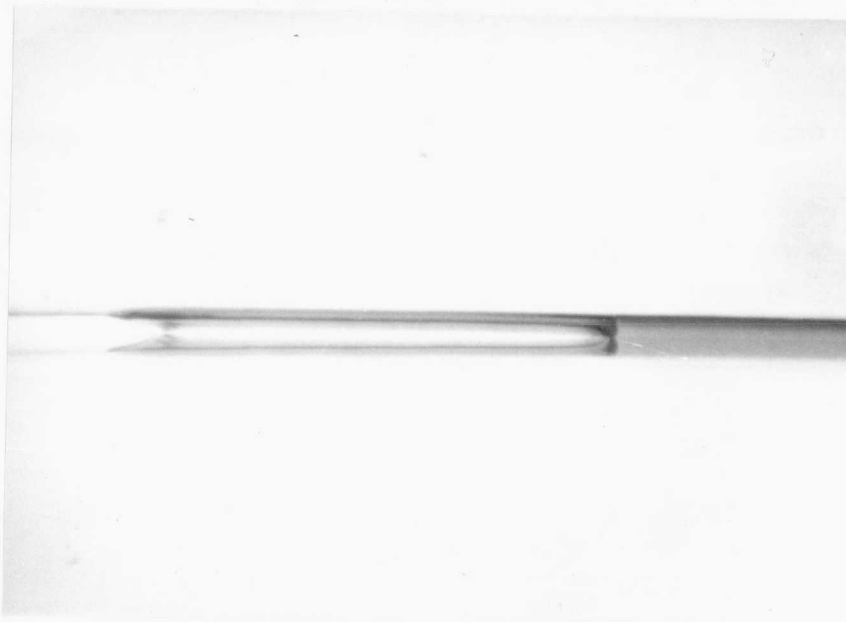


figure 7.25: Slow Crack Propagation - producing mirror surface

completely mirror-smooth and featureless or it would be patterned with a series of "stripe" marking traversing the section - as shown schematically in figure 7.23(b).

In the first case, high magnification microscopy showed that the surface was indeed smooth and a stereoscan microscope was unable to distinguish any type of regular structure or pattern - see figure 7.24 - opposite surfaces were exactly the same and it was thought therefore that the surfaces are the product of fracture straight through the centre of the craze. For some time it was presumed that the crack velocity was high since no slowly growing cracks had been observed immediately prior to total specimen failure. The difficulties in observing any type of fracture process when viewing the craze from above are ever-present - since the craze itself appears crack-like to the naked eye.

However, when the craze was observed from the side at high magnification it was seen that the crack started by growing at a very slow speed - fracture being observed to occur straight through the middle of the craze - as shown in figure 7.25. It can also be seen that the crack grows only through the central sections of the craze, a 'plane stress skin' being left intact on the surfaces - this skin only breaking when the crack had grown by a millimetre or so. By improving the normal optics on the travelling microscope and altering the lighting conditions, the progression of such a crack could be distinguished on the craze surface. Measurements of the crack length versus time characteristics showed that for the constant loading conditions the growth rate accelerated continuously until total fracture had occurred.

On the above evidence, it is postulated that this type of growth and fracture surface pattern (or non pattern to be more precise!) is caused by void coalescence on a microscale. In this region, the craze is relatively thick ($\sim 100\mu$) and any micro-features which might have been apparent immediately following cracking are probably masked by the relaxation of the highly stretched craze.

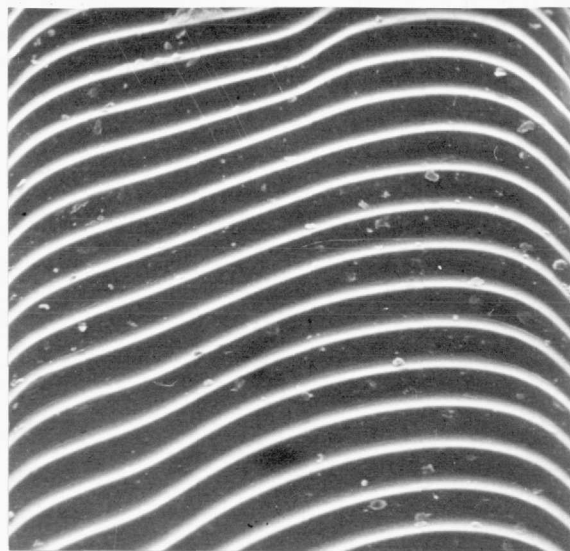


figure 7.26: 'Gear-Teeth' Markings (x 20)

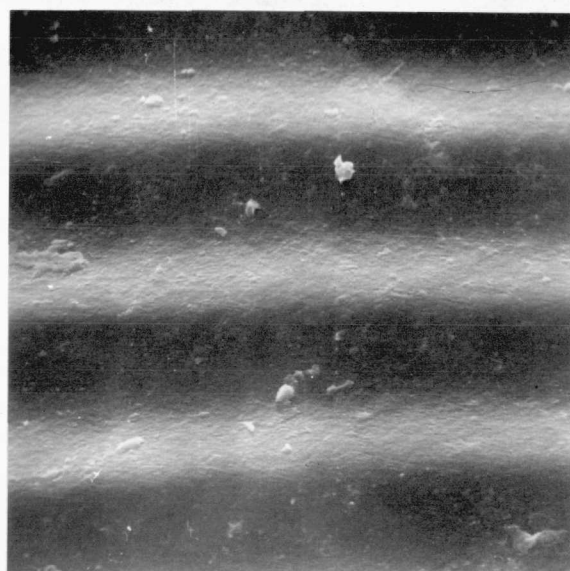


figure 7.27: 'Gear-Teeth' Markings (x 200)

7.9.2 Region A - "corrugated" surface

For the second type of fracture surface, the stereoscan revealed that the 'stripe' markings are really gently undulating corrugations caused by the crack progressing through the craze in an oscillatory fashion - see figures 7.26 and 7.27. The 'hills' and 'valleys' on opposite surfaces formed a complementary pair, the surfaces, when together, effectively meshing together like gear teeth.

This type of feature is similar to the 'mackerel' pattern observed by MURRAY and HULL [1970b] in polystyrene craze failures. They have explained the polystyrene features in terms of the crack propagating between opposing craze/matrix boundaries at high speed, as shown schematically in figure 7.28.

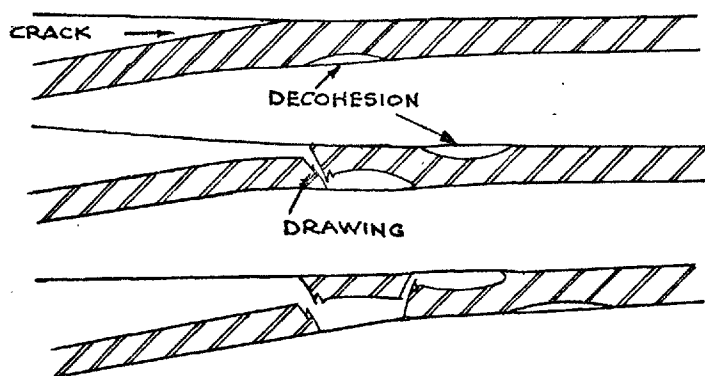


figure 7.28: Model for Fast Fracture within a Craze - HULL 1970

They proposed that the stresses generated ahead of a 'fast' crack moving along the craze/matrix interface would cause decohesion of the craze from the matrix as shown. Once such a weak zone is created, they argued that the crack would switch over onto the opposite interface; and would therefore propagate in a cyclic manner down the craze. GREEN [1971] invoked this argument to explain the 'gear teeth' pattern in the PMMA 'wet' craze case. Although this argument may be true for polystyrene, it is not a correct description of the PMMA failure.

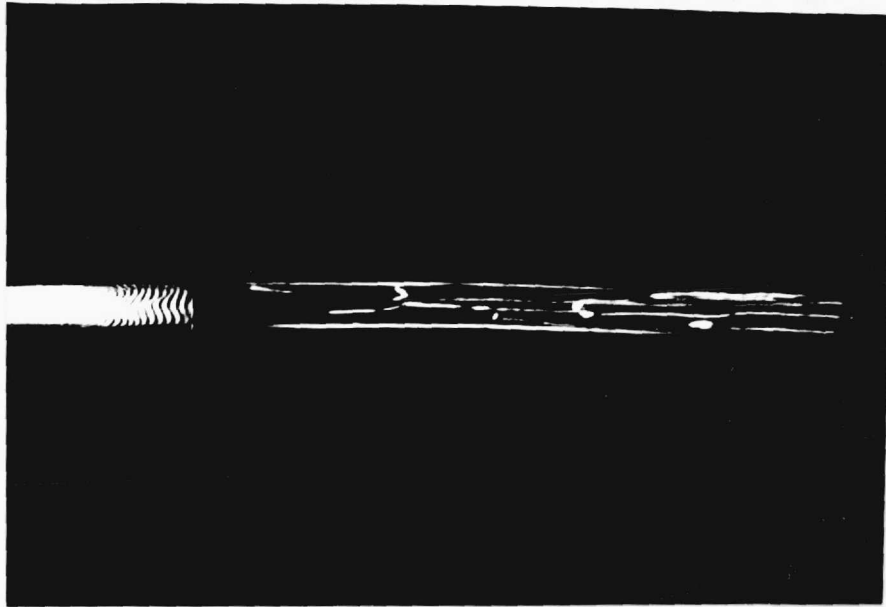


figure 7.29: Oscillatory Fracture and Residual Markings
- illustrated in a 'dried' craze

Figure 7.29 shows a photograph of the crack tip region in a specimen containing a long dried-out craze. The specimen had been inadvertently removed from the methanol just as a crack had started to grow through the craze. The 'gear teeth' pattern is clearly visible on the surface of the crack growing within the craze. The chances of having removed the specimen during 'fast' fracture - thereby halting the crack as shown - are extremely unlikely and it was inferred that this type of failure also takes place at slow speed. Direct evidence of the slow speed oscillatory motion of a crack through the 'wet' PMMA craze has since been obtained by GRAHAM [1972] using a high powered microscope/T.V. system. The crack has been seen to oscillate between the craze/matrix boundaries - though without any sign of large scale decohesion.

The reasons for the production of this type of failure are not yet fully understood. It is thought that the cyclic motion is initiated by a fault in the craze causing the crack to deviate from the central plane, since fault marks ("bumps" in

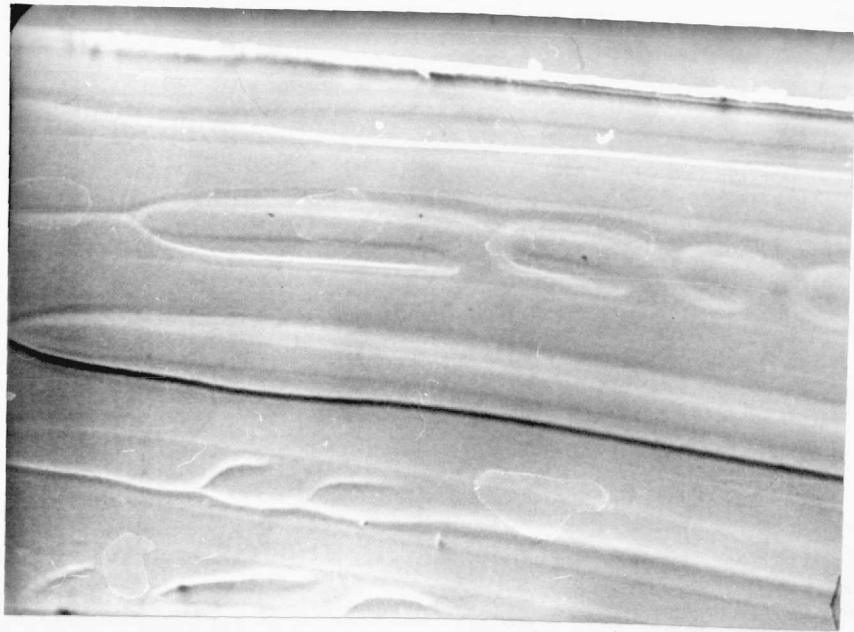


figure 7.30: Features on Central Region of Fracture Surface

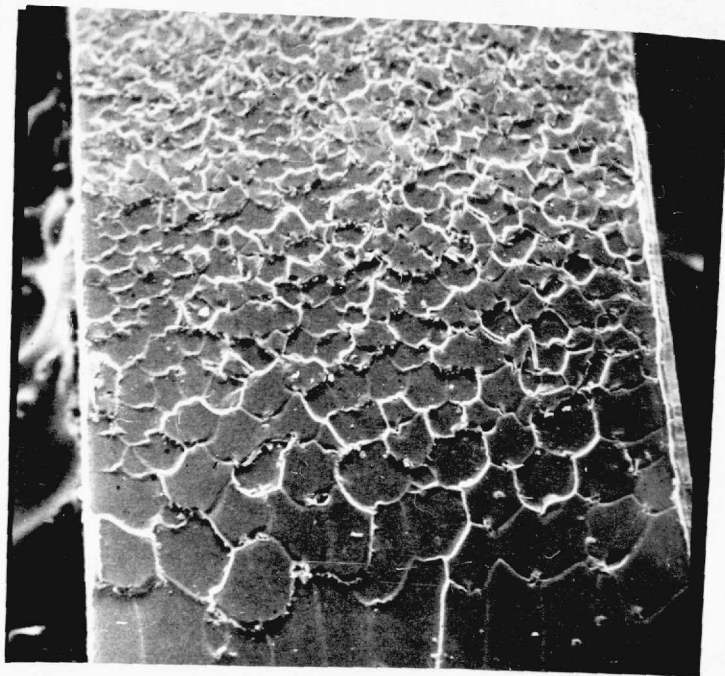


figure 7.31: Features at End of Craze Region

the craze) are nearly always observed when the "gear teeth" pattern occurs.

Further work on this subject is now in hand and Ph.D. copyright precludes further discussion at this stage.

7.9.3 Additional fracture surface markings

The markings in the central and end regions of the broken craze which have been illustrated schematically in figure 7.23 (B and C) are shown in more detail in the stereoscan micrographs of figures 7.30 and 7.31.

In both cases, as before, the opposite fracture surfaces mate exactly, the relief features on one surface corresponding to depressions on the other surface.

The 'line' markings of region B (figure 7.23) which are shown in figure 7.30 are analogous to the 'river' patterns observed in the air fractures (figure 4.16), in that they are thought to be caused by crack propagation on slightly different levels across the section thickness. The reasons for the transition from either the slow growth through the centre of the craze or the oscillatory motion between the craze/matrix interfaces are obscure as yet since the speed of crack propagation in this region is too high for easy visualization. It is, however, possible that the crack is forced onto the different levels because of an inhomogeneous craze structure in this region since this type of line marking has been observed within the structure of dried, unbroken crazes (e.g. figure 7.29).

The 'island' structure of region C (end of craze), may also be explained by the propagation of a crack through a pre-existing type of structure such as that shown in figure 7.31, since the grainy features observed on the surfaces of slowly propagating 'thin' crazes are similar in nature. The definitive type of 'island' and 'crater' features on the surface are also a definite indication that there has been discontinuous propagation along the craze/matrix interface, the crack transferring across the craze thickness in an irregular manner. Again,

the reasons for the transition of types of marking are not clear but in this case it is possible that because of the marked change in type of feature, the onset of region C represents the point of crack instability within the craze and that there is a transition in crack velocity at this section. For a full interpretation, much further work will obviously need to be done.

7.10 CLOSURE

It has been found that stressing notched specimens of PMMA in a methanol environment gives rise to craze formation and growth. Tests at a range of applied stresses on specimens containing different notch lengths have shown that the growth behaviour of the craze is controlled by the level of the 'initial' stress intensity factor K_O . For those tests where the craze ceased to grow it has been demonstrated that the rate of craze propagation is governed by the rate at which the environment can flow through the end face of the crack, and that for those tests where the craze propagated at a constant speed until eventual failure the growth rate is governed by side flow through the surface of the specimen.

The flow analysis which has been developed using simple fluids mechanics theory in conjunction with a fracture mechanics approach has provided equations which may be used to predict craze speeds. The analysis and experimental data on growth rates are in excellent agreement, as are the predictions for void sizes and spacings. The calculation for the craze stress has shown that these zones are capable of carrying considerable stresses — 3.5 MN/m^2 — although this value is much smaller than that calculated for a 'dry' craze in polystyrene ($\sim 40 \text{ MN/m}^2$) — thereby reflecting the softening action of the environment. There are aspects of the environmental attack fracture behaviour which have been ignored in this treatment, in particular the effects of pre-soaking and chemical attack have not been considered. This work is now in hand in conjunction with a detailed analysis of the initiation and propagation of cracks through environmentally induced crazes. Although the single edge notch specimen geometry which has been used in the present tests is a slightly artificial situation since both end and side flow can occur simultaneously at the crack tip, it is thought

that the basic equations and ideas which have been outlined in the preceding sections can be readily translated to describe more realistic practical situations (e.g. notches in the surface faces of sheet specimens), since the basic flow solutions should still be valid. Again, this aspect is now being investigated.

In an attempt to see how the predictions of the craze growth model would work in a different situation, it was decided to investigate the effects of cyclic load on craze propagation in PMMA in methanol.

A description of the experimental work and use of the flow model to describe the interaction of fatigue and environment follows in Chapter 8.

CHAPTER 8. PMMA IN METHANOL - EFFECT OF CYCLIC LOADING

8.1 FATIGUE TESTING

Applications in which plastics may experience fatigue failure due to the effects of cyclic loading are now becoming quite common as these materials are used more and more as loading bearing members. As it is also known that the presence of organic media is often the instigator of brittle failure at times and stress levels far below expectation, it would seem likely that the simultaneous combination of both cyclic loading and environment would result in a further acceleration of failure. It is therefore surprising to find that an examination of the literature reveals that virtually no work has been published on this combination of effects. The only reference to fatigue and environment is in some work by PRINGLE [1969] who tested PMMA in distilled water. This work is not one of the better examples of materials research since 75% of the paper is taken up by a statistical analysis of the huge scatter on his results and there is very little discussion of material response, cracking, crazing etc. Various commercial laboratories have made half-hearted attempts to carry out fatigue tests in various organic environments but have, in general, reverted to tests in air - daunted by the huge scatter produced on conventional S-N curves. The plastics manufacturers have tended to turn a blind eye to corrosion fatigue because they argue that there have not been many applications of plastics where this type of failure has arisen. This may well be true at the present time although the situation is not likely to last.

Because of this lack of data on fatigue in environments, it was decided that in view of the success in explaining the effects of methanol on PMMA under constant load, much useful information could be gleaned by extending the work to include cyclic loads. Before describing the project a brief review of the nature of

fatigue in plastics in air is given so as to familiarise the reader with some of the processes which can be involved.

8.1.1 Fatigue of plastics

Fatigue tests on plastics are carried out on a routine basis by most of the major manufacturers and other interested groups. The tests are often performed on suitably modified conventional metals testing machines which, in general, apply sinusoidally varying loads or displacements to the specimens at a range of frequencies. Reverse cycle tests, using axial loads, are quite difficult to carry out satisfactorily because of buckling problems during the compression cycle although some data is available - GOTHAM [1969]. It is generally desirable to cycle with an equal tensile and compressive stroke since this leads to a stable operating condition which is relatively simple to control. The use of bending tests to accomplish this is routine practice in metals testing, and machines for loading plastics in both rotational bending and simple flexure are now available and are frequently described in the literature. Such tests are run until some evidence of failure is detected; either in the form of microscopic cracks or complete specimen rupture. The results are usually presented in the form of S-N curves, i.e. graphs of stress amplitude versus number of cycles to failure, and these may be used in design calculations.

It is well known in metals testing, that such data is not very reliable although it is often argued that bending tests are satisfactory for measuring crack initiation. In plastics, the failures are started at inherent flaws in the material and most of the fatigue life is crack propagation from the initial flaws. It would therefore appear more logical to induce an initial crack of pre-determined size and measure its propagation behaviour, rather than rely on some natural and undetermined effect.

With metals, the stresses encountered in fatigue tests are generally well within the elastic region and consequently hysteresis effects are small. Changes

in test frequency have a minimal effect on the cyclic behaviour and the life (cycles to failure) at a given stress level is independent of frequency. Because of this, machines can be designed to run at very high speeds in order to reduce testing times and accelerate the fatigue programmes. Waveform also has little effect on the material behaviour.

