THE ENVIRONMENTAL STRESS CRACKING OF POLYETHYLENES - A FRACTURE MECHANICS APPROACH

by

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ABSTRACT

The environmental stress cracking of polyethylenes is a slow speed cracking phenomenon to which the applicability of fracture mechanics is studied in this work. A critical review of available literature is given in which particular reference is made to methods of testing.

It is shown that when the stress intensity factors (K_1s) required to cause cracking are compared on a crack speed basis, there is no specimen geometry effect. This leads to the conclusion that there is a unique relationship between K_1 and crack speed for each polyethylene, environment and temperature, and that the application of fracture mechanics is justified.

The practical work is based on polyethylenes for use as gas pipes. The materials selected for testing are therefore mainly very crack resistant copolymers and the work is extended to include surface cracks in plates and the insides of pipes.

The K_1-crack speed approach is used to study material, environmental and temperature effects. A relationship between K_1 and density is shown for copolymers, and two failure mechanisms are identified for all the materials tested. These are correlated with material relaxation and tentatively with environmental flow. The relaxation controlled cracking is used to define a critical crack opening displacement which is independent of temperature.

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NOTATION

Summary of definitions of symbols used repeatedly in the main text

a	crack length or half crack length
A_{gross}	cross-sectional area of a specimen
A_{net}	A_{gross} minus cracked area
ABS	acrylonitrile-butadiene-styrene
c	half crack width
CMC	critical micelle concentration
CN	centre notch(ed)
COD	crack opening displacement
DEN	double edge notch(ed)
E	modulus
E_y	yield modulus
$E_{2\%}$	2% modulus
ESC	environmental stress cracking
f ( )	function
G	strain energy release rate
G_c	critical G
HDPE	high density polyethylene
K	stress intensity factor
K_1	K for mode 1 stressing
K_{1c}	critical K_1
LDPE	low density polyethylene
MFI	melt flow index
MPVC	modified polyvinylchloride
MW	molecular weight
MWD	molecular weight distribution

P	pressure in pipe
PE	polyethylene
PIB	polyisobutylene
PMMA	polymethylmethacrylate
PVA	polyvinylacetate
PVC	polyvinylchloride
r_i	radius of pipe (bore)
r_o	radius of pipe (outer)
r_y	Irwin plastic zone size
SEN	single edge notch(ed)
SN	surface notch(ed)
t	specimen thickness or time in modulus data
t_o	crack initiation time
UPVC	unmodified polyvinylchloride
w	specimen width
Y	geometric factor in K_1 calculation or surface tractions
γ	surface energy
ϵ	strain
ϵ_y	yield strain
ϵ^*	failure strain
η_o	opening of semi-elliptic crack
ν	Poissons ratio
σ	stress
σ_h	Lamé circumferential stress
$\sigma_{h_{Total}}$	total circumferential stress for crack opening calculation
σ_{h_K}	total circumferential stress for K calculation
σ_l	longitudinal pipe stress
σ_y	yield stress
Φ	elliptical integral

CHAPTER 1

INTRODUCTION

1.1. BACKGROUND TO THIS WORK.

The environmental stress cracking (ESC) of polyethylenes (PEs) has been the subject of a great deal of study since its first identification. Many tests have been developed which have been considered satisfactory for giving qualitative comparisons of materials. These test methods were normally developed with a specific end purpose in mind. They used either constant load or constant displacement to cause failure and only the times for crack initiation or specimen failure were measured. These times could only be used to rank materials for end uses with similar loading conditions to those used in the tests. The different tests gave contradictory results for many aspects of ESC, particularly where materials of different modulus were tested.

With the increasing use of PE for engineering purposes, and in particular for piping in the gas industry, the data obtained from available test methods were unsatisfactory. The times for crack initiation or specimen failure provided only a very general and not always correct assessment of the relative crack resistance of PEs. The results were affected by the method of loading and the specimen preparation ; both the thermal history of the specimens and the quality of the surface finish or notching technique influenced the test times. In spite of all the attempts to standardise testing procedures and specimen preparation there was always a very large scatter on results and the average of 10 or 20 results was normally used as the cracking time. A further factor which made the development of a new test necessary was the failure of many of the available methods to give results for very crack resistant materials. Even those test methods which would give results could not be related precisely to the end use, and the only choice for an important engineering application such as gas systems was to select the most crack resistant material from the available PEs. This 'best available' approach was likely to prove at best more expensive than necessary and at worst dangerous in the long term.