In testing plastics, special care must be taken in interpreting the results of fatigue tests because the material properties are extremely sensitive to both time and temperature and hysteresis effects cannot be ignored. Any study of the dynamic fatigue of plastics involves consideration of variables such as frequency, the use of continuous or discontinuous cycling, the level of the applied stress and whether cycling is at variable stress or strain. Different loading waveforms, e.g. sinusoidal, saw tooth, square wave etc. can all affect the results.

An additional factor which has bedevilled conventional testing is that the visco-elastic nature of plastics gives rise to the generation of heat during cycling. The effect is compounded by the low thermal conductivity of plastics which results in considerable temperature rises. CONSTABLE et al. [1970(a)] tested PMMA in rotational bending and flexure and found that it was possible to produce "thermal" failures in which the material became so hot that it produced a localized plastic hinge. The occurrence of such failures is a function of the heat loss from the specimen surface and as such is determined by factors such as the area to volume ratio of the specimen. By judicious choice of specimen dimensions and/or the ambient temperature, it is possible to ensure that the failure is always of the 'true' fatigue type. However the uncertainty of the original inherent flaws still remains and an examination of the fracture mechanics approach is worth pursuing.

8.1.2 Fracture mechanics and fatigue

The simplest way of using a fracture mechanics approach is to perform the usual rotating bending or flexure tests with a range of initial notch sizes.

CONSTABLE et al. [1970(b)] have performed such tests on many plastics, using notched rotational bending specimens to obtain curves of K_{IC} versus Cycles to failure (N). This data is more useful than the normal S-N curves not only because the experimental scatter is rather less, but also because the curve effectively includes the flaw growth.

In the metals field, the fracture mechanics approach has been instrumental in correlating and explaining many of the problems encountered in the interpretation of data. In notched tensile tests, it has been shown by PARIS [1965] that a substantial portion of the crack growth history can be described by the power law:-

$$da/dN = A(\Delta K)^m \quad (8.1)$$

where ΔK is the amplitude of K level and A and m are experimentally determined constants (m is usually found to have a value around 4).

It is now known that the behaviour as described by equation 8.1 is not quite the whole story since there is evidence, GALLAHER [1970], that the power-law region is segmented into a low and high ΔK region due to changes in fatigue growth mechanisms.

A similar type of power-law relationship has been shown to apply to fatigue crack growth in rubber (LAKE [1969]) as follows:

$$da/dN \propto T^2$$

where T is the 'tearing energy' ($\equiv G$ in fracture mechanics terminology).

Because of the success in applying this form of analysis to crack growth in both metals and rubbers, attempts have been made to apply similar concepts to

plastics. BORDUAS et al. [1968] carried out centre notched tension tests using PMMA at low frequencies and found that the Paris-law holds for this material. This work was later extended by MUKHERJEE et al. [1969] who confirmed the PMMA results on other glassy plastics. The values of m (the exponent in equation 8.1) as determined from these tests was somewhere around 5. Various interpretations can be put on the values of A and m , but it is probably best at this stage to regard the equation as an experimental fact, as did Paris. Interpretations in terms of visco-elastic analyses and ductile hole growth have been mooted and while they have some interest they are certainly not proven.

8.1.3 Environmental fatigue

As far as environmental fatigue is concerned, the literature for plastics is unusually barren, as previously stated. In metals testing, recent studies have led to the suggestion of a simple, quantitative method for estimating the effects of aggressive environments on fatigue crack growth in some ultra high strength steels, WEI and LANDES [1969] have suggested a model which proposes that the rate of crack growth in a corrosive environment is considered to be the algebraic sum of the rate of growth in an inert reference environment and that of an environmental component computed from load profile and sustained crack growth data obtained in an identical environment.

$$\text{Viz: } \frac{da}{dN}_{\text{(corrosion fatigue)}} = \frac{da}{dN}_{\text{(env)}} + \frac{da}{dN}_{\text{fatigue (no env)}}$$

This simple result has been shown by Wei's experiments to be substantially correct.

With plastics, a similar procedure would be exceedingly difficult to apply as a general criterion, because one is not always sure of obtaining the same type of behaviour in air and environments. For example, PMMA fails in air by crack pro-

pagation whereas in alcohol etc. craze formation and growth occurs. Because of the previous experience with PMMA in both air and methanol it was felt that a study of the PMMA/methanol system provided the best opportunity for making significant progress in tackling corrosion fatigue in plastics. A description of this investigation now follows:

8.2 EXPERIMENTAL PROGRAMME

Because of the dearth of information available on the effects of cyclic loading on plastics in organic environments, it was felt that most progress would be made by considering only one type of loading/specimen system. For all the tests now reported, SEN specimens were used (dimensions as before - figure 4.1) and only tensile loads were applied. The only machine available which could control the low loads expected with the small PMMA specimens was the Instron Universal machine, and hence this restricted the range of test frequencies. Most of the tests were performed on this machine at frequencies $5 \times 10^{-4} \rightarrow 3 \times 10^{-1}$ Hz although a small number of specimens were tested on a prototype energy cycling machine at 30 Hz (courtesy Instron Ltd.).

A few preliminary tests on the standard Instron soon showed that at low frequencies, tensile cyclic loads produced the same type of craze growth as had been observed in the constant load tests, i.e. a single craze of considerable dimensions was grown at the crack tip - the crack remaining stationary for the majority of the test.

Before modifying the model for craze growth under constant loads to accommodate a varying load history, it was necessary to have some information on the response of craze propagation rates to a more simple type of varying load than the ramp system imposed by the Instron. Accordingly, a short series of variable load tests was conducted on the constant load machines.

8.3 CRAZE GROWTH UNDER VARYING LOADS

8.3.1 Varying K_O tests

The general test procedure was to load a notched specimen at a given K_O value ($> K_n$) and then allow the growth rate to settle at a constant speed. Having accurately measured this speed (allowing at least 3 mm of growth at constant speed) the load was changed to give a different K_O value and hence a different speed which was again measured. The K_O value was then changed once more - and so on.

Three main K_O variation patterns were used viz.

- (i) $K_O = 0.4; 0.5; 0.6; 0.8; 0.3; 0.6; 0.5 \text{ MN/m}^{3/2}$
- (ii) $K_O = 0.8; 0.6; 0.5; 0.4; 0.3; 0.4 \text{ MN/m}^{3/2}$
- (iii) $K_O = 0.3; 0.8; 0.6; 0.4; 0.5; 0.6 \text{ MN/m}^{3/2}$

Each loading pattern was repeated twice using specimens with different initial notch lengths - all the specimens being 1.5mm thick.

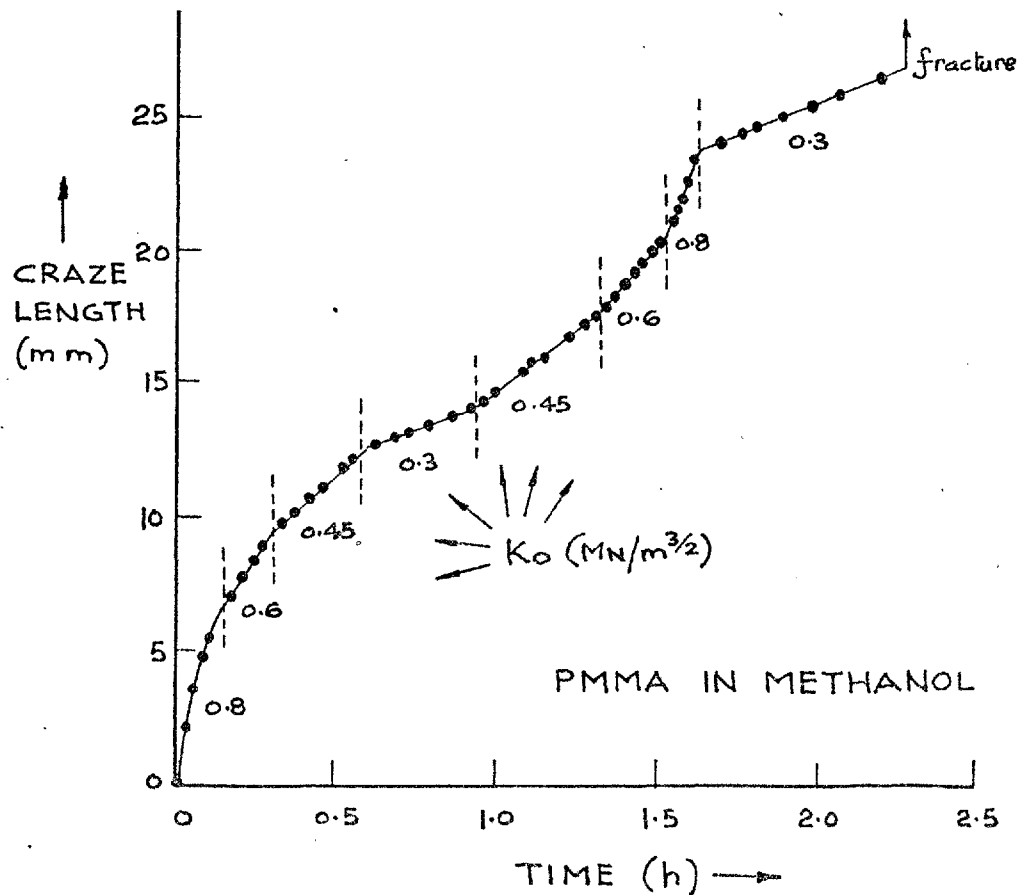


figure 8.1: Effect of Varying K_O on Craze Propagation

A typical craze growth history obtained from part of one of these tests (using variation pattern (ii)) is shown in figure 8.1. It can be seen that there is a distinct response in the growth rate to varying K_o values. The constant speeds obtained at each K_o value were measured and found to be entirely consistent with the values obtained in the conventional static load tests - reported in Chapter 7. There was no noticeable difference produced by changing the load variation pattern, a given K_o value always gave the same speed (within $\pm 8\%$) irrespective of whether the test was run after an increase or decrease in the loading condition.

On changing the K_o values, although the response of the craze growth rate was almost immediate, there was usually a short delay before a steady-state speed was achieved (as shown in figure 8.1). In constructing an analysis in a ramp loading test, these short delays would tend to be self-compensating on the loading and unloading cycles and it is thought that their effect would be small at low test frequencies.

The explanation of the changes in velocity with K_o changes is clearly that the void area (ψ) is still determined by the current K_o value and that the observed speed changes are merely responses to changes in the void area. Changes in K_o simply produce different craze tip deflections and hence different void areas.

8.3.2 Load/unload tests

As a further test on craze growth recovery, a number of ancillary tests were conducted. In the first tests, specimens with crazes growing at a constant rate were unloaded, left to stand in the methanol for short periods and then re-loaded again at the same K_o condition. For unloading periods of less than 20 minutes the craze maintained its silvery appearance (even though the relaxations within the craze must have been 'squeezing' alcohol out of the voids) and on re-load the craze started to grow once more at the same speed as before - shown in figure 8.2.

Unloading for longer than 20 minutes allowed for much more complete evacuation of the alcohol, and the craze began to lose its silver-like appearance, e.g. unloading for 30 mins produced a time-lag of 20 mins in craze re-initiation.

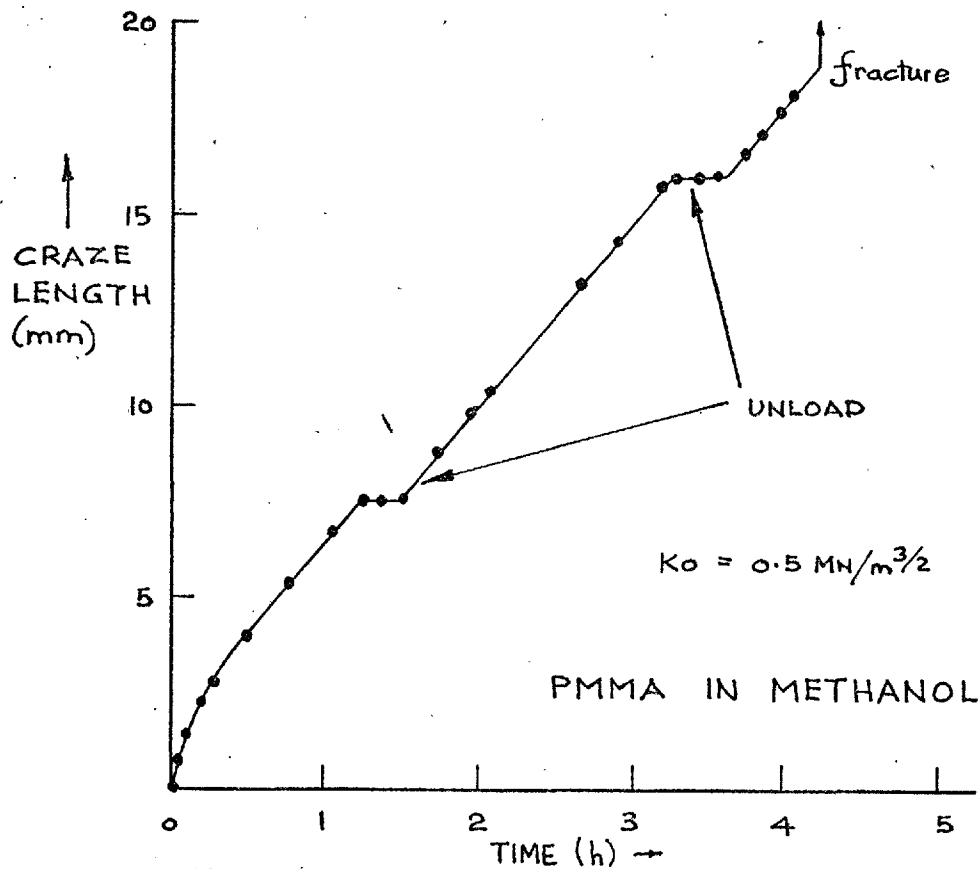


figure 8.2: Effect of Unloading on Craze Propagation

To investigate the effects of long periods of unloading and complete alcohol evacuation, specimens which had been maintaining constant speed growth were removed from the loading stations and allowed to stand unloaded for periods of up to 10 weeks, when they were again re-loaded. In most of the cases it was found that the main craze gradually regained its silvery appearance over a 2-3 hour time period (the time depending on the craze length). The only exceptions to this form of 'recovery' were two specimens in which the crazes had been grown to extreme lengths ($\approx 0.8 W$) before load removal. After twenty hours in the methanol no recovery was observed and since it was thought that soaking effects would have distorted the behaviour by this time the tests were discontinued.

In general then, it would appear that the deflection at the craze tip (which controls the growth rate), responds in an essentially elastic manner to quite drastic changes in both loading variations and load removal. This does not infer that all the deflections down the main craze are necessarily recoverable since the extensions which are imposed during craze propagation will almost certainly produce permanent 'plastic' deformation - on top of that which exists as a virtue of the very existence of the craze. The response of these deflections to changes in loading will be a function of the craze stress/strain behaviour and to date, no information is available on this subject for a 'wet' craze, although KAMBOUR et al. [1967(b)] have given some results for a dry polycarbonate craze, showing that permanent deformations were produced by comparatively small craze thickness extensions.

As a whole, however, the elastic-like response of the craze growth rate to changes in load gave good hope that a simple modification of the model derived for constant load behaviour could be used to accommodate a constant rate of change in load and hence provide some insight into the effects of cyclic fatigue on craze propagation in PMMA in methanol. The analysis of a ramp load input cycle is now given:

8.4 ANALYSIS OF CRAZE GROWTH - CYCLIC LOADING

The tests on the constant load machines have shown that the craze speed in a varying load test remains a function of the K_O level. In deriving an analysis for predicting the craze speed it is presumed that the environmental attack occurs, as before, by either side or end flow and the equations derived previously for static loads are valid at any instant in time. It is also presumed that the K_m and K_n limitations will again be operative and the analysis is derived for the particular case of zero minimum load and the more general case where the lower limit (K_O) is any value of $K_O > K_n$.

8.4.1 Cyclic Craze Growth for $K_O = 0$

The loading history is as illustrated in figure 8.3 with zero initial load.

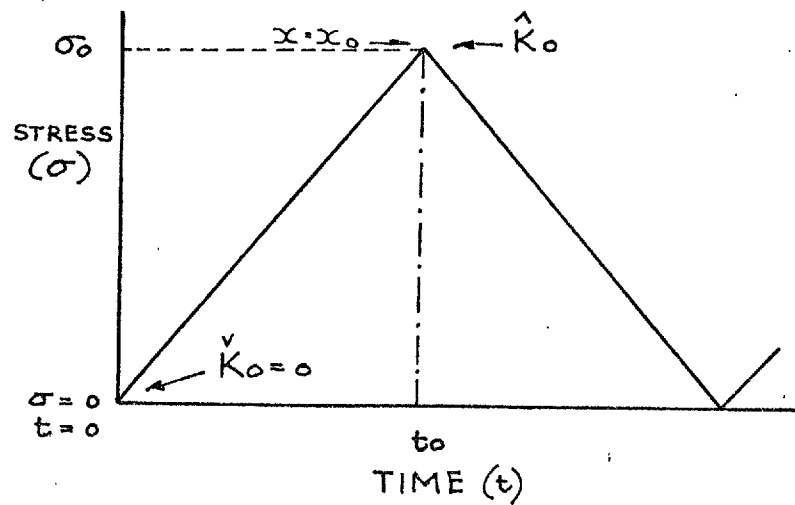


figure 8.3 Loading Pattern for $K_O = 0$

For a ramp load input:- $\sigma = At$ (8.2)

where σ is the gross stress and t , the loading time.

At maximum stress, let. $\sigma = \sigma_0$ and $t = t_0$.

Hence: $\sigma = \sigma_0 t / t_0$ (8.3)

Using equation 8.3 together with the fact that at any time:-

$$K_o^2 = \sigma^2 Y^2 a_o \quad \text{gives:-}$$

$$K_o^2 = \frac{\sigma_o^2 Y^2 a_o \cdot t^2}{t_o^2} = \frac{\hat{K}_o^2 t^2}{t_o^2} \quad (8.4)$$

where $\hat{K}_o$ is the maximum value of K_o in any cycle of loading.

From the constant load analysis (equation 7.16) the craze growth rate for side flow conditions (dx/dt) is given by:-

$$dx/dt = C(K_o^2 - K_n^2) \quad (\text{Ignoring } K_m) \quad (8.5)$$

where C is a constant.

Substituting for K_o (from equation 8.4) in equation 8.5, gives the growth rate under cyclic loading $(dx/dt)_{cyclic}$ as:-

$$(dx/dt)_{cyclic} = C \left\{ \hat{K}_o^2 \cdot t^2 / t_o^2 - K_n^2 \right\} \quad (8.6)$$

Now it will be assumed that constant speed growth only occurs for $K_o > K_n$ i.e. when $t > t_n$.

Integrating equation 8.6 and using the condition $x = 0$ until $t = t_n$ and that a mean craze speed per cycle is defined by:

$$\bar{x} = x_o / t_o \quad (x_o \text{ as in figure 8.5) gives:-}$$

$$\frac{d\bar{x}}{dt} = C \left\{ \frac{\hat{K}_o^2}{3} - K_n^2 + \frac{2}{3} \frac{K_n^2}{\hat{K}_o} \right\} \quad (8.7)$$

where $d\bar{x}/dt$ is the average speed over a complete loading cycle.

$$\text{Now let } \frac{d\bar{x}}{dt} = C(\bar{K}_o^2 - K_n^2) \quad (8.8)$$

where $\bar{K}_o$ is the "equivalent" K_o value which gives a speed $d\bar{x}/dt$ in a constant load test.

From equations 8.7 and 8.8 :-

$$\bar{K}_o = \frac{\hat{K}_o}{\sqrt{3}} \left\{ 1 + 2 \left\{ \frac{K_n}{\hat{K}_o} \right\}^3 \right\}^{\frac{1}{2}} \quad (8.9)$$

8.4.2 Cyclic craze growth for $\check{K}_O > K_n$

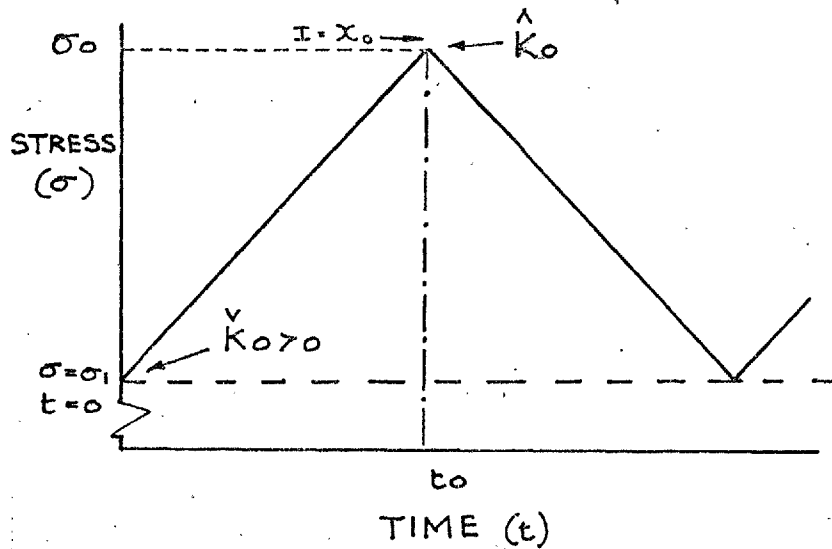


figure 8.4: Loading Pattern for $\check{K}_O > K_n$

In any given test presume cycling between stresses σ_1 and σ_0 (σ_0 = maximum stress in cycle - at $t = t_0$ and σ_1 = min. stress - figure 8.4)

i.e. $(\sigma - \sigma_1) = A't$

At $\sigma = \sigma_1$, $t = 0$ and at $\sigma = \sigma_0$, $t = t_0$

whence: $\sigma = \sigma_1 + (\sigma_0 - \sigma_1) t/t_0$

i.e. At any time:-

$$K_O = \check{K}_O \frac{(t_0 - t)}{t} + \hat{K}_O \cdot \frac{t}{t_0} \quad \{\check{K}_O = \text{Min } K_O\} \quad (8.10)$$

As before, combining equations 8.5 and 8.10 and using the boundary condition

$x = 0$ at $t = 0$ gives:

$$\frac{dx}{dt} = C \left\{ \frac{\check{K}_O^2}{3} + \frac{\hat{K}_O^2}{3} + \frac{\check{K}_O \hat{K}_O}{3} - K_n^2 \right\} = C \{ \bar{K}_O^2 - K_n^2 \}$$

where $\bar{x} = x_0/t_0$ as before

i.e. $\bar{K}_O = \frac{1}{\sqrt{3}} \left\{ \check{K}_O^2 + \hat{K}_O^2 + \check{K}_O \hat{K}_O \right\}^{\frac{1}{2}} \quad (8.11)$

Thus an analysis of this form allows for the comparison of constant load and cyclic load tests. By choosing the K_o limits from equations 8.9 and 8.11 it is possible to run cyclic tests at $\bar{K}_o$ values for which results are available from constant load tests and the rates of craze growth can be compared. To enable such a comparison to be made, two test series were conducted - using both zero and non zero minimum loads.

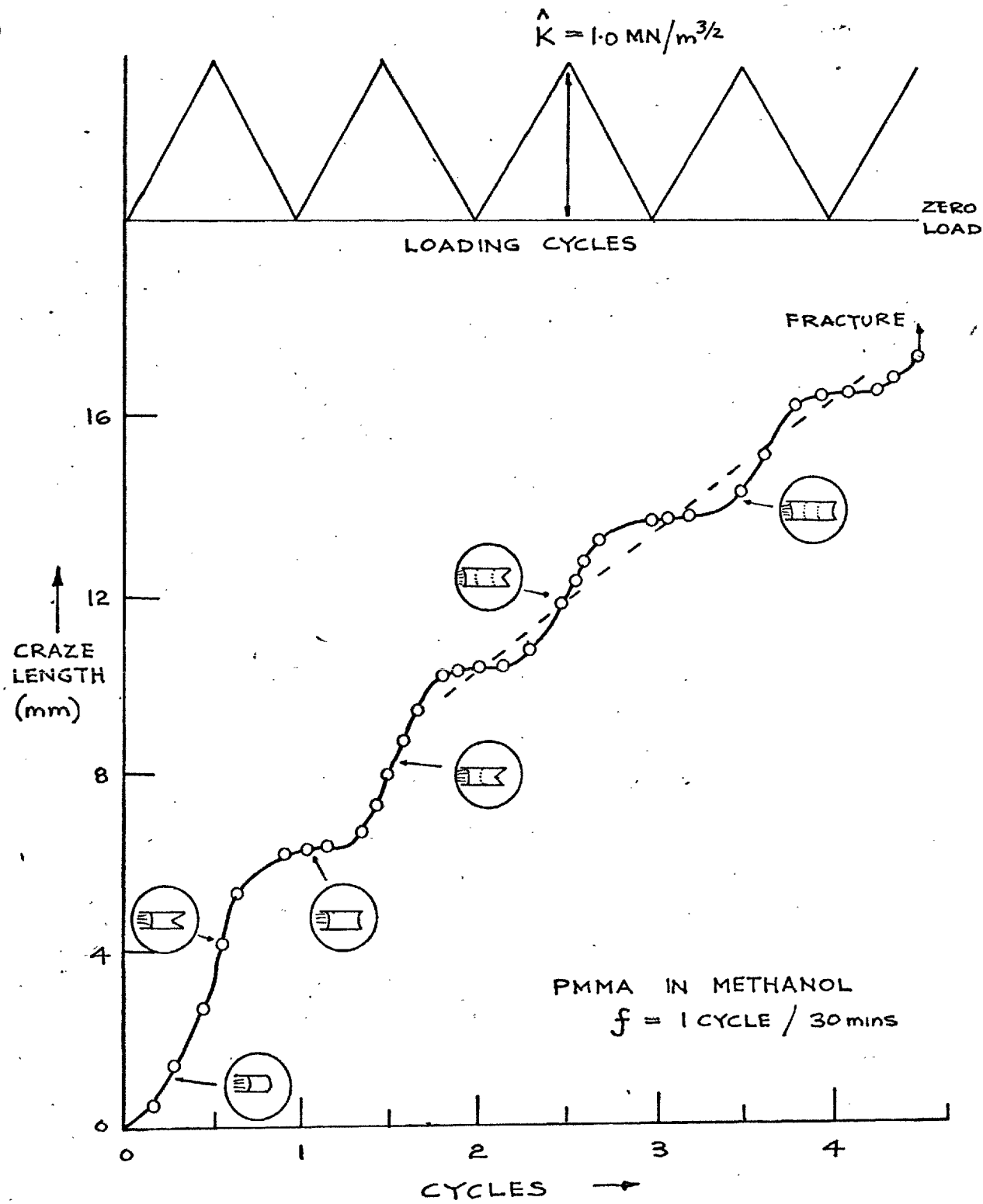


figure 8.5: Craze Growth Pattern - Very Low Cyclic Frequency

8.5 RAMP LOADING TESTS

8.5.1 Very slow cycling rates $\sim (5 \times 10^{-4} \text{ Hz})$

In order to examine the craze growth pattern in detail, an initial series of tests was performed (using the SEN specimen) at very low cycling rates (viz. $5 \times 10^{-4} \text{ Hz}$) on the Instron. The load was varied from zero to some positive tensile value (at which $K_O = \hat{K}_O$) and then decreased again, giving a ramp cycle of K_O values as shown in figure 8.5, which also illustrates the craze growth behaviour for $K_O = 1.0 \text{ MN/m}^{3/2}$. During the loading half of each cycle, the craze growth rate gradually accelerated as expected until the maximum K_O value was reached; the growth rate decreasing thereafter until the craze eventually stopped growing at $K_O = 0.24 \text{ MN/m}^{3/2}$. The cycle was then repeated as shown.

The initiation and arrest points were somewhat difficult to define precisely, since the microscope had to be re-zeroed (on the tip of the original crack) before each reading, because the specimen tended to move slightly in the grips during loading. Nevertheless, sufficient readings were obtained to show that the craze initiation and arrest condition were tolerably close to the value of K_n (e.g. $K_O = 0.24 \text{ MN/m}^{3/2}$ for arrest here c.f. $K_n = 0.21 \text{ MN/m}^{3/2}$ from constant load tests!).

The insert sketches show the form of the craze front profile and it can be seen that the side-flow "vee" pattern becomes pronounced as K_O increases and then less apparent as K_O decreases. When fracture eventually occurred, there was no obvious change in the craze growth behaviour and the process took place without any visible warning sign.

8.5.2 Cyclic loading at 10^{-1} Hz

Most of the cyclic loading tests have been performed at 10^{-1} Hz since this was a reasonably convenient frequency for the Instron to maintain for long time periods. The two main test series involved testing a large number of specimens at both zero and non-zero minimum loads. Equations 8.9 and 8.11 were then used to deduce equivalent static K_o values, $\bar{K}_o$.

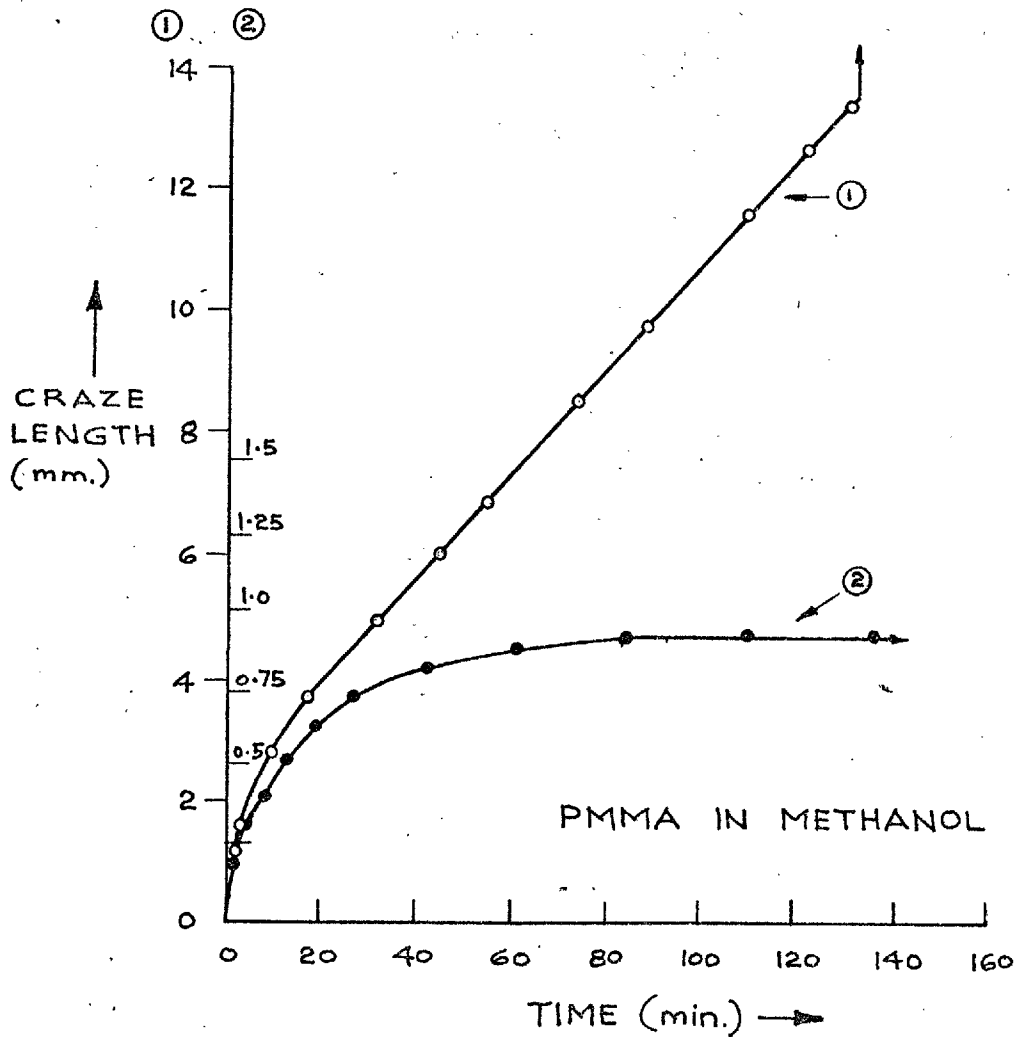


figure 8.6: Typical Craze Length vs Time Curves - $f = 10^{-1}$ Hz

As in the constant load tests, there were two types of craze growth history produced - depending on the level of K_o and these are shown in figure 8.6. For $\hat{K}_o < K_n$, craze growth started at a high rate and then eventually slowed until craze growth ceased altogether. In the second type ($\hat{K}_o > K_n$) the growth rate

eventually settled to a constant value (as before - in the constant load tests).

If it is assumed that the craze velocity is fixed by the current value of K_O at any given time, then clearly $\dot{x}$ will decrease as observed and the crazes will stop for $\hat{K}_O < K_n$. For any value of K_O , local variations in craze growth pattern - shown in figure 8.5 would not be apparent at the present cycling frequency (10^{-1} Hz) and only the average form of curve - shown as the dotted line in figure 8.5 would be apparent - as in figure 8.6).

8.5.3 Craze appearance

In broad terms, the crazes grown under cyclic loading conditions were very similar in appearance to those grown in the constant load tests. For values of $\hat{K}_O < K_n$ there was no sign of the inverted 'vee' front associated with side flow - hence lending support to the assumption that once again this behaviour is caused by end flow alone. At the craze arrest condition however, it was noticed that the craze front became very irregular and small line markings gave the front a non-uniform appearance. It would appear that the craze propagates in a most irregular manner in the last few minutes of true growth - indicating some degree of heterogeneity in the craze tip region.

In those tests growing to failure (i.e. $\hat{K}_O > K_n$), the general craze appearance was as before - the inverted 'vee' pattern asserted itself during the constant speed history. However, at slow speeds ($< 4 \times 10^{-4}$ mm/s) the grain markings, first noticed in the constant load tests (figure 7.8) once again appeared. Under cyclic conditions, this graininess was far more pronounced and widespread and did not disappear as in the constant load tests. If the hypothesis that these marks are caused by the craze being heterogeneous is true, then it would appear that cyclic loading enhances the effect because of the disturbances to the microstructure caused by the continual load reversals.

8.5.4 No side flow tests

The observed craze arrests when $\hat{K}_O < K_n$ and the craze front patterns produced, all suggest that once again the growth of the crazes is controlled by the flow of the environment with the craze. To provide a conclusive check, a short series of tests in which the side flow was cut off by greasing the specimen surfaces, was conducted. In all cases the crazes stopped growing after a short time, irrespective of the value of K_O . It is therefore concluded that the processes involved in craze growth under cyclic loading in PMMA in methanol are controlled by the flow processes and that the transposition of the constant load model is valid.

8.6 CRAZE BREAKDOWN

The onset of ultimate craze failure was more readily apparent under cyclic loading at 10^{-1} Hz. In the constant load tests, the crack growth through the craze was normally smooth and continuous and rather difficult to discern when the craze was viewed from above. Also, the crack growth period was usually short c.f. the total testing time. In the cyclic tests, failure occurred by a more random mechanism of void coalescence within the craze. The first signs of failure were the appearance of small dark 'finger' markings growing from the crack tip. These markings - representing regions of local void coalescence - would grow in a rather haphazard manner and did not usually spread across the whole section. Instead, other 'dark' regions would appear some way ahead of the crack and the various regions eventually moved towards one another - as shown in figure 8.

Eventually the regions would coalesce to spread straight across the specimen thickness and failure would occur almost immediately - by fast crack propagation. It is almost certain that the dark regions shown in the photographs are regions of void coalescence since in some cases, when the regions had started to join together, alcohol could be seen "bubbling" in and out of the regions - as the load was cycled.



figure 8.7: Void Coalescence - 10^{-1} Hz

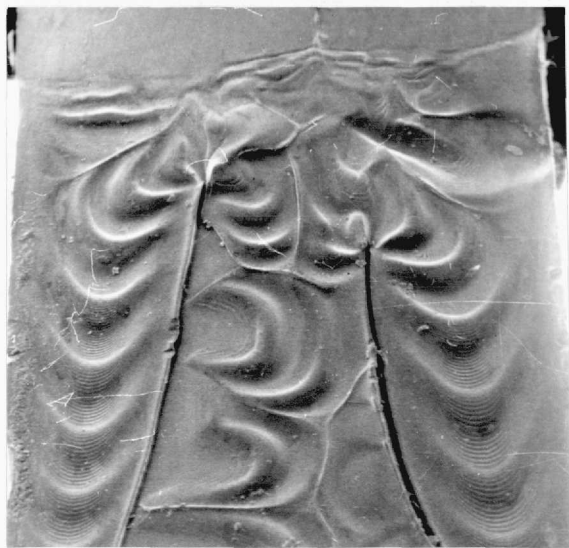


figure 8.8: Fracture Surface Markings - 10^{-1} Hz

Also, photographs taken from the side showed that at this stage, considerable crack extension had taken place. In some cases this process would take as long as 40 mins. to occur and there was a marked effect on the craze growth rate, especially during the later stages when the voids had coalesced across the section - hence increasing the effective $\overline{K}_O$ value.

The fracture surfaces of the slowly cycled specimens showed ample evidence of the void coalescence. A typical example is shown in figure 8.8. The outline of the "puddles" formed by the void coalescence are clearly visible. The repeated ripple markings on the surfaces indicates the gradual progression of both the primary and the secondary cracks. These marks are typically observed on the fracture surfaces of specimens which have failed by fatigue. In metals it has been observed that the crack growth/cycle occurs as a repetitive process of crack tip blunting followed by re-sharpening - it being this process which causes the characteristic marks on the surface. It is interesting to note that it has been shown that the crack growth part of the cycle occurs on the unloading cycle - no explanation yet being forthcoming for this somewhat surprising result.

A similar process of blunting and re-sharpening is thought to occur in the present case - although from the appearance of the islands of material left on the surface it would appear that the crack growth path is rather tortuous, the crack probably branching between the craze/matrix interfaces and the centre of the craze.

8.7 MODELLING THE RESULTS

The cyclic model was found to give a most satisfactory prediction of the growth rates in these tests - figure 8.9 shows a typical curve from a cyclic loading test ($\Delta K_O = 0 \rightarrow \hat{K}_O$) and the experimental points obtained from a constant load test conducted at the equivalent $\bar{K}_O$ value deduced from equation 8.9. Figure 8.9 also shows the curve obtained when the mode of loading was changed from constant load at $K_O = 0.45 \text{ MN/m}^{3/2}$ to cyclic load at 10^{-1} Hz - the cyclic limits as indicated giving $\bar{K}_O = 0.45 \text{ MN/m}^{3/2}$ (i.e. the same predicted condition). In both these cases the agreement is excellent.