This work was therefore commenced with the objectives of developing a test method which could be used for comparison of materials and, more important, could be used to give failure criteria upon which engineering decisions could be made.

The design life of gas distribution pipes is 50 years and, if good predictions of the likelihood of ESC in this period can be obtained, then the primary objective of this work has been achieved. The second objective of the work, if the first part was successful, was to study some of the variables in ESC. It was necessary to study the aspects of cracking more closely than previous workers because there were so many differences of opinion in the available literature that there were probably unidentified factors affecting the results. These factors had to be realised if a full analysis was to be made. It was therefore important that the test method investigated was not another 'time to fail' determination but included continuous monitoring of cracking.

1.2. USE OF PLASTIC PIPES FOR CONVEYANCE OF GAS

The rapid growth in the use of plastics for engineering purposes has been reflected over the past 16 years by the adoption and expansion of the use of plastic pipes by gas industries throughout the world. The primary advantages of plastic pipes are their resistance to corrosion and the ease with which they can be laid. These factors make plastics economical for the lower pressure gas piping systems where the weakness of plastics, relative to ferrous materials, can be overcome without using very large quantities of polymer.

The British gas piping system is divided into two parts. The transmission system consists of the National Grid and the high pressure regional grids. The distribution system is the lower pressure network of feeder mains, district mains and services which take gas from the grids to the consumers. It is in this distribution system that plastic pipes are being used, both to replace old mains and for extensions of the network. The plastic materials at present being used are PEs.

1.3. ADVANTAGES OF PE FOR GAS DISTRIBUTION SYSTEMS

The ferrous materials used for gas distribution are cast iron, ductile iron and steel. The iron systems are made up of short lengths of pipe with mechanical joints which make laying difficult and give the possibility of leaking joints. The cast iron and to a lesser extent the ductile iron, can be fractured by relatively small impacts or by land subsidence, although the short lengths of pipe ensure that no fracture can run very far. Steel pipe systems can be welded so they have no leaking joint problems and they are less prone to fracture than cast iron. The disadvantages of steel are the cost of the material and of welding and the lack of resistance to corrosion which means that a protective coating has to be used.

The first moves to use plastic pipes were made with unmodified polyvinylchloride (UPVC). Systems were easily glued giving leak-proof joints and because of this and their lightness the pipes were easy to lay. This made the overall costs very competitive and the corrosion resistance of PVC meant that it should be much safer than the other systems in the long term. There were however some potential disadvantages with UPVC systems. Although PVC was found to suffer only pigment discolouration from the earth environment which caused the problems with ferrous materials, it was not totally resistant to the aromatic hydrocarbons in the towns gas which was passed through the pipes. It was known that these aromatics would be slightly absorbed and might cause cracking or crazing (8, 15, 82). At the time little UPVC was used in Britain but with the increase in the use of natural gas to replace the aromatic-rich towns gas, UPVC might have been used again but for its brittleness. At low ambient temperatures and internal pressures at the higher end of the range used by the gas industry, it was found that an impact could lead to a propagating crack failure.

The long term strength properties of UPVC could not be utilised fully because of the possibility of an impact initiating a running crack, so the system had to be 'over-designed' and therefore became uneconomical. The brittleness of PVC is often reduced by modification of the structure by the incorporation of energy absorbing materials such as chlorinated polyethylene, acrylonitrile-butadiene-styrene (ABS) or polyvinylacetate (PVA). The addition of these materials, within limits, increases the fracture toughness and the ductility of the modified PVC (MPVC) but also reduces the strength. The strength reduction is not a major handicap; it means that a greater wall thickness has to be used. As MPVC is a more expensive material and more of it has to be used to give the same pipe strength, much of the economical advantage of PVC is lost, but pipe costs are not the main factor in gas systems. The cost of the pipe itself is small compared with the cost of digging the trench, refilling it and reinstating the surface, so the advantages of MPVC can be utilised with only a small percentage price increase. These advantages are its resistance to crazing and the reduced likelihood of fracture ; it is because of these that MPVC pipes have been used to a far greater extent than UPVC in Britain. MPVC has however been superceded by PE.