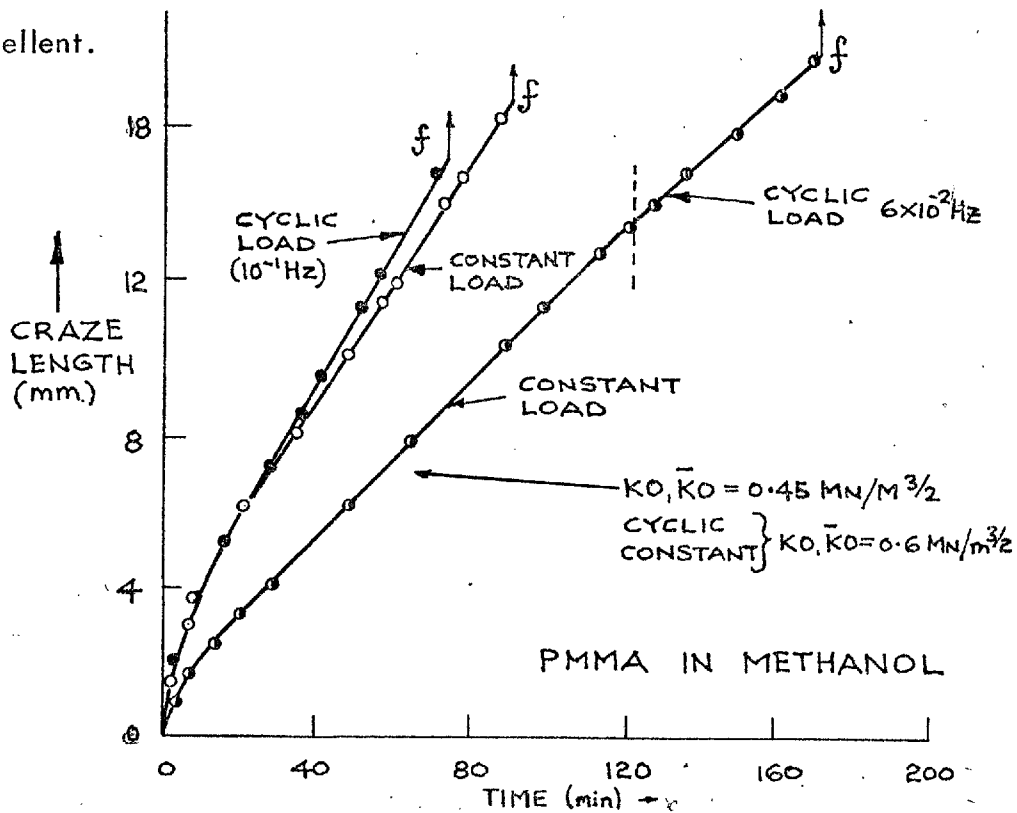


figure 8.9 Comparison of Craze Growth Due to Constant and Cyclic Loading

The comparison of the results from the main body of tests, with their constant load counterparts, is shown in figure 8.10 where the equivalent static $\bar{K}_O$ values have been calculated from equations 8.9 and 8.11 and then plotted versus the observed cyclic craze speeds.

The results of the previous constant load tests (the predicted lines of figure 7.7) are shown superimposed on the same graph, and once again the agreement is seen to be excellent for both specimen thicknesses and both types of minimum load conditions.

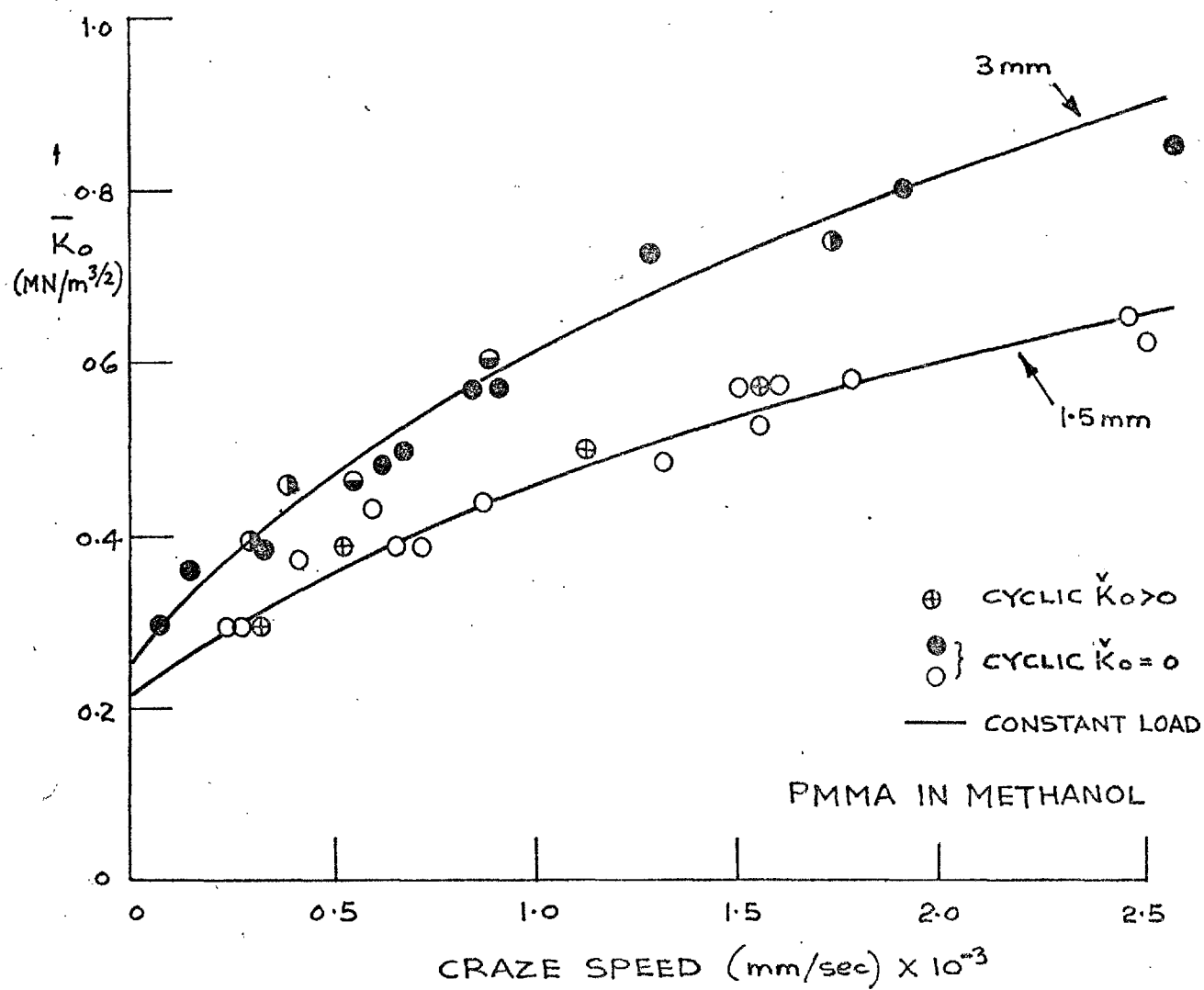


figure 8.10: $\bar{K}_0$ vs Final Craze Speed - constant load cf. cyclic load

Thus, knowing the constant speed behaviour of the PMMA craze, use of the simple modifications given in the present analysis, allows for the prediction of the craze speed for any type of ramp loading condition - at this frequency.

The validity of the assumption that the craze velocity is solely dependent on the current K_O value was further confirmed by conducting an experiment where the loading condition (i.e. ΔK_O) was changed for set periods during the test so as to observe the effect this would have on the velocity. The resulting growth rate curve is shown as figure 8.11 and it can be seen that for each change in ΔK_O value there was an equivalent change in the craze speed. The changes in velocity were almost immediate and the speeds were as would have been expected from tests at a single loading condition. Again, the change in ΔK_O is seen to reflect changes in the average void area - to which the craze responds as shown.

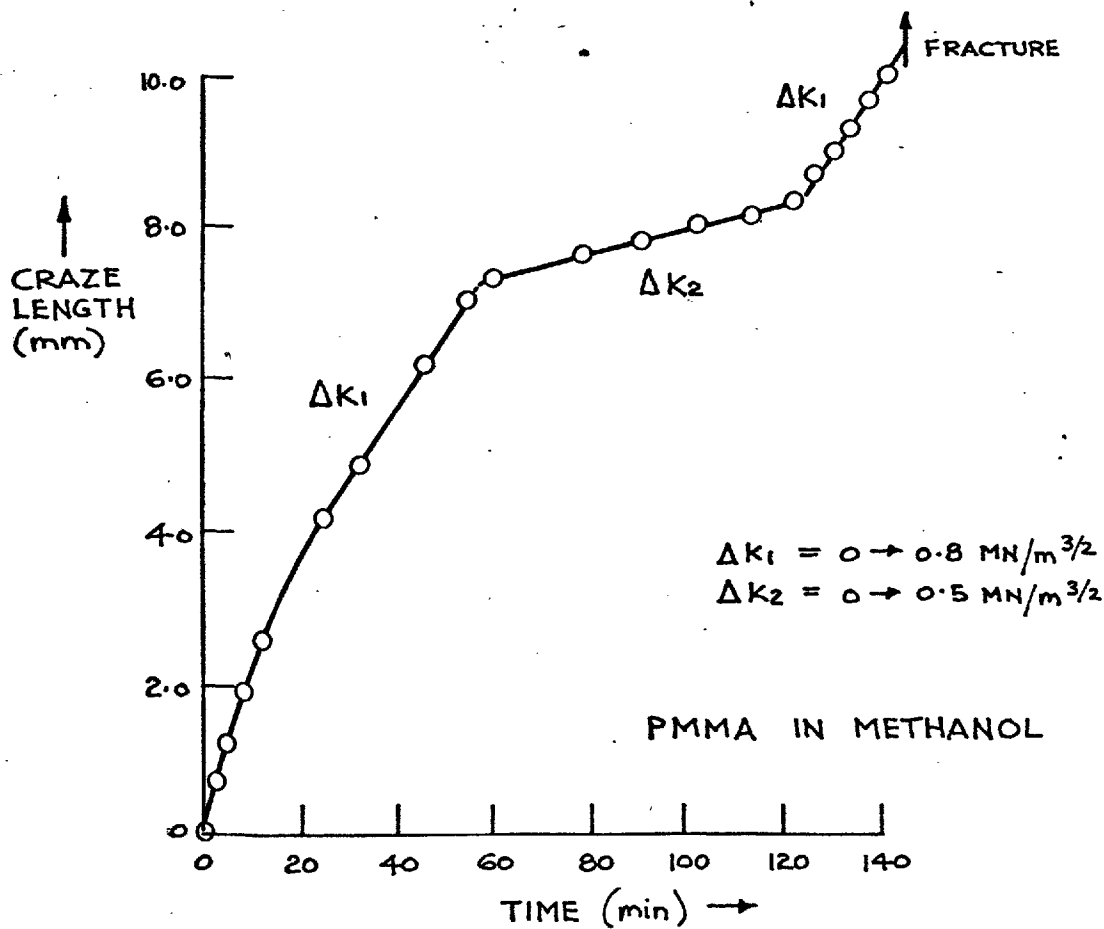


figure 8.11: Effect of Changing Load Amplitude

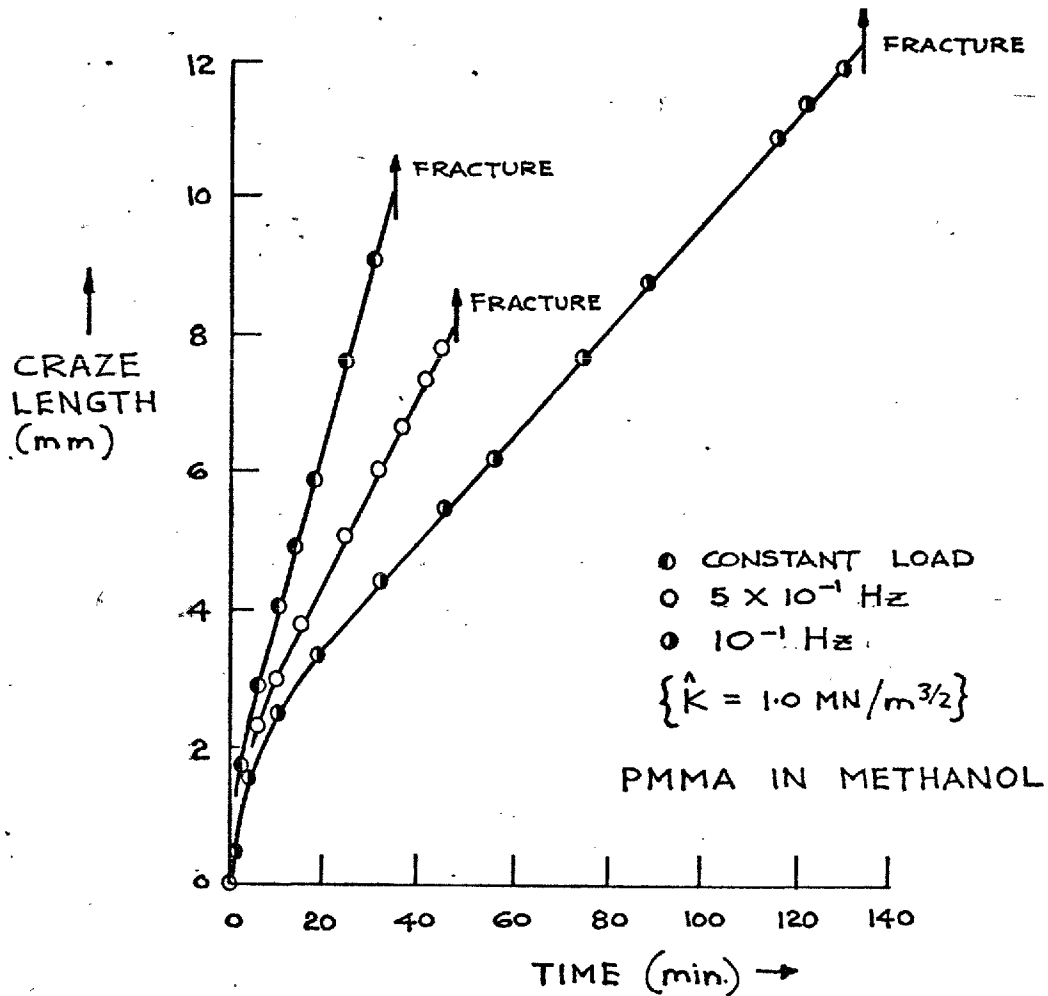


figure 8.12: Effect of Frequency on Craze Growth - $\bar{K}_0 = \text{constant}$

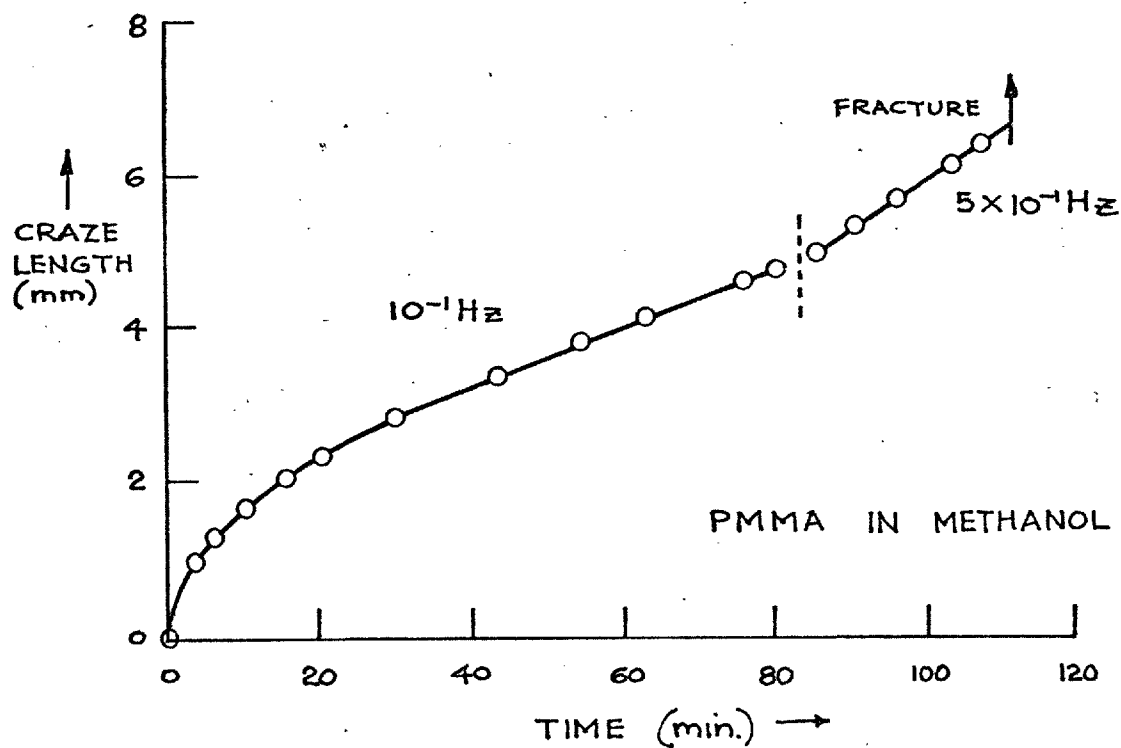


figure 8.13: Effect of Changing Frequency During a Test

8.8 FREQUENCY EFFECTS

As previously explained (page 195), because of the rate and temperature dependence of the properties of plastics, cyclic frequency can have a considerable effect on the results of tests - crack growth/cycle usually decreasing with increasing frequency although crack initiation occurs at lower K_{IC} values.

Because of the difficulties in cycling at "high" frequency on the conventional Instron (5×10^{-1} Hz is the limit - and even then the machine 'complained') only a limited series of exploratory tests have been run so as to assess the possible consequences of varying the frequency of load application.

Two brief series have been conducted. In the first case, tests were run as before on the Instron at frequencies $10^{-1} \rightarrow 5 \times 10^{-1}$ Hz; and in the second, a few tests have been made using a prototype Instron "Dynamic Energy Cycler" machine at 30 Hz (using 6 mm specimens since it was difficult to control the machine at low loads').

8.8.1 Tests at frequencies $10^{-1} \rightarrow 5 \times 10^{-1}$ Hz

All tests used 1.5 mm thickness specimens and cycling ranges were for $\hat{K}_O > K_n$. The same type of craze growth pattern as before was obtained - craze speeds settling at a constant value until final fracture. The effect of test frequency on these final speeds is illustrated in figure 8.12 which shows craze length/time curves for three frequencies - all tests being for the same loading condition. The curve for 10^{-1} Hz represents a lower bound since below 1.5×10^{-1} Hz, frequency had no obvious effect on the results (within experimental accuracy). However, it can be seen that for frequencies greater than 1.5×10^{-1} Hz there is a pronounced effect - the speeds increasing with frequency, although the final speed value is still somewhat below that obtained in a constant load test (run at $K_O = \hat{K}_O$) which could be considered in this context as being run at an infinitely high frequency. The frequency effect which is shown is certainly not due to normal variations in the tests, since the effect was observed in a single test in which the frequency was altered in the middle of the test. The result is shown in figure 8.13 and clearly illustrates the increased growth rate produced at higher frequencies.

8.8.2 High frequency tests (30 Hz)

Because of difficulties in obtaining time on a suitable testing machine, only a limited number of tests have been performed. The results on 6 mm thick specimens showed that for the initial period of the test the craze growth pattern is as before: the growth rate being greater than any previously noted - as expected from the trends in the lower frequency tests. However, the craze growth pattern was not maintained for the whole of the test as before. After a few millimetres of craze growth it could be seen that a crack was growing through the craze. When this crack approached the craze tip (within 300 μ), then instead of fast fracture occurring - as in all previous tests - the crack and craze proceeded to grow together across the specimen until eventually fast fracture occurred at some undefined instability point.

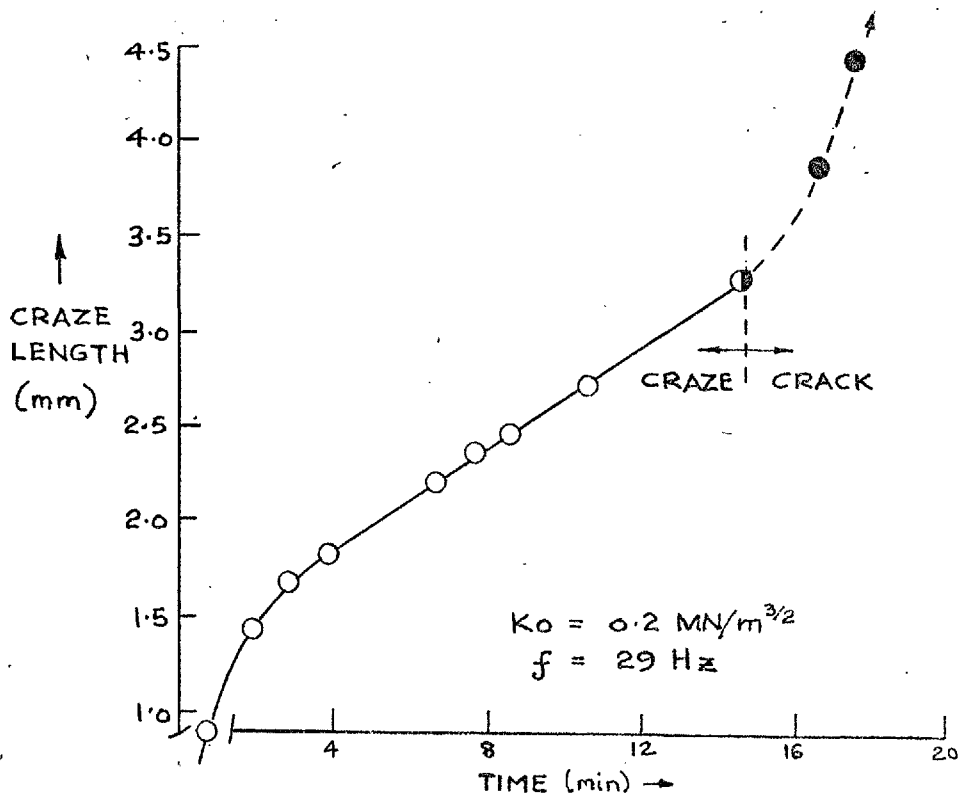


figure 8.14: Crack and Craze Growth at High Frequency ($f = 30 \text{ Hz}$)

The nature of the joint crack/craze growth portion of the test history is shown in figure 8.14. It can be seen that the growth rate accelerated as the crack traversed the specimen - presumably due to the high ΔK value since the load cycling range was held constant all through the test.

8.8. 3 Discussion of results

From the way in which the craze growth rate responds to changes in loading in both the variable static load tests and the cyclic tests below 10^{-1} Hz , it appears that there is an apparently elastic response to deformation of the material at the craze tip.

At higher frequencies, it would seem that there is a pronounced viscoelastic response and the deformations at the craze tip are not fully recoverable during the unloading half of the cycle. As a consequence, it would follow that the average void opening is greater - hence allowing an increased flow rate of the alcohol through the craze, thereby giving a higher craze speed. As the frequency is increased, the effect would be expected to become more pronounced until eventually the deformations are cycled so quickly that there is zero material response and the voids remain permanently open as in the constant load tests.

A second factor affecting the results could be the effects of viscous damping. KOSTEN and ZWICKER [1939] have proposed a model for the viscoelastic behaviour of a rubber foam and they showed that viscous damping at high frequency can alter the flow characteristics of air flowing through the foam. Converting their argument to the case of alcohol flow in a craze it can be postulated that at low cyclic frequencies the alcohol flow is slow and the viscous damping is correspondingly small. As the deformation frequency rises, the damping increases due to the increased flow of the environment through the craze pores. The viscous resistance increasingly constrains the environment within the craze and the flow rate diminishes - thereby leaving a reservoir of alcohol, which is free to attack the unconverted plastic zone. (The decrease in flow rate will reduce the damping once more and so the pattern would also be cyclic in nature.) Although this argument does have some merits the two cases are not strictly analogous since the compressibility of the air will affect the results more drastically in the rubber foam case.

It is thought the viscoelastic response is by far the more important of the two possible sources of explanation.

8.9 CLOSURE

The results of both varying static load and ramp loading tests at low frequency have shown that craze growth is again the precursor of failure in PMMA in a methanol environment. The effects of cyclic frequency can alter this pattern, but only when loading rates are of the order of 30 Hz , when a mixed mode of continuous crack and craze growth can occur.

At the low frequencies ($< 10^{-1} \text{ Hz}$) it has been shown that the craze growth rates are controlled by the 'initial' stress intensity factor, K_0 , and that the processes of end and side flow again govern craze speeds - as in the constant load tests. The modified flow model has been shown to give excellent agreement with the rates of craze propagation at different levels of loading, thus lending confidence to the analysis. The fracture through the crazes macroscopically occurs in a slightly different manner under cyclic load however, since the effects of void coalescence within the craze are much more readily apparent and cracks seem to propagate through the craze in a more irregular and haphazard manner.

Before a complete description of the effects of fatigue and environment can be obtained, much further work obviously needs to be done - in particular on the effects of cyclic frequency - and it is not imagined that the present work presents a closed book on the subject. However, as a first step, good progress has been made and it would appear that there are no fundamental difficulties in interpreting data which cannot be overcome. In examining the effects of craze growth, the most complex situation has been attempted, since failure by crack growth in an environment should be capable of interpretation by the more conventional type of

fracture mechanics approach which has been successful in explaining fracture in air. Whether cracking or crazing occurs, the effects of soaking on both the bulk and crack/craze tip material will obviously play an important role in evaluating data, since conventional fatigue tests normally run for many times the time scales used in the present tests and this aspect would also seem to be worthy of further study.

CONCLUSION

Although each of the preceding chapters of this thesis has been closed with specific conclusions relating to details of the tests and results, it is pertinent at this stage to make a few general comments which may help to provide a broader perspective on the work as a whole.

The projects which have been attempted in this work have been successful in that it has been demonstrated that fracture mechanics can be an extremely powerful tool for the analysis of failure in different polymer/environment combinations. Previously, the data which has been available on fracture processes in even the more 'brittle' glassy plastics such as PMMA and polystyrene, has been of a variable quality and the discrepancies in the numerical values of γ_p and K_{Ic} have prompted doubts as to the relevance of linear elastic theory in describing the fracture of viscoelastic materials.

The work on PMMA in air has shown that a consideration of the interrelation of crack speed and 'crack toughness', $K_{(I)c}$, has allowed for viscoelastic effects and has adequately served to correlate previous results on this material. The data presented in this work has been shown to be self-consistent in that different test systems/specimen geometry combinations have given compatible results for the slow crack propagation regime.

The extension of this approach to polystyrene has been particularly successful in that realistic test data has at last been achieved. The lower bound $K_{(I)c}$ values obtained here, are thought to be entirely consistent with practical cracking situations and the combination of these numbers with the unnotched tensile test data has provided a good working model for discussion of possible failure mechanisms. The use of a Dugdale model to assess craze

strengths has led to the proposal that there are two competing failure criteria. When 'inherent' flaw sizes are very small ($< 0.1 \text{ mm}$) the effect of flaw size becomes less critical since the prime failure mechanism is via craze instability rather than slow, controlled, viscoelastic crack propagation. This is not to imply that fracture mechanics is useless for polystyrene since there is always the possibility of large flaws occurring because of the combination of residual stresses and environments. It is obviously pertinent therefore, to extend the work in future towards an examination of sources of flaw generation, since practical failure stresses are often much lower than the value of 34.6 MN/m^2 obtained here - suggesting that environments play a significant role in initiating the fracture process.

The effects of environment on the stress cracking of polyethylene has been investigated using the same test techniques, analyses etc. as those employed for the 'brittle' glassy plastics. This is the first time fracture mechanics has been seriously used to describe crack growth in this normally ductile material. The results have given good hope that the consistency of data achieved here can be repeated on most commercial types of material to allow for a detailed examination of the nature of the environmental attack. The K_{Ic} /crack speed approach allows for the discussion of material characteristics directly, since the use of pre-notched specimens overcomes the usual difficulties associated with the effects of the nature of the surface condition in unnotched tests. (As a direct result of the present work, the fracture mechanics approach to ESC is now being used by at least one commercial laboratory to evaluate the fracture of polyethylene and it is hoped that others will follow in the future.)

The other major plastics 'failure' problem which has been investigated with some success is that of environmental stress crazing of glassy plastics. The PMMA/^{system} methanol was found to be ideal for evaluating the mechanics of craze growth under different loadings since long, single crazes were readily produced at the tips of induced flaws. The fluid flow model which has been proposed to account for the different types of craze growth pattern appears to work well for constant loading and gives a realistic picture of the ways in which environments can attack glassy plastics. Again, the use of pre-notched specimens has enabled the effects of different crack sizes to be evaluated, and incorporated in the model for growth. The derived values of voiding parameters have been shown to be compatible with values measured directly by other workers, thereby lending confidence to the validity and applicability of the model. It is hoped that the work can now be extended to account for craze growth from surface notches (rather than through-thickness cracks) to give a description of more realistic practical crazing situations. The effects of temperature, pre-soak, different environments all need to be considered to provide a more complete explanation of crazing mechanics.

The extension of the present work to account for the effects of cyclic loading has provided a cross check on the craze growth model. The case of crazing under cyclic loading is considerably more complex than is the cracking situation since the analysis is not quite so straightforward. However, the 'flow' model has been shown to give excellent correlation of data for craze growth at low cyclic frequencies - mainly because the viscoelastic response of the craze is small for slow rates of loading. It is known that frequency will have a pronounced effect on the mode of craze propagation and will obviously have to be investigated in greater detail in future.

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PAPERS 1 and 2

Paper 1 : "The Fracture of PMMA in Air - A Fracture Mechanics Approach".

- G.P. MARSHALL; L.E. CULVER; J.G. WILLIAMS - Plastics
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Paper 2 : "The Environmental Stress Cracking of Polyethylene - A Fracture
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Crack and craze propagation in polymers: a fracture-mechanics approach

I. Crack growth in polymethyl methacrylate in air

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Abstract: Crack and craze growth in polymers is of major importance in the exploitation of polymers. The concepts of fracture mechanics provide a useful framework in which to study these phenomena and in particular the effects of environments. As a first step in this study, crack growth in polymethyl methacrylate in air has been examined and a curve of fracture toughness as a function of crack speed has been determined. Of the three test methods evaluated, namely notched tension, parallel cleavage and tapered cleavage, the last is superior to the other two because crack speed can be determined with greater precision and studied more easily over a wide-range.

1 Introduction

This is the first paper to be published on a programme of studies the authors are making to examine the usefulness of the concepts of fracture mechanics when applied to a number of phenomena encountered in polymers. The concepts were developed for metals, although there is ample evidence^{1,4} that polymers obey the same over-all rules for brittle crack propagation. Certainly these concepts have not provided all the answers even in the limited fields where they have been applied, but they are the only ones to give a consistent and logical framework in which the phenomena may be discussed. The over-all simplicity of the basic metals-based theory must be modified when polymers are discussed to include rate effects. The concept of a fracture-toughness parameter which is a function of crack speed has been shown³ to be applicable and previously encountered difficulties can be overcome.

Armed with this concept the authors propose to examine environmental stress cracking in polymers. In such cases a crack or craze will grow under low stresses in the presence of certain environments. This mode of failure is of great importance for the future exploitation of polymers and it is considered that this approach provides meaningful parameters and test methods for their determination.

This paper examines the crack growth of polymethyl methacrylate (PMMA) in air and determines fracture toughness as a function of crack speed with particular emphasis on the low-speed region. Three test methods will be examined and their relative merits will be discussed.

2 Fracture-mechanics concepts

Fundamental work on the use of energy methods for investigating fracture problems is attributable to Griffith.⁵ He suggested that the difference between experimental and theoretical values of tensile strength is due to the presence of small flaws which act as stress raisers in a loaded specimen. For the case of an infinite plate containing a central crack and loaded in tension, he postulated that unstable fracture would occur if, for a small increase in crack length, the

energy released became equal to or greater than the energy required to form new surfaces, namely if

$$\frac{\partial u}{\partial a} \geq \frac{\partial \gamma}{\partial a} \quad (1)$$

where u is the elastic strain energy, γ is the surface energy, and a is the crack length.

This led to a critical stress criterion of failure, namely

$$\sigma_c = (2\gamma E/\pi a)^{1/2} \quad (2)$$

where σ_c is the critical stress, E is Young's modulus and γ is the surface energy.

Equation 2 cannot fully describe the fracture process since it neglects the effects of irreversible work in the plastic zone which is formed at the tip of a crack. However, the influence of the plastic zone on the stress field is small and solutions of the form of eqn 2 may be used where the parameter replacing γ incorporates the plastic work effect.

Irwin,⁶ following Westergaard,⁷ gave stress-function solutions relating the stress field in the vicinity of the crack tip to the applied stress in this form. Referring to FIGURE 1, the stresses may be expressed thus:

$$\begin{aligned} \sigma_x &= \frac{K \cos(\theta/2)}{(2\pi r)^{1/2}} [1 - \sin(\theta/2) \sin(3\theta/2)] - \sigma_{ox} \\ \sigma_y &= \frac{K \cos(\theta/2)}{(2\pi r)^{1/2}} [1 + \sin(\theta/2) \sin(3\theta/2)] \\ \sigma_z &= \frac{2\nu K \cos(\theta/2)}{(2\pi r)^{1/2}} - \nu \sigma_{ox} \text{ (plane strain)} \\ \text{or } \sigma_z &= 0 \text{ (plane stress)} \\ \tau_{xy} &= \frac{K \cos(\theta/2) \sin(\theta/2) \cos(3\theta/2)}{(2\pi r)^{1/2}} \\ \tau_{yz} &= \tau_{zx} = 0 \end{aligned} \quad (3)$$

where σ_x , σ_y , σ_z and τ_{xy} , τ_{yz} , τ_{zx} are the direct and shear stresses in Cartesian co-ordinates, ν is Poisson's ratio, r and θ are polar co-ordinates with an origin at the crack tip (FIG 1) and K and σ_{ox} are stress field parameters.

Close to the crack tip σ_{ox} is very small compared with σ_x and is neglected. K is designated the stress field intensity factor and is the only parameter which relates the stress field in the vicinity of the crack tip

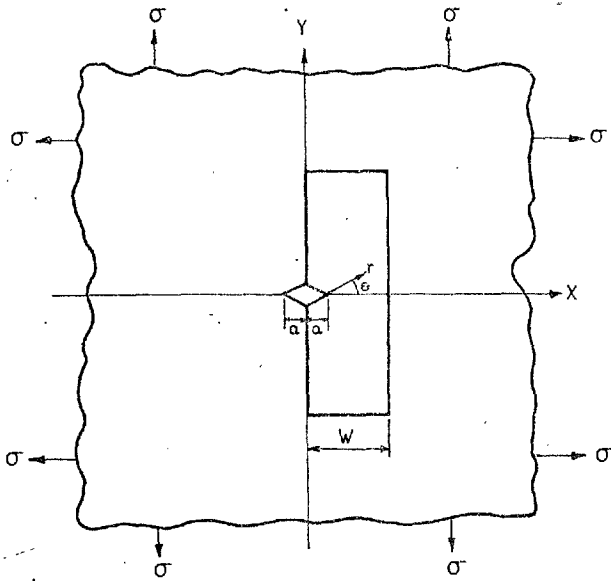


FIG 1 Single-edge-notch specimen in relation to infinite plate

to the loading and geometry of the system. Its value needs to be determined for the particular model being considered.

Since the elastic stress field is essentially described in terms of K , any fracture criterion must be related either to K or to the applied stress σ . At fracture, experience shows that σ is not constant on either the gross or the net area and it is therefore postulated that $K = \text{constant} = K_c$ at fracture.⁶ Although K_c is a material property it is not implied that its numerical value is necessarily constant. As with other material properties, its value is dependent upon a number of variables, eg temperature, strain rate and previous history.

An excellent summary of K_c concepts is to be found in Reference 1.

Three modes of cracking may be envisaged, namely opening, sliding and screw sliding. When a crack propagates in the opening mode the crack surfaces are displaced normally to one another, whereas in the two sliding modes the surfaces slide one over the other either in the direction of the crack growth or normal to it.

However, for a given mode of crack extension, K_c should be independent of the testing system used if fracture mechanics concepts are justified. The three test methods considered in the present paper, all causing the opening mode of crack extension, use plate specimens in (1) single-edge-notch tension, (2) parallel cleavage, and (3) tapered cleavage.

3 Application of concepts

3.1 Single-edge-notch tension

With reference again to FIGURE 1, for an infinite plate containing a central crack of length $2a$,

$$K_c = \sigma(\pi a)^{1/2} \quad (4)$$

In a plate of finite width W , where $a/W > 0.1$, the proximity of the free edge of the plate influences the elastic strain energy field in the vicinity of the crack tip. Eqn 4 is then no longer valid, but a more exact solution⁸ gives

$$K_c^2 = \frac{P^2}{B^2 W} [7.59 (a/W) - 32 (a/W)^2 + 117 (a/W)^3] \dots (5)$$

where P is the applied load, B is the specimen thickness, W is the specimen width and a is the crack length.

3.2 Parallel cleavage

For the configuration shown in FIGURE 2(b) a first approximation to the value of K_c , obtained by regarding the specimen as a pair of built-in cantilevers, is, for small ratios of H/a ,

$$K_c = 2\sqrt{3} \cdot \frac{Pa}{BH^{3/2}} \quad (6)$$

where P is the applied load, B is the specimen thickness and $2H$ is the specimen width.

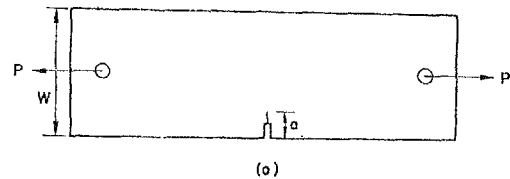


FIG 2 Specimen shapes

- (a) Single-edge-notch
(b) Parallel cleavage
(c) Tapered cleavage

The built-in cantilever assumption is not strictly justified for such a cleavage specimen, however, and a more exact solution,⁹ using a boundary collocation procedure, gives

$$K_c = \frac{Pa}{B_c H^{3/2}} [3.46 + 2.38 (H/a)] \quad (7)$$

where B_c is the crack width.

There are limitations on this solution. It is not valid for $a/H < 2$, physical considerations suggesting that an interaction between the stress fields from the applied load and the crack tip is likely to occur.⁹ The influence of the remote edge of the plate also limits the validity to cases where $a/H < (q/H) - 1$ (FIG 2).

The bending stresses in the arms of a cleavage specimen can cause a propagating crack to deviate from the line of symmetry, and it is necessary to impose some form of restraint on the crack. A simple solution suggested by Berry¹⁰ is to machine side grooves along the line of symmetry to constrain the crack along that axis. Such grooves could disturb

the stress field, however, and the numerical solution is no longer valid. It is then necessary to express K_c in a more general form.

In terms of specimen compliance the Irwin-Kies¹¹ relation gives

$$K_c^2 = \frac{P^2 E}{2B_c} \frac{dc}{da} \quad (8)$$

where c is the specimen compliance.

An approximate compliance calibration, from beam theory,¹² is given by

$$\frac{dc}{da} = \frac{8}{EB} \left(\frac{3a^2}{H^3} + \frac{1}{H} \right) \quad (9)$$

but in the absence of an exact solution an experimental calibration is necessary for this type of specimen.

3.3 Tapered cleavage

For the configuration shown in FIGURE 2(c) a combination of eqns 8 and 9 yields

$$K_c^2 = \frac{4P^2}{BB_c} \left(\frac{3a^2}{H^3} + \frac{1}{H} \right). \quad (10)$$

Hence, if a specimen is designed such that

$$\left(\frac{3a^2}{H^3} + \frac{1}{H} \right) = \text{constant} = M \quad (11)$$

the stress intensity factor is independent of crack length and a more stable test can be achieved.

The relationship in eqn 11 is strictly satisfied only by a curved profile but it is possible to produce a straight-edged tapered specimen in which dc/da will vary only marginally over comparatively large crack growths. A numerical solution, using boundary collocation methods, of such a specimen is available¹³ from which compliance calibration data may be obtained and a choice of specimen configuration may be made.

Side grooves to control the crack are necessary, as before, but in this respect also the tapered specimen has an advantage over the parallel one. The tensile stress due to bending is

$$\sigma_x = \frac{6Pa}{BH^2} \quad (12)$$

which, with eqns 10 and 11, gives,

$$\sigma_x = \frac{3a}{H^2} \left[K_c^2 \left(\frac{B_c}{B} \right) \times \frac{1}{M} \right]^{1/2} \quad (13)$$

Differentiation shows that the maximum value of σ_x occurs when $a = H/\sqrt{3}$, i.e. for a tapered specimen the risk of the crack deviating from the axis of symmetry reduces if the crack propagates beyond that value.¹²

4 Test programme

A diagram of the loading apparatus used in the crack propagation tests is shown in FIGURE 3. It is basically a batch of single-lever loading systems incorporating pre-tensioning and constant-load devices. Crack extension measurements were made with a travelling microscope when the crack propagation speed was below 10^{-3} in/s but above this limit a cinematograph-camera technique was employed.