1.4. PE GAS PIPE SYSTEMS

When considering any material for gas piping the primary requirement is that it must be safe. Only if it is safe can it be compared on a cost basis with other materials. For PE the advantages from the safety view point are :-

a) Toughness - even under impact loading PE pipes have not developed running cracks and it is difficult to even penetrate the pipe wall.

b) Resistance to corrosion from the external environments which may be acid or alkaline and may contain micro-organisms capable of damaging other plastics.

c) Ductility which enables PE pipes to absorb all normal land subsidence, such as mining subsidences, without inducing large stresses.

The cost advantages come mainly from the lightness and ductility, which make laying easy, and they are :-

a) Coils of pipe can be used to eliminate many of the joints which make laying time consuming. This applies to pipes up to 90 mm diameter.

b) Many bends can be made simply, without special fittings and extra joints.

c) Fusion joints can be made without skilled labour and without the possible leak problems of mechanical joints.

d) Insertion-replacement and extraction-replacement of old mains by PE mains removes the necessity to dig up the old main.

The disadvantages of PE are :-

a) Its relative lack of strength.

b) Its susceptibility to permeation by hydrogen.

c) Its absorption of aromatic hydrocarbons and resulting reduction in mechanical properties.

The first of these disadvantages is no problem because in the low pressure systems the cost of increasing pipe wall thicknesses to give massive safety factors on the predicted 50 year strength is of little consequence. The other two problems were removed with the introduction of natural gas so the international adoption of PE for gas piping has a very well founded basis.

1.5. USAGE OF PLASTIC GAS PIPES

In Britain PVC was first used approximately 16 years ago but only about 1180 km of pipe were laid, the vast majority of this being MPVC laid in the last nine years. PE has gained much wider acceptance since its introduction in 1969 and the rate of increase in its usage is shown in Table 1 below which gives the quantities of PE pipe laid in consecutive years.

TABLE 1 QUANTITIES OF PE PIPES LAID IN BRITAIN

Year	Km of PE pipe
1971-2	870
1972-3	2500
1973-4	3747

The 1973-4 figure represents approximately 2800 tonnes of polymer. Most of the pipe is in small sizes ; systems consist of pipes from four inch* mains through to one inch or three-quarter inch services to houses. Some large diameter pipe has been used for insertion-replacement of old mains.

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* Imperial dimensions used for pipe sizes are a measure of the nominal bore. It is considered inappropriate to convert these to metric units because these sizes should not be confused with those of the metric systems now being introduced in which the size is a measure of the nominal minimum outside diameter.

The available figures for the American Gas Industry (1, 41) are for distribution systems of all plastics. The quantities used were :-

TABLE 2 QUANTITIES OF PLASTICS USED FOR GAS PIPE IN THE U.S.A.

Year	Tonnes of plastic
1964	860
1968	3900
1970	5290
1972	8970

The 1972 figure represents 16,900 km of pipe, the majority being two inches diameter and smaller. Plastic is the only material to show growth throughout the period from 1964 to 1972.

1.6. DESIGN CRITERIA FOR PE PIPES

Plastic pipe systems for gas distribution are required to have a level of performance specified by the appropriate national and international standards organisations. The specifications are generally performance orientated with minor material requirements where necessary to ensure long term stability. The performance tests in specifications can be divided into two categories - type tests and quality control tests. The latter are not important to the present work but the type tests which are the tests designed to ensure a safe 50 year working life are very much concerned with ESC.

The most important tests included in the British and American standards are the hydrostatic pressure tests. The failure mode of PE pipes under internal pressure changes with time. High pressures give ductile failures in relatively short times but lower pressures, which give longer failure times, can result in brittle failure. A plot of log of circumferential wall stress against log of time to fail generally results in two approximately straight lines with the second line, representing brittle failures, having a much steeper negative slope. This means that if brittle failures can be induced in tests, which will not normally run for more than one year, the material is unlikely to be suitable for 50 years service. The corollary of this is that specifications must be written which ensure that the 'knee' in the log stress versus log failure time graph is close to the minimum service life of 50 years. In order to do this any brittle failure at 20°C during a test must constitute failure of the pipe to comply with the specification, but this is not a good enough test so brittle failure must be induced in short times. This is done by testing at high temperatures. Normally hydrostatic pressure testing at 80°C is used to give a 'knee' in the failure curve and this 'knee' is related to that at 20°C by assuming relationships known to apply to similar materials. The type of failure which can occur at short times in an unsatisfactory material during 80°C testing is shown in figure 1.