All specimens were carefully machined from sheet material and allowed to normalize at a temperature of 20°C and a relative humidity of 50 per cent. Pilot tests indicated the necessity of having perfectly formed

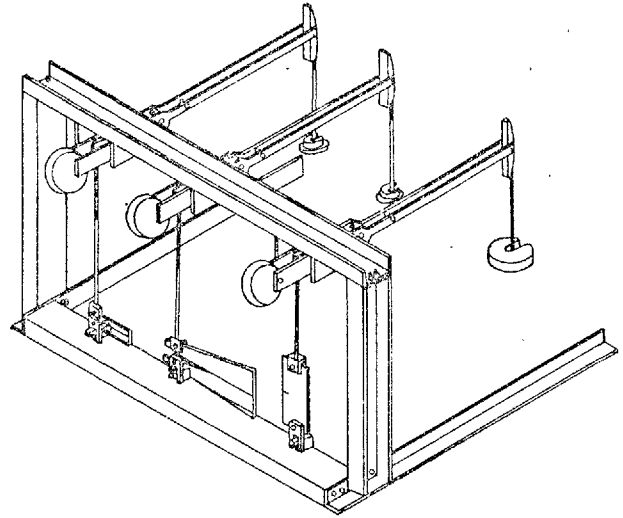


FIG 3 Testing apparatus

and orientated notches, and for this reason several different known techniques were tried. A more successful one, however, was developed to use a razor blade in a jig mounted in a Vickers hardness-testing machine. The notch was started with a saw cut, the specimen was lightly held in a vice on the machine table and the table was then raised until the blade entered the material. A natural crack whose

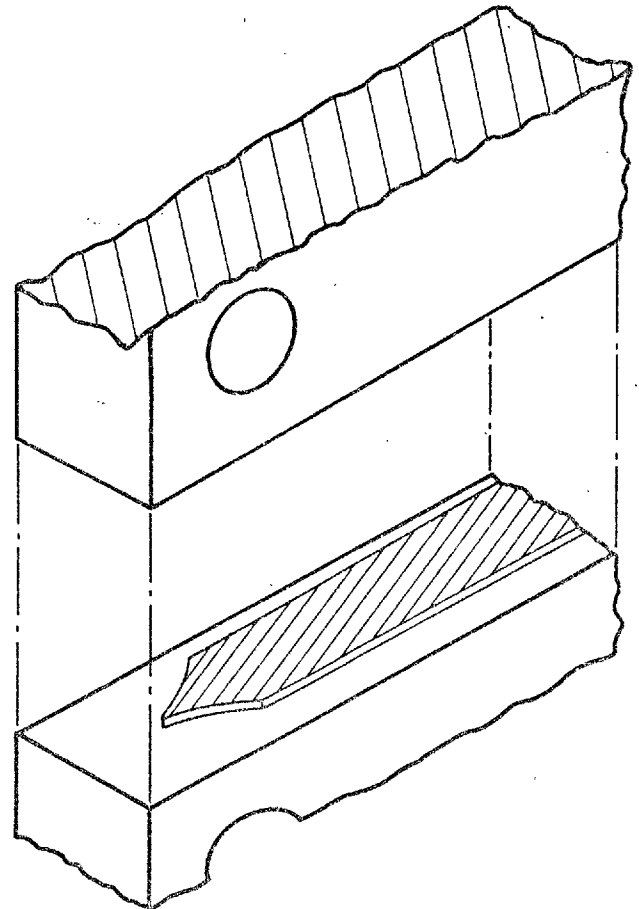


FIG 4 Section through parallel-cleavage specimen showing swallow-tail effect

length could be controlled was thus formed ahead of the blade.

The side grooves in the cleavage specimens should be as narrow as possible for complete crack control, and a width of 0.006 in was used. Their depth was 0.060 in, this having been found by experience to be the minimum for full crack restraint. To initiate the cracks in these specimens the side slots were milled to the centre line for a short distance near the point of loading, thus producing a swallow-tail section as shown in FIGURE 4. Pre-loading in an Instron Universal TT-C testing machine initiated a crack having a uniform front.

4.1 Calibration tests

The same Instron testing machine was also used for

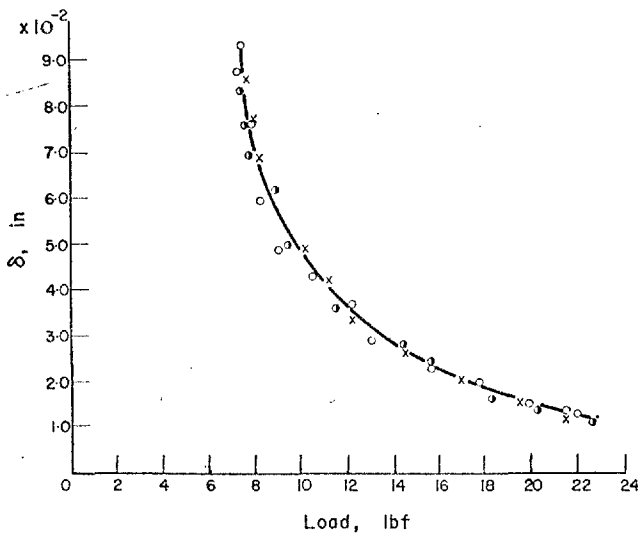


FIG 5 Load/deflexion calibration curve for parallel cleavage tests

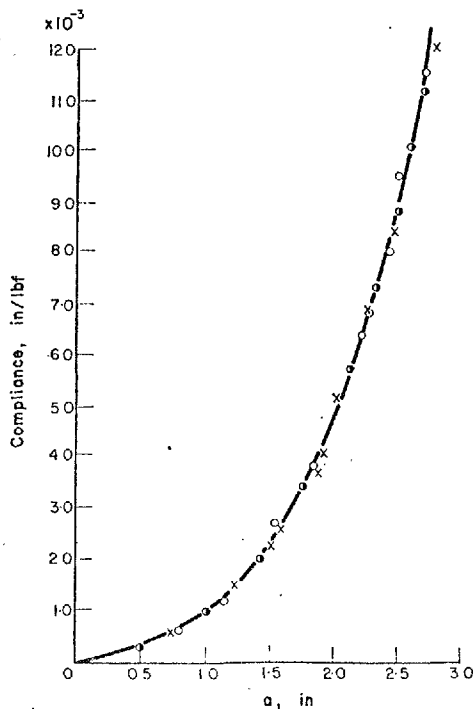


FIG 6 Compliance/crack-length curve for parallel cleavage

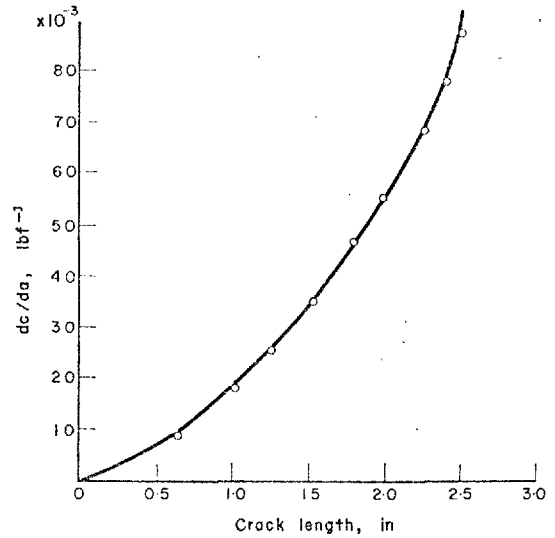


FIG 7 Calibration curve for parallel cleavage

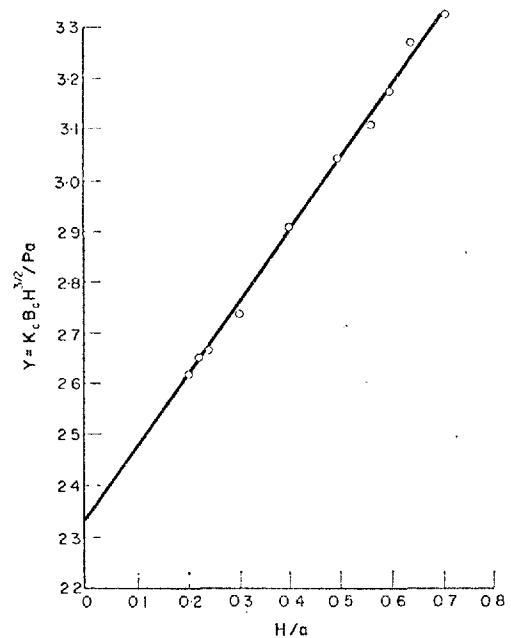


FIG 8 Dimensionless stress-intensity coefficient as a function of reciprocal of relative crack length (parallel cleavage)

these tests on the cleavage specimens, load and corresponding deflexion being recorded continuously. To avoid the possibility of stress relaxation in the specimen near the crack tip, a constant crosshead speed of 0.2 in/min was used and the load/deflexion chart was marked at intervals as the crack extremity passed gauge marks on the specimen. The load/deflexion curve obtained for the parallel cleavage specimen, FIGURE 5, was used to calculate compliance values for different crack lengths; the results are given in FIGURE 6. The slopes of this curve give dc/da which was then plotted against crack length in FIGURE 7.

The factor K_c was calculated using FIGURE 7 and the Irwin-Kies¹¹ relation

$$K_c^2 = \frac{P^2 E}{2 B_c} \frac{dc}{da} \quad (14)$$

Gross & Srawley⁹ in their boundary collocation analysis express K_c in terms of a dimensionless parameter

$$Y = \frac{K_c B_c H^{3/2}}{P a} \quad (15)$$

which, when plotted against H/a yields the relation

$$Y = \frac{K_c B_c H^{3/2}}{P a} = 3.46 + 2.38(H/a). \quad (16)$$

From the calibration data obtained here a similar function Y' may be calculated and plotted against H/a (FIG 8) yielding

$$Y' = \frac{K_c B_c H^{3/2}}{P a} = 2.33 + 1.5(H/a) \quad (17)$$

whence $Y' = 0.67 Y$

A similar experimental technique was used for the tapered-cleavage calibration tests, the variation of deflexion with load being as indicated in FIGURE 9. The load remains sensibly constant over a wide range of deflexions, the oscillations about the mean reflecting slight deviations of the crack about the central plane. The slopes dc/da were obtained from corresponding values of compliance and crack length (FIG 10) and used to calculate K_c from the Irwin-Kies relation eqn 14 which yields

$$K_c^2 = 3140 P^2 \quad (18)$$

for the particular specimen geometry.

Boundary collocation computations¹³ give, for a tapered specimen, a dimensionless calibration factor

$$Y = \frac{K_c B_c W^{1/2}}{P}$$

which varies with a/W to a greater or less extent depending on the specimen geometry. The geometry for the present tests was chosen such that Y varied least over the range $0.2 < a/W < 0.7$ which ensures a minimum change in compliance. The boundary collocation computations for a specimen having a geometry similar to that used in these tests but without side slots yields

$$K_c^2 = 5050 P^2. \quad (19)$$

The effect on K_c of introducing side slots is thus obtained by comparing eqns 17, 18 and 19; i.e. the effect is to reduce K_c by factors of 0.63 and 0.67. Use of beam theory would have shown a reduction factor of 0.71, $[\sqrt{(B_c/B)}]$. The discrepancies between this and the experimental values is thought to be due to variations in slot geometry and stress field effects.

4.2 Crack propagation tests

The single-edge-notch specimens used, shown in FIGURE 2(a), were all 6×2 in but of three thicknesses, namely 1/4, 1/8 and 1/16 in. A constant load was applied to each in turn and the resulting crack growth with time was measured. A typical set of results is indicated in FIGURE 11. From such curves corresponding values of crack speed (da/dr) and K_c were determined using computer techniques, and the values were plotted as in FIGURE 12.

Calibration marks were engraved on the parallel cleavage specimens, FIGURE 2(b), to assist in crack-growth measurement, and the test was then completed as outlined above. The change of crack extension with time is shown in FIGURE 11 and the K_c /crack-speed relationship is shown in FIGURE 13.

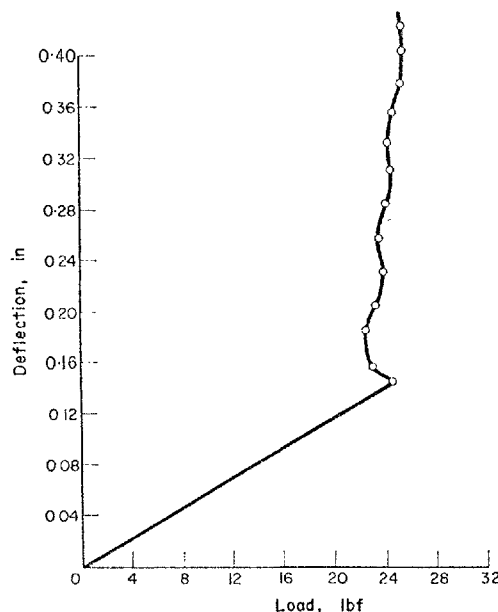


FIG 9 Load/deflexion calibration curve for tapered cleavage tests

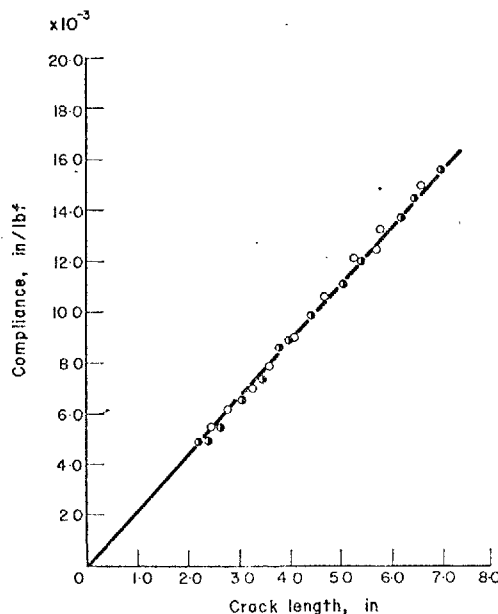


FIG 10 Compliance/crack-length curve for tapered cleavage

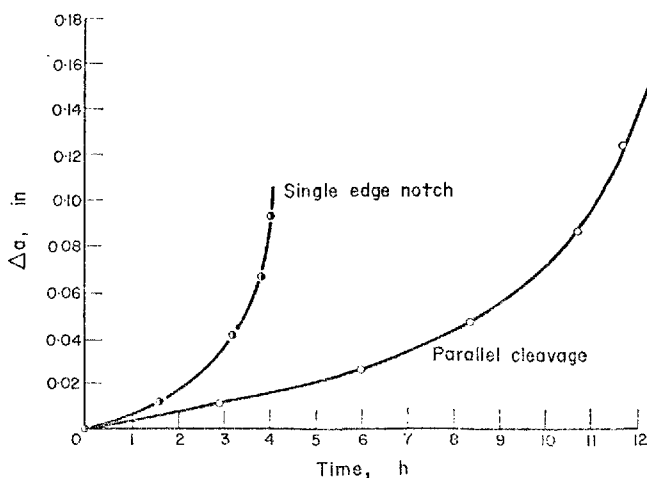


FIG 11 Typical curve for change in crack length against time for similar starting values of K_c

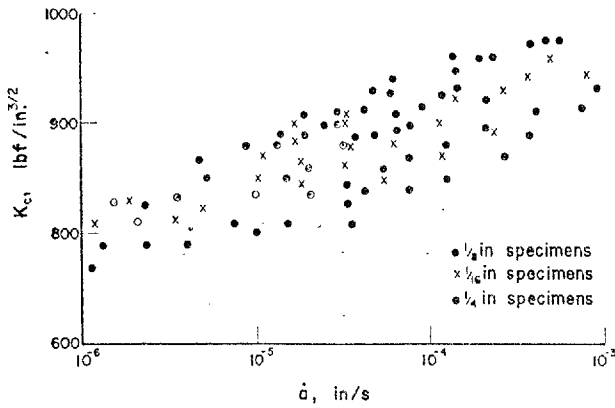


FIG 12 Effect of crack speed on fracture toughness in single-edge-notch specimens

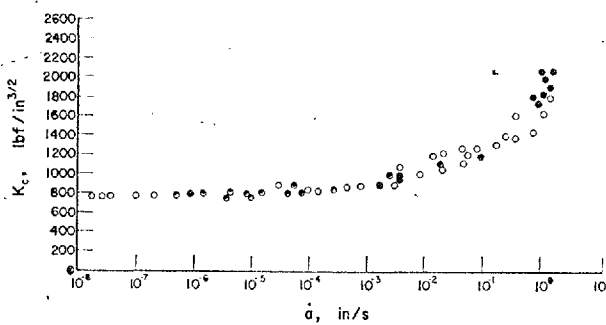


FIG 13 Effect of crack speed on fracture toughness in parallel-cleavage specimens

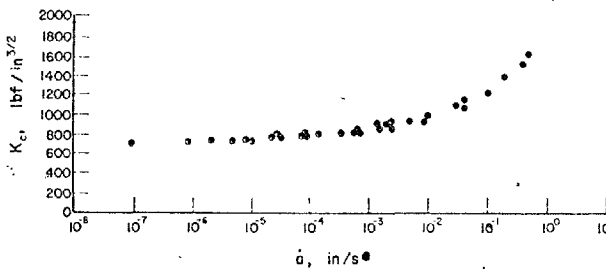


FIG 14 Effect of crack speed on fracture toughness in tapered-cleavage specimens

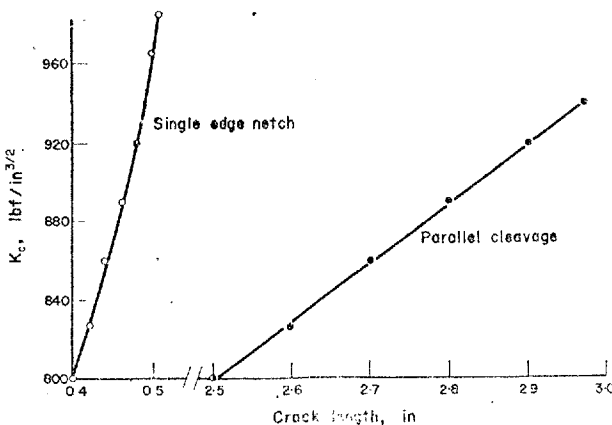


FIG 15 Variation of fracture toughness with crack length

Tapered-cleavage specimens having dimensions as in FIGURE 2(c) were tested in the same manner, the corresponding curve of K_c versus crack-speed appearing as in FIGURE 14.

5 Discussion

The single-edge-notch tension test has the obvious attraction of simplicity. That there are serious drawbacks to this configuration, however, is evident from a study of FIGURES 11 and 15. FIGURE 11 shows that the test is basically unstable in that the crack accelerates continuously to fracture, and the slow-growth regime is of short duration. Using the maximum permissible crack length⁸ of 0.4in the maximum measurable amount of crack growth was only 0.1in and the range of speeds measurable from a single specimen was limited. The results (FIG 12) indicate a scatter of some ± 15 per cent which is attributable largely to the inherent inaccuracies of slope-taking techniques necessary in determining values of crack speed, and to the high degree of sensitivity to notch form in tension tests. This sensitivity is a reflection of the fact that, in this type of test, the loads required are comparatively large and the resulting deflexions are small.

It was because of the above problems that cleavage tests were considered. The parallel specimen produces continuously accelerating crack growth but the amount of slow crack growth is considerably more than in the single-edge-notch test and allows a wider range of crack speeds to be studied. A comparison of the sensitivity of K_c to changes in crack length (FIG 15) between these two types of test reveals a 5:1 advantage in favour of the cleavage specimens. Furthermore, the cleavage tests, involving low loads and large deflexions, are less sensitive to notch form. Nevertheless, the difficulties in slope-taking techniques remain, and FIGURE 13 reveals a scatter of ± 9 per cent.

The use of a tapered-cleavage specimen, in which K is independent of crack length, gives a constant crack speed and allows its magnitude to be determined with greater precision. A wide range of crack speeds can be easily studied and, since the effect of the side grooves is conveniently allowed for in the calculations, the relationship between K_c and crack speed, (FIG 14) may be established - in this case with a scatter of ± 5 per cent.

Crack behaviour at very low speeds ($< 10^{-7}$ in/s) presents special problems in that the time involved in producing appreciable crack growth (3h to produce 0.001in) allows viscoelastic stress relaxation to occur such that the crack is effectively blunted and this leads to crack arrest. It seems possible that this may provide an explanation of the threshold phenomenon. Clearly, however, provided that a satisfactory crack can be grown, the tapered-cleavage test is the best for this type of determination, the precision achieved being better than in any other form of fracture test.

For comparative purposes the curves showing the dependence of K_c on crack speed, as obtained from the three tests, are superimposed in FIGURE 16. Within the limits of experimental accuracy a unique relationship exists independent of test method. There is some evidence that the cleavage results are slightly lower than those in tension, but the difference is very

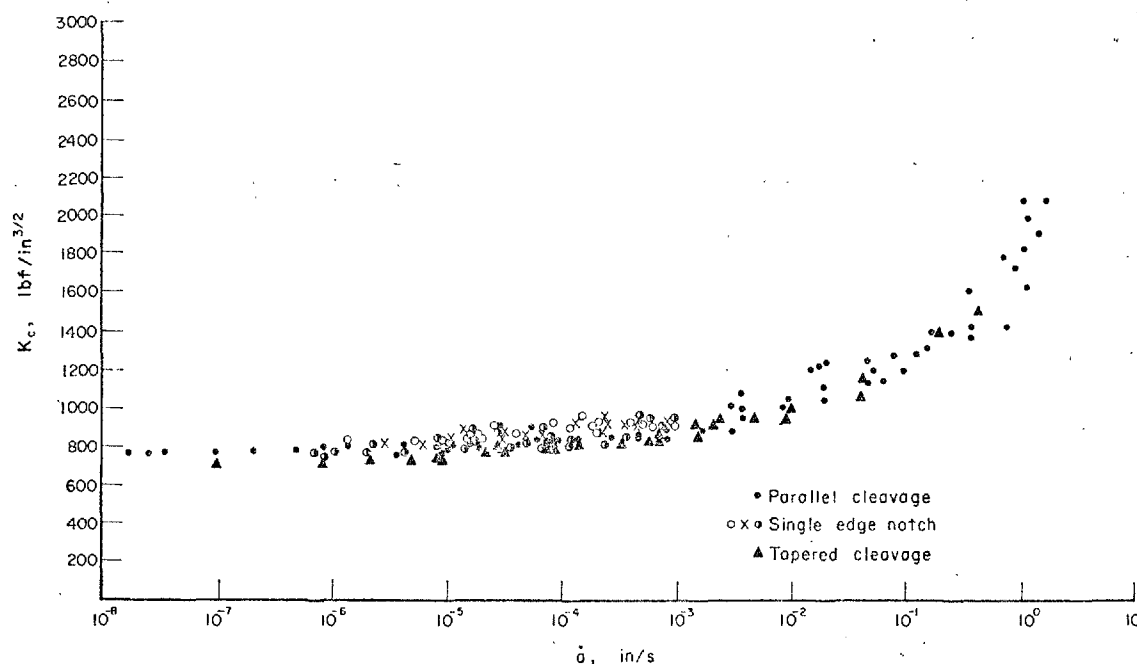


FIG 16 Results from FIGS 12, 13 and 14 combined

small. This difference could be attributed to a slight variation in stress distribution at the crack tip or to some influence of the side grooves, but the differences are marginal and do not warrant further discussion at this stage.

The curve is in good agreement with previously published figures,¹⁴ and in particular the threshold value of $750 \text{ lbf/in}^{3/2}$ agrees closely with that suggested for design purposes.³ The results (FIG 12) also show that there is no appreciable dependence on specimen thickness within the limits examined. Fracture mechanics postulates that a transition from plane-strain to plane-stress conditions will occur when the specimen thickness approaches the plastic zone size. For PMMA such a transition would be expected for a thickness of approximately 0.002 in , i.e. well below the thicknesses used in these tests, and plane-strain failures would thus be expected throughout with no variation with thickness.

6 Conclusions

Three test methods, aimed at studying crack and craze propagation in polymers, have been adequately evaluated. Tapered-cleavage tests have considerable advantages over parallel-cleavage and single-edge-notch tension tests for a study of the behaviour of PMMA in air.

A unique relationship between the fracture-mechanics parameter K_c and crack speed has been

shown to exist. The relationship agrees well with previously published work.

This background is of considerable value in the evaluation of crack growth under other conditions.

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Environmental stress crack growth in low-density polyethylenes

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Abstract: If full use is to be made of the properties of polymers it is necessary to understand the factors governing the growth of cracks and crazes in them. As part of a broad study of these phenomena the growth of cracks in two grades of polyethylene in two different environments has been examined. The results have been analysed using fracture-mechanics concepts. Within the limits of the tests made, there was a unique relationship between the crack-tip stress intensity factor and the crack speed, and neither thickness of the specimen nor long pre-soaking in the environments affected the crack growth properties. Strain rate effects have been investigated and this allowed a comparison of theoretical and experimental results to be made. Very good correlation was achieved.

1 Introduction

If the application of polymers in engineering is to be fully exploited it is necessary to determine and to understand their behaviour under stress in different environments. Their growing use in the fields of, for example, containers, packaging, piping and insulation brought them into contact with environments other than air and revealed the possibility of unsatisfactory behaviour. In particular, polymers may crack or craze when subjected to low stresses in the presence of certain environments, and, although such failures are seldom catastrophic, it is important to recognize the possibility of their occurrence and hence to understand their cause. A good review of polymer behaviour is given in the papers of Reference 1.

Several variants of the stress cracking phenomenon have been noted in polyethylene, and a considerable amount of research effort has been expended upon them in the past. Previous workers have studied the environmental stress cracking behaviour of polyethylene but their attention has been largely confined to obtaining data concerning the polymer properties which affect its resistance to this mode of failure or to devising and standardizing test methods for producing satisfactory correlation of results.

The work now reported is part of a broad examination of the usefulness of fracture-mechanics concepts when applied to environmental stress cracking and crazing in polymers. These concepts, although developed for metals, have been shown to be applicable to brittle crack propagation in polymers and, in particular, have been applied to the examination of crack growth in polymethyl methacrylate (PMMA) in air.²⁻⁵ It is thought that the subject will also produce meaningful parameters for the analysis of crack and craze growth in polymers subjected to stress in different environments.

This paper examines the crack growth of polyethylene in alcohols, and values of stress intensity factor, as functions of crack speed and strain rate, are determined for two grades of the polymer.

2 Fracture-mechanics concepts

Experience shows that fracture cannot, in general, be predicted by simple calculations based on either gross or local stresses. Some materials, although normally ductile when tested in simple tension, fail in a brittle manner if tested after notching, and one object of fracture mechanics is to forecast the circumstances in which slow or fast low-stress fractures will occur. Fracture mechanics is thus based on the strength of a flawed member which in turn is represented by a notched specimen.

The notch, or flaw, will have an elastic stress pattern associated with it (except immediately adjacent to the tip where a plastic zone may form) and stress-function solutions for these stresses, in terms of the applied stress, are available for various specimen geometries. These show that there is one parameter K , the stress field intensity factor, which relates the elastic stress field near the crack tip to the loading and geometry of the system. Any fracture criterion should thus be related to K or to the applied stress p , but since p is not constant on either gross or net area it is postulated that K be constant and equal to K_c at fracture. K_c is a measure of the 'fracture toughness' and is a material constant having the value

$$K_c = p(\pi a)^{1/2} \quad (1)$$

for an infinite plate containing a central crack of length $2a$.

For a single edge notch specimen of width W , thickness B and crack length a , subjected to a load P as in these tests (FIG 1) the fracture toughness has been shown⁶ by boundary collocation methods to be

$$K_c = \frac{P}{BW} a^{1/2} \left[1.99 - 0.41 \left(\frac{a}{W} \right) + 18.70 \left(\frac{a}{W} \right)^2 - 38.48 \left(\frac{a}{W} \right)^3 + 53.85 \left(\frac{a}{W} \right)^4 \right] \quad (2)$$

which may be represented by

$$K_c = Y p a^{1/2} \quad (3)$$

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Earlier work in this field was based on energy considerations and the theory was phrased in terms of the 'surface energy' G_c (or γ). The surface energy is related to K_{Ic} by

$$K_{Ic}^2 = E G_c \quad \text{for plane stress}$$

and $K_{Ic}^2 = E G_c / (1 - \nu^2)$ for plane strain

where E and ν are Young's modulus and Poisson ratio respectively.

The crack toughness of strain-rate-sensitive materials has been considered by Irwin⁷ who suggested that the effective stress rate around the crack tip was

$$\dot{s} = \frac{2f}{t} + \frac{f}{2r} \dot{a}$$

where f is the yield stress,

t is the testing time,

r is the radius of crack-tip plastic zone, and

$\dot{a}$ is the crack speed.

If one assumes plane strain conditions,

$$2r = \frac{1}{2\sqrt{2\pi}} \left(\frac{K_{Ic}}{f} \right)^2$$

An 'apparent' crack speed can be determined by equating the two conditions before and after cracking occurs; i.e. before cracking occurs

$$\dot{a} = 0$$

and

$$\dot{s} = \frac{2f}{t}$$

and at the onset of cracking

$$\dot{s} = \frac{f}{2r} \dot{a}$$

Thus, by eliminating $\dot{s}$

$$\dot{a} = \frac{4r}{t} = \left(\frac{K_{Ic}}{f} \right)^2 \cdot \frac{1}{\sqrt{2\pi}t} \quad (4)$$

This derived crack speed for a given K_{Ic} value may be compared with the experimental results.

3 Test programme

3.1 Choice of material and environment

Earlier workers¹ have shown that the resistance of polyethylene to environmental stress cracking is a function of molecular weight, of which the melt flow index is a (reciprocal) measure. The resistance to attack of this nature increases with increase in molecular weight. In the present work, in order to achieve failures within practical time limits, the materials selected were compression-moulded grades of polyethylene of density 0.912 and melt flow indices 20 and 7, although it was realized that the most serious problems of environmental stress cracking occur in polyethylenes of much lower melt flow indices. Tests on these latter materials are in progress.

True environmental stress cracking is a purely physical phenomenon involving no chemical changes, swelling or similar mechanical weakening of the material. Care is therefore necessary in selecting suitable environments to eliminate the possibility of solvent stress cracking. For the present work alcohol was chosen since it is a precipitant for polyethylene; two grades were used, namely ethanol and methanol.

3.2 Choice of specimen geometry

A feature of the literature on stress cracking is the number of specimen geometries and loading systems which have been used in an effort to obtain consistently repeatable results. The more popular in current use are:

- constant load tests using straight, dumb-bell or Maltese-cross-shaped specimens,
- constant strain tests with the same specimen geometries, and
- 'Bell Telephone' tests using bent strip specimens.

Results from such tests are usually plotted on a time-to-failure basis and the confidence limits often leave much to be desired.

In a previous paper⁴ the present authors described tests on crack growth in PMMA in air using three types of specimen commonly used in fracture toughness testing, namely:

- the single-edge-notch tension specimen,
- the parallel cleavage (double beam cantilever) specimen, and
- the tapered cleavage specimen.

Each of these specimens, used in constant-load tests, proved satisfactory, but the two cleavage types were superior for slow growth tests. Attempts to use these latter two specimens in the testing of polyethylene have so far proved to be impracticable, in that the low rigidity of the material allows the arms of the specimen to twist, thus causing crack arrest. However, single-edge-notch specimens proved highly successful in preliminary tests with polyethylene, in that large amounts of slow crack growth were obtainable and growth measurements were easily made. This type of specimen was therefore decided upon for all tests reported in this paper.

3.3 Specimens and equipment

The specimens, $6 \times 2 \times \frac{1}{16}$ or $\frac{1}{8}$ or $\frac{3}{16}$ in, were knife-cut from sheet material which had been allowed to normalize for two months at a temperature of 20°C and a relative humidity of 50%. Preliminary tests revealed that annealing of the specimens produced no significant effects on the test results, possibly because of overriding notch effects, and all sheets were therefore used in the normalized condition. These preliminary tests also revealed the importance of standardizing the

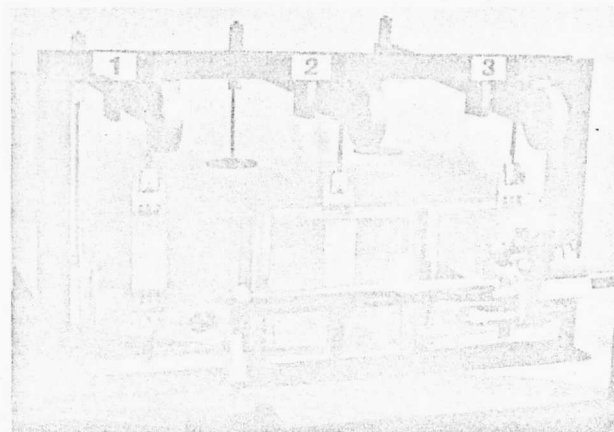


FIG 1 Dead-weight loading apparatus

notching technique and the procedure finally adopted was to use a razor blade to make a notch from which a 'sharp' crack was induced by pre-loading the specimens for approximately 10s. The specimen was then allowed to recover for 10 min before the test proper was carried out. This procedure was used throughout this work.

A view of the dead-weight loading apparatus used for the crack growth tests is shown in FIGURE 1. It consists essentially of a batch of single-lever systems incorporating pre-tensioning and constant-load devices. The specimens were mounted in glass tanks which allowed for their complete immersion in the fluid environments used.

For the tests at various strain rates, use was made of the Instron TT-C universal testing machine, fitted with immersion testing equipment as necessary (FIG 2).



FIG 2 Instron immersion testing equipment

3.4 Crack-growth tests

If the fracture characteristics of a material are to be analysed using fracture-mechanics concepts it is necessary that the fracture toughness parameter K_{IC} is independent of the initial crack length a_0 .

Single-edge-notch tension specimens $6 \times 2 \times \frac{1}{16}$ in were prepared, as indicated above, from each grade of polyethylene, melt flow indices 20 and 7, and separate series of specimens were notched to give crack lengths in the ranges $a_0 = 0.05$ – 0.1 in, 0.1 – 0.2 in, 0.2 – 0.3 in, 0.3 – 0.4 in and 0.4 – 0.6 in. These were then assembled in the loading rigs and immersed in methanol or ethanol immediately prior to applying the predetermined load. The resulting crack growth with time was measured using a travelling microscope and stop-watch. All the tests were conducted at 20°C .

To evaluate the effects of specimen thickness, further series of tests in methanol were performed on polyethylene of melt flow index 7, having thicknesses of $\frac{1}{8}$ and $\frac{3}{16}$ in and initial crack lengths in the range 0.2 – 0.4 in.

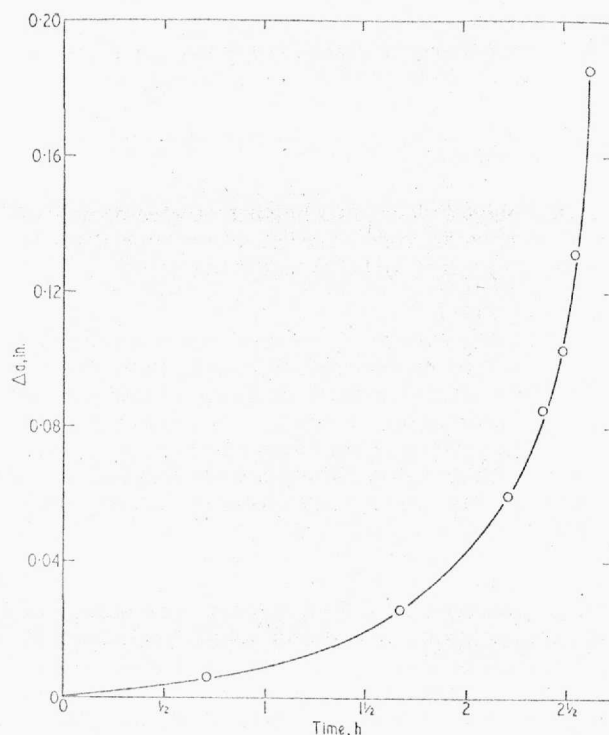


FIG 3 Crack-growth tests: typical curve of change in crack length against time

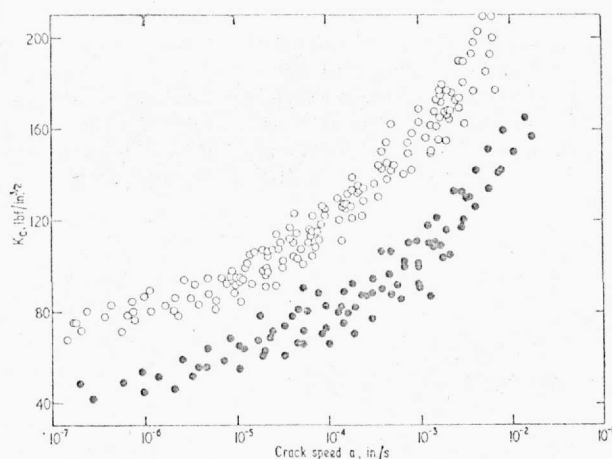


FIG 4 Effect of crack growth speed on fracture toughness

○ Polyethylene MFI 7 in methanol
● Polyethylene MFI 20 in methanol

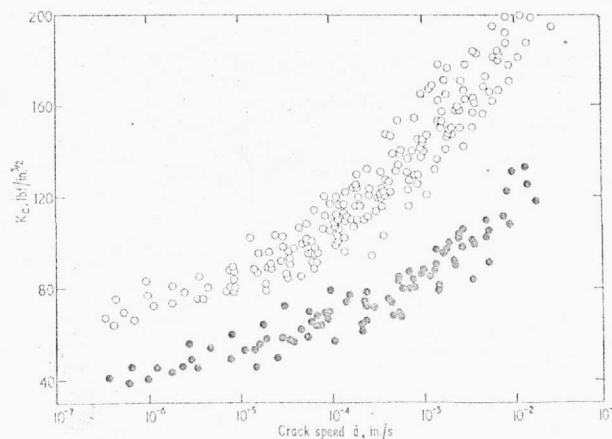


FIG 5 As Fig 4 for polyethylene in ethanol

In all, some 250 tests of this nature were completed and a typical curve of crack growth with time is shown in FIGURE 3. From such curves corresponding values of the crack growth rate da/dt ($=\dot{a}$) and K_c were determined with the use of computer techniques and they are shown in FIGURES 4 and 5.

Finally, to investigate the effects, if any, of pre-soaking polyethylene, two batches of specimens from the melt-flow-20 grade were left to soak in ethanol for periods of up to 300 h before testing as above.

3.5 Strain-rate tests

Polyethylene is known to be very strain-rate-sensitive and it was thought desirable to investigate its fracture behaviour at various rates of straining. This was seen to have a double value, in that by using Irwin's theory⁷ another curve showing the relationship between K_c and crack growth rate, $\dot{a}$, could be obtained for comparison with that obtained directly from the crack-growth-rate tests previously described. Furthermore, additional evidence on the notch-length-sensitivity of polyethylene in alcohol would be obtained.

A series of specimens $6 \times 2 \times \frac{1}{16}$ in was prepared from each grade of polyethylene and notched in the manner previously described, the initial crack lengths varying within the range 0.05–0.8 in. These specimens were initially cut at random from several sheets of the polymer. The specimens were mounted in turn in the immersion equipment in the Instron TT-C testing machine, immersed in methanol and strained in tension at a constant rate of crosshead movement. The clamping arrangements were such that the specimens had a gauge length of 2 in, and the crosshead movements used in the various tests corresponded to strain rates on the specimen of 0.25, 0.1, 0.05, 0.025 and 0.01 per min.