The design criteria for a plastic pipe system cannot be based upon the pipe alone but must involve testing of all the fittings - the complete system. The performance specification applicable to the pipe must be applied to the system and the hydrostatic pressure tests are again of primary importance. Pipe extrusion should give a smooth, notch-free product and therefore reduce its susceptibility to brittle failure initiations. The specifications require this high quality of production. The complete system however must, by virtue of its design, have stress-raisers at the changes of section and may have notches caused by the fusion process. This makes the material's resistance to crack initiation and growth particularly important. An example of the type of failure which can be induced in a socket fusion joint by testing at high temperature and pressure is shown in figure 2 which is a photograph of a section through a straight coupler.

It was with pipe failures in accelerated tests in mind that this study of the ESC of crack resistant PEs was initiated. During the work, accelerated test failures of the type shown in figure 2 occurred and the relevance of crack growth studies of notched specimens was fully realised.

CHAPTER 2

THE ENVIRONMENTAL STRESS CRACKING OF POLYETHYLENE

2.1. INTRODUCTION

The environmental stress cracking of PE was first reported by Richards in 1946 (90) and the early interest in the phenomenon was generated by the telephone cable industry after the recognition of environmental failures in cable sheaths by Mougey (see 22). It was De Coste et al. (22) who stated that the embrittlement of PE by certain environments, which Richards defined as 'polar organic liquids', was not in fact embrittlement because there was no general stiffening of the material as shown by impact tests. They advanced the term 'environmental cracking' as being preferable.

A definition of ESC has been given by Howard (50) viz :
'ESC is the failure in a surface initiated brittle manner of a PE 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 stress may be involved and the sensitizing medium may be gaseous, liquid, semi-solid or solid.'
This definition based upon conclusions from early tests covers the main aspects of the phenomenon but omits the generally accepted points that the environment does not chemically change the polymer nor is it absorbed to any appreciable extent.

Reviews of stress cracking literature are available in published literature notably by Howard (49-54) and Vincent (102) and although these cover all recorded variables affecting the ESC of PE it is considered necessary here to overlap these reviews. The main reason for the present work is the study of a new test method and, although the previous reviews comment upon the differences in results obtained by different test methods, it is thought necessary here to put much more emphasis upon the test methods used by other workers in the field. It is also necessary to include more recent work although little has been published since 1968 and the bulk of testing PE has been of a fairly routine nature based upon the ASTM testing procedures.

There are two ASTM test methods for the ESC of PE materials, one (2), which is based upon the tests of De Coste et al. (22), provides essentially a measure of crack initiation time for specimens bent to a constant strain. The second method (3) is a constant load test for type III PEs based upon the method of Lander (67). These and similar test methods were used by many of the authors referenced in the following sections in which the main variables affecting ESC are described.

2.2. CRACKING CHARACTERISTICS

2.2.1. Surface Initiation

ESC is a surface phenomenon because there is, by definition, little penetration of the environment into the material. It has been found that cracks originate from surface defects or the edge of a specimen and that they invariably propagate at right angles to the major principle stress direction.

Carey (17) compared injection moulded and die cut specimens and concluded that flame polishing specimens or injection moulding them, rendered even susceptible PEs immune to cracking unless the surface was scored. This does not however correlate with the results of O'Connor and Turner (79) who found that flame polishing reduced the likelihood of cracking but did not render the material immune. The above conclusions led to the authors of both papers using 'stress raisers' in their constant load tests of plate specimens.

The importance of surface stress raisers is one of the variables dependent upon the exact method of testing. Suezawa et al. (99), studying tubes in torsion and tension, found that higher stresses led to the formation of more cracks suggesting that more surface imperfections reached a critical growth state. For uniaxial tension tests of notched specimens Marshall et al. (71) found that materials were notch sensitive but yielded at the notch tip when high net section stresses were applied to specimens. If only high stresses were used in tests this yielding could lead to the conclusion that PE is not notch sensitive and this was the conclusion of Isaksen et al. (61). Uniaxial tension tests on very thin specimens gave failure times for notch specimens which were the same as those for unnotched, because of yielding, leading to the conclusion that PE is not notch sensitive. This particular conclusion is considered rather negative but the microscopic studies reported in the paper are important because they show that PE is not notch sensitive in the sense that cracks grow from a prenotch. Voids were observed ahead of the notch which became blunt. These voids then coalesced and grew back into the blunt initial notch.

2.2.2. Applied Stress

Tensile stress is a pre-requisite of ESC. It is debatable whether this stress must be polyaxial. A susceptibility of PE to rapid brittle failure under biaxial stress, when no aggressive environment is present, has been found by Hopkins et al. (48) and although this has been related to ESC susceptibility there is a much greater molecular weight (MW) dependence than with the non-environmental failure. Ellis and Cummings (29) found that cracking did not occur in uniaxial tension and Heiss et al. (43) found it necessary to longitudinally notch tensile specimens in order to make them crack. McFedries et al. (76) used biaxially stressed Maltese Cross shaped specimens. They considered that the stress distribution in these was much more relevant to the majority of end uses, such as cables and pipes, because of the biaxial stress components. Also they thought that the most critical loading conditions would be defined by these tests.

Many authors disagree with this (17, 25, 28, 61, 98). The importance of polyaxial stressing is difficult to assess from these reports because conflicting arguments can be put forward to explain both conclusions. The lack of cracking in uniaxial tension could be regarded as a yielding effect, caused because the tests were not conducted at sufficiently low stresses. This point was made in the first section of this chapter and also was illustrated by Howard and Gilroy (54) who found for tensile specimens no cracking occurred in yielded material, but with specimens which had necked, failures occurred in the material between the yielded and the 'undisturbed' polymer.

The argument against those who have observed uniaxial tension failures is that, in practice, the attainment of the true uniaxial tension is almost completely limited to monofilaments and fibres.

The above-mentioned work of Howard and Gilroy could be interpreted as a demonstration of the effect of biaxial stressing because the necking region of a specimen is the section where the polyaxial stress components will be greatest.

As a result of the present work, which will be discussed later, and because of the results of Isaksen et al. (61) who tested specimens only 0.0125 mm thick, it is concluded that failure does occur in uniaxial tension but that yield is much more readily reached in the absence of the other stress components so much lower applied stresses and much longer times have to be used in testing.

Failure by yielding has been assumed in the above to be the opposite of ESC but in fact ESC is to a large extent a yielding phenomenon. The brittle nature of failures observed with the naked eye or under low magnifications is shown to be cold drawing on a very small scale when observed under higher magnification. De Coste et al. (22) illustrate the brittle appearance of cracks in low density PE (LDPE) cable sheath and refer to the rib and hackle pattern characteristic of glass fractures. Clegg et al. (19) illustrate the microscopic drawing of an apparently brittle failure as do O'Connor and Turner (79) who found, in tests on flat sheets, that the first part of the failure appeared brittle although it was semi-ductile and later the amount of cold drawing increased until conventional yielding was observed. It was found that cracks propagated further and there was less cold drawing when low stresses were applied to specimens.

2.3. MATERIAL VARIABLES

2.3.1. Molecular Weight

2.3.1.1. Average Molecular Weight

The effect of MW on ESC resistance of PE was realised by Richards (90) when he found high MW grades immune to cracking. Since these findings, grades of all MW have been cracked. The reviews of the influence of MW and molecular weight distribution (MWD) in polymers by Martin et al. (73, 74) cover ESC quite thoroughly so this section will only be a short review. Both constant strain tests (5, 22, 47, 64) and constant stress tests (7, 17, 45, 46, 67, 71, 76) showed that increasing weight average MW, or decreasing melt flow index (MFI), led to better stress crack resistance, all other things being equal. Some reservations have been shown regarding the generalisation that decreased MFI leads to increased stress crack resistance since abnormal circumstances can have effects. Notable amongst these are processing and addition of other materials. Howard and Gilroy (54) found that the working of material led to rapid decreases in MFI. The special effects of copolymerisation will be mentioned in a separate section.

The quantitative effect of MW changes in PEs is dependent upon density. Lower density materials (67) and copolymers (33) show much more dependence upon MW than high density in which it may be almost negligible.

2.3.1.2. Molecular Weight Distribution

Although there generally appears to be a good correlation between MFI and crack resistance it is not simple, since MWD and chain branching affect crack susceptibility. Herman and Biesenberger (44) showed that broader MWD Phillips polymers had worse ESC properties than similar Ziegler polymers.

It has been found that the low MW fractions have the greatest influence upon cracking and their extraction greatly increases times to failure (46, 48, 51). There are anomalies in results when quenching is used to solidify the polymer but this is likely to be an effect of internal stress rather than a material property. Zabusky and Heitmiller (114) found, however, that the importance of MWD was rather more complicated than previously thought. By fractionating commerical and experimental polymers, having essentially the same weight average MW and number average MW, and applying bent strip tests and tests on blow moulded bottles, they found that the experimental polymers with bimodal MWD had much better stress crack resistance. If this finding is interpreted in the same manner as the low MW extraction results it would show that the middle of the MW distribution is the most susceptible to cracking.

These MWD effects are utilised during the production of polymers since the idealised Gaussian distribution of MWs can be modified during polymerisation, or possibly in the future by fractionation (64), to produce a resin which will have a combination of properties to best fit an end use.

The processing work of Davies and Evans (21) had the effect of reducing the MWD of their material and after annealing, to remove the physical entanglements, it was found that stress cracking times were increased.

2.3.2. Blending and Copolymerisation

The other approach to the tailoring of polymers to give ESC resistance stems from the influence of additives. The addition of low MW linear hydrocarbons was found to have little effect upon cracking particularly at long times (61). The addition of Silanes was found by Schonhorn et al. (93) to have any of a number of effects ranging from virtual destruction of the PE to crosslinking. If the correct Silanes were chosen cracking resistance was greatly increased (not because of crosslinking). Similar results have been obtained with the addition of sulphonates (see for example 26), Polyisobutylene (PIB) and butyl rubber (22) and although all of these were tested in constant strain, and the modulus of the blended material is likely to have had an influence upon the results, the increases in failure times are considered to reflect significant increases in ESC resistance.

The same effects as blending of PIB can be obtained by copolymerisation. The addition of 5-10% PIB to high density PE (HDPE) has been shown (49) to greatly increase cracking resistance while also increasing processability.

Most examples of the effects of copolymerisation concern the ABS polymers. McFedries (75), in stress relaxation tests with styrene-acrylonitrile copolymers and a homologous series of straight chain alcohols as environments, found that low acrylonitrile content led to brittle failures (i.e. ESC rather than the solvent stress cracking experienced in other cases) particularly with short chain alcohols. Similarly Dixon (24) concluded from constant strain and creep rupture tests, in a number of environments, that ABS materials were better than impact polystyrenes. Stolki (97), again working with ABS but in a lard environment, found that as acrylonitrile content increased the crack resistance increased and there was a critical value of about 23% above which the time to crack increased by several decades.

2.3.3. Crystalline Structure

2.3.3.1. Quantity of Crystallinity

The potential for crystallization of a particular PE is a function primarily of its chain branching and, to a lesser extent, its MW. This potential is controlled by the thermal history of individual specimens which affects both the amount and character of the crystalline phase. Density provides a convenient, if not totally accurate, assessment of the total amount of crystalline phase but it does not reflect variations in crystalline texture which have an important bearing upon ESC. The molecular difference between LDPE and HDPE homopolymers is primarily that the chain branching decreases from about one branch per 10 carbon atoms to one branch per 1000 (44), the branches being primarily methyl groups, enabling the crystallinity and therefore the density to increase.

The exact effects of quantity of crystallinity are difficult to determine because of the effects of other variables. In constant stress tests increasing density in low density materials with the same MFI was found to slightly increase resistance to cracking but for all densities there was found to be little effect. In constant strain tests, or where stress or strain were allowed to decay at rates dictated by the creep behaviour of the polymer, a distinct relationship was found (see for example 50). This was presumed to result from the increased stiffness which accompanied increased density and constituted the primary reservation of the ASTM on their bent strip test (2). For biaxial tensile tests (76) increasing density was found to greatly increase times to failure but how relevant this, which is an effect of biaxial stressing (48), is to ESC depends upon the importance of biaxial stress components.

2.3.3.2. Crystalline Texture and Thermal History

The crystalline structure of crystallizing polymers is very dependent upon the thermal history to which they have been subjected. Because of this and other effects, such as the production of internal stresses, which can occur in all plastics, thermal history is of prime importance when considering ESC and many other factors involving plastics (28, 91).

In order to remove thermal history effects it is best to remelt the polymer since in the molten state 'memory' is lost and the temperature does not have any effect (22) assuming there is no degradation. It is the cooling rate which is of primary importance. Rapid cooling of PE leads to a more refined crystal structure whilst slow cooling permits the growth of larger spherulites and annealing permits the thickening of the fibrils within the spherulites if properly performed, or to a secondary