From the beginning of each test the end of the crack in the specimen was carefully observed through a

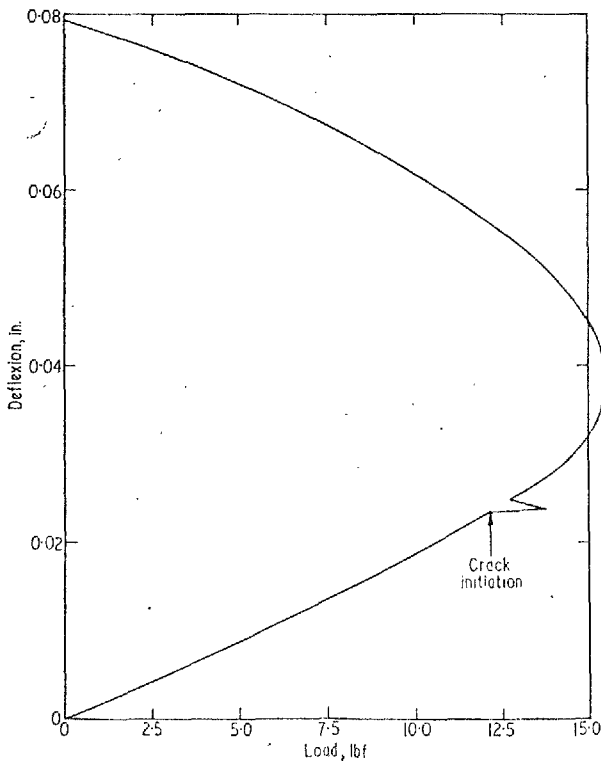


FIG 6 Strain-rate tests: typical deflection/load curve

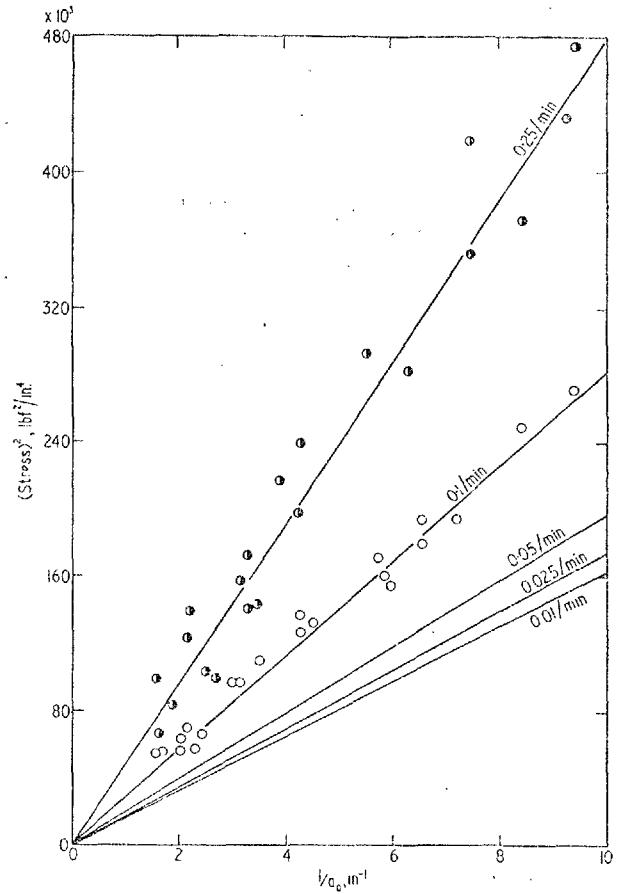


FIG 7 Effect of strain rate on fracture toughness of polyethylene MFI 20 in methanol

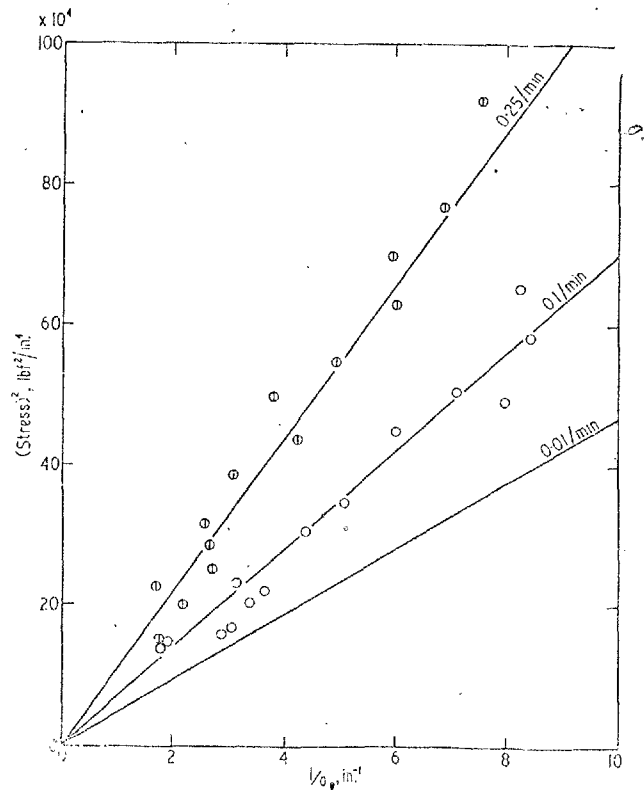


FIG 8 As Fig 7 for polyethylene MFI 7 in methanol

microscope, the point of initial crack growth being recorded by activating the event recorder on the autographic load/crosshead-displacement chart.

In all, some 300 tests of this nature have been completed and a typical load/extension curve is shown in FIGURE 6. From these results curves were also plotted (FIGS 7 and 8) to show the relationship between $(p_1)^2$ and $(a_0)^{-1}$ where p_1 is the stress at the instant the crack begins to propagate.

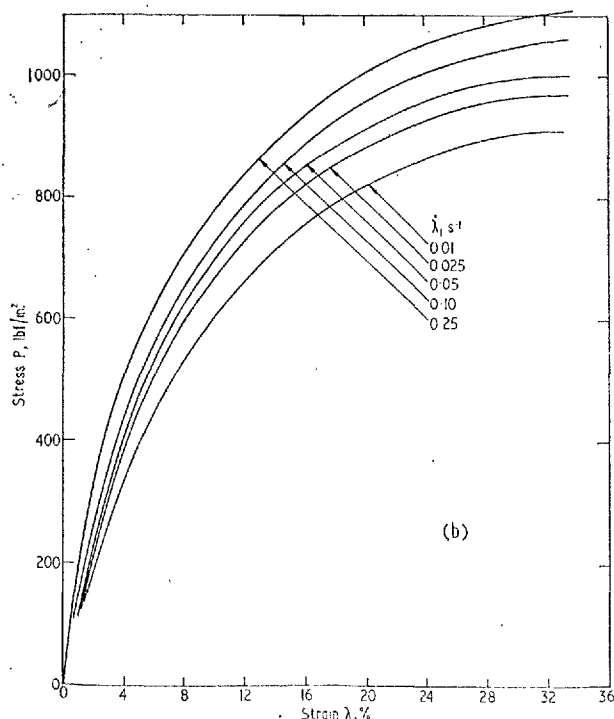
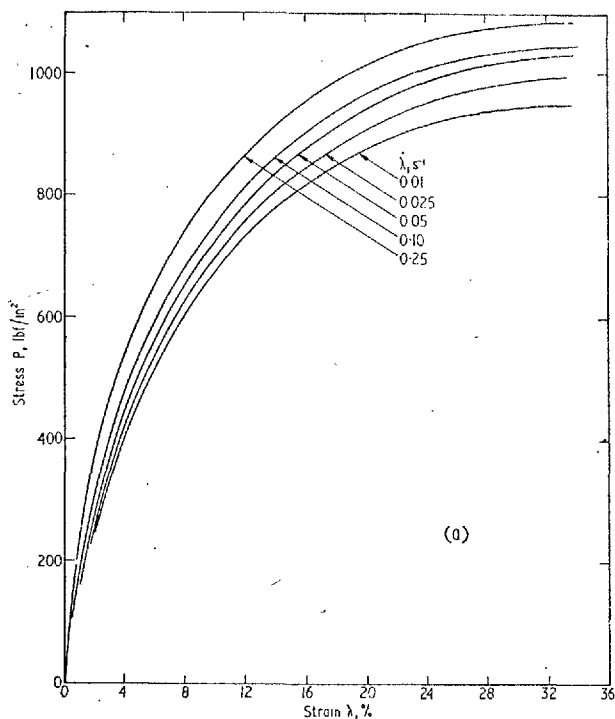


FIG 9 Effect of strain rate on stress/strain curves

(a) Polyethylene MFI 7 in methanol
(b) Polyethylene MFI 20 in methanol

In order to apply Irwin's theory it is also necessary to know the yield stress of the materials in alcohol at the various strain rates. A series of normal tensile tests was therefore made, in the same Instron testing machine, to establish the stress/strain curves for both grades of polyethylene in methanol. The results of these tests are shown in FIGURE 9.

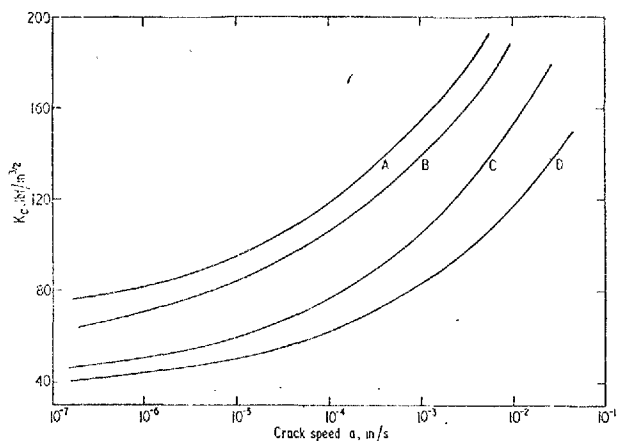


FIG 10 Comparison of crack-propagation data

A Polyethylene MFI 7 in methanol
B Polyethylene MFI 7 in ethanol
C Polyethylene MFI 20 in methanol
D Polyethylene MFI 20 in ethanol

Finally, for comparative purposes, representative stress/strain curves for the materials in air were also obtained.

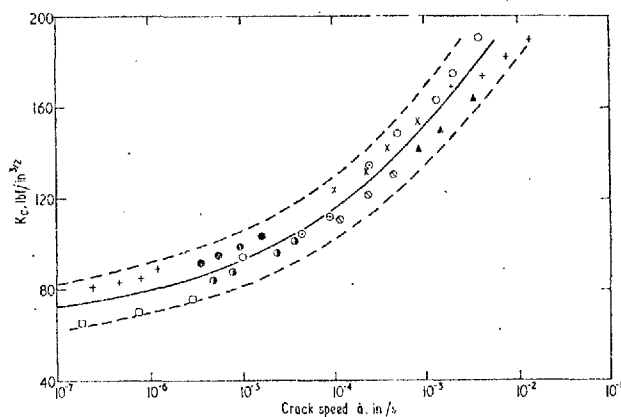


FIG 11 Fracture-toughness/crack-speed curve for polyethylene MFI 7 in methanol

4 Discussion on results

The curve showing the growth of crack length with time (FIG 3) on which, for the sake of clarity, very few data points have been indicated, is typical of such curves obtained using single-edge notch specimens of brittle materials. Such materials may exhibit sudden crack growth at a point of instability, but polyethylene in alcohol behaved in a very stable manner and allowed careful measurements to be made over long periods of slow crack growth. On the other hand, a disadvantage of using this polymer was the difficulty encountered in clearly defining cracks because of its low translucence; good lighting conditions were found to be essential.

The large number of results showing the relationship between the fracture-toughness parameter K_{IC} and

crack speed $\dot{a}$ (FIGS 4 and 5) indicate that, within the limits of these tests, a unique relationship exists for each grade of material in each environment. The curves are shown superimposed for comparative purposes in FIGURE 10. As would be expected, the melt-flow-7 grade is more resistant to both types of alcohol and the crack speed increases rapidly with K_{Ic} for all the material and environment combinations used. It should be noted that, in principle, a complete curve as in FIGURES 4 and 5 would be obtained from each specimen. This is not practicable, however, but FIGURE 11 shows that each specimen does form a part of the general curve.

There are limitations to the 'uniqueness' of the $K_{Ic}/\dot{a}$ curves. In other tests, not reported here, it became apparent that if a comparatively large gross-section stress (in excess of 100 lbf/in²) was applied to a specimen having a large a/W (crack-length/plate-width) ratio (say > 0.25) a crack speed very much lower than expected was achieved for the particular K_{Ic} value. This phenomenon would appear to be a result of the combination of a large gross-section stress and a large crack length, which causes a high net-section stress, and this in turn leads to a complex situation and to eventual breakdown of the basic equations as plasticity and finite-plate-width effects become predominant. This finite-width effect can be seen in the specimen shown in FIGURE 12.

In general, therefore, tests were performed with gross-section stresses below 100 lbf/in² and this had an additional advantage in that it minimized the effects of non-linearity in the stress/strain relationship for the material. By suitably limiting the stress it was found possible to achieve good correlation of data for specimens having a/W ratios up to 0.4. It is interesting to note, however, that the data giving the upper bounds of the curves in FIGURES 4 and 5 were achieved from specimens in which either the stress or the crack length was large.

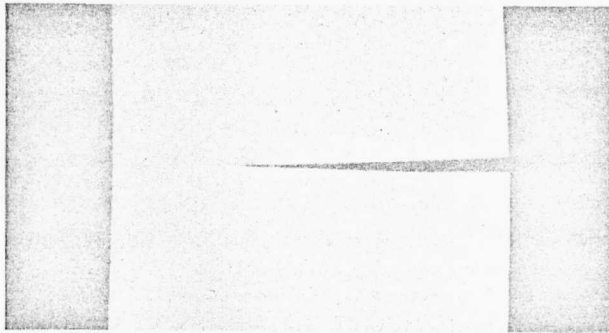


FIG 12 Typical specimen fracture

The results in these Figures show a scatter of the order of ± 12 per cent which is attributable to possible small variations in polymer properties resulting from the deliberate random cutting of specimens, to the high degree of sensitivity to the form of the notch, and to the difficulties encountered in measuring crack lengths as explained earlier. These limits were considered acceptable, however, particularly when compared with the scatter of ± 15 per cent obtained when conducting similar tests on PMMA¹.

Additional tests showed that the thickness of the specimens had no significant effects, at least within the range considered (FIG 13). Other results (FIGS 14 and

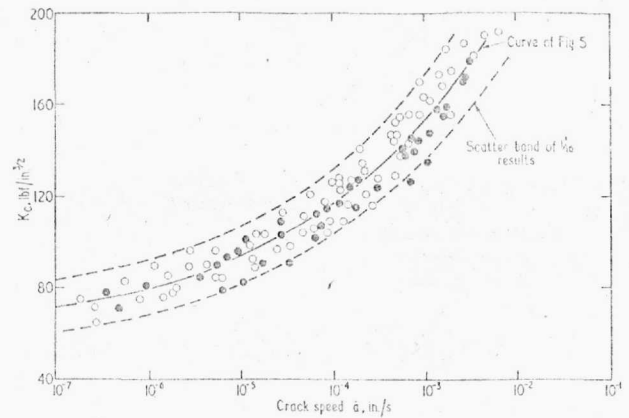


FIG 13 Effect of varying specimen thickness on crack propagation for polyethylene MFI 7 in methanol

○ 1/8 in specimens
● 1/16 in specimens

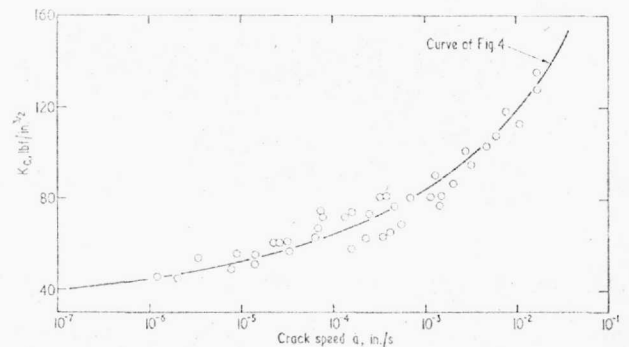


FIG 14 Effect of soaking on crack propagation: polyethylene MFI 20 in ethanol

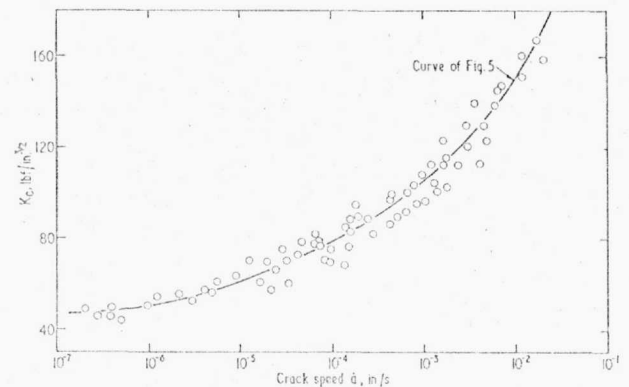


FIG 15 Effect of soaking on crack propagation: polyethylene MFI 20 in methanol

15) also clearly indicate that pre-soaking the polymer for up to 300 h in the alcohols used has no effect on the crack propagation properties. This was to be expected since alcohol is a precipitant for polyethylene, but further tests, involving very much longer soaking times, are in progress to check this point further.

Turning now to the tests to study the effects of strain rate, a typical load/deflexion curve for this material is shown in FIGURE 6. The discontinuity in the curve was caused by the actuation of the event recorder at the observed initiation of crack growth. This initiation occurred well before the point of maximum load which must therefore represent an instability condition.

The observation of the initiation of growth was difficult, and at high strain rates, where the growth was particularly fast, it led to a consistently higher degree of scatter in the results, as may be seen in FIGURES 7 and 8 in which the data for strain rates of 0.25/min and 0.05/min only are shown, for the sake of clarity. However, the scatter was favourable when compared with that found in similar tests on polymethyl methacrylate in air.⁴ The equipment used in the strain-rate tests required the ends of each specimen to be clamped and produced a uniform stress field. This allowed the infinite-plate solution of eqn 1 to be applied directly, in contrast to the earlier constant-load tests, in which the specimens were pin-loaded, carried a non-uniform stress and required the use of the finite-plate-width correction factor (Y) of eqn 3. The slopes of FIGURES 7 and 8 were used to determine the fracture-toughness parameter K_{Ic} , to be employed with the Irwin theory⁷ previously outlined.

To enable the analysis to be completed, the yield stress of polyethylene in methanol was obtained at

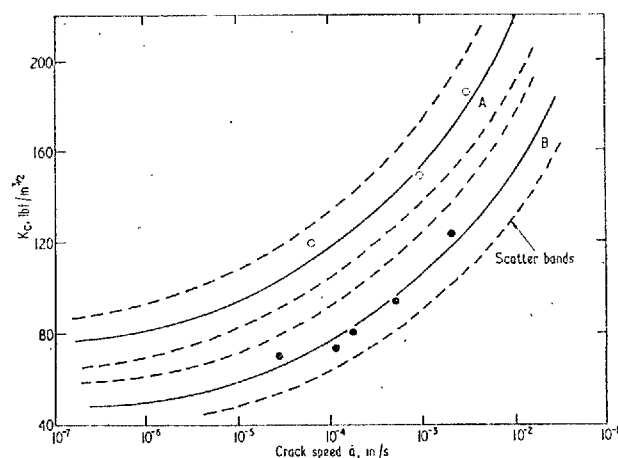


FIG 16 Comparison of theoretical and experimental results

- A Polyethylene MFI 7 in methanol (from Fig 4)
 B Polyethylene MFI 20 in methanol (from Fig 4)
 ○ } Calculated from Irwin's theory
 ● }

various strain rates. A comparison with similar stress/strain curves obtained in air showed that there was no difference, although in alcohol cracking occurred just before yield conditions were reached.

The apparent crack speeds obtained from the Irwin analysis are shown superimposed on the experimental $K_{Ic}/\dot{a}$ curves in FIGURE 16. The agreement between them is excellent thus lending confidence to both the analysis and the present experimental work.

5 Conclusions

Many tests have been completed to study the effects of environments on crack growths in different grades of polyethylene. Fracture-mechanics concepts were used in the analysis of the results and a unique relationship has been shown to exist between the fracture-mechanics parameter K_{Ic} and the crack speed. Strain-rate effects have been evaluated and good correlation is shown to exist between theoretical analysis and experimental results.

It is anticipated that these concepts will be widely applicable in the evaluation of crack and craze growths under other conditions.

Acknowledgements

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DISCUSSION

DR J. ROBERTS (*ERDE, Waltham Abbey, Essex*): Could the authors indicate how a choice of strain rate is made for the yield stress to be used in Irwin's equation? Should one have to use the strain rate at the crack tip?

—The relationship which Irwin has derived from obtaining the 'apparent' crack speed is couched in terms of the uniaxial tensile yield stress, σ_y . We admit that in strain-rate-sensitive materials

this value may be different from that which is obtained in the region of the crack tip in practice. Because the value of σ_y at the crack tip is unknown, however, we are forced to use the value obtained from conventional tensile tests as being the closest approximation available. The errors involved in this procedure would appear to be small in that excellent agreement is obtained when theoretical and experimental results are compared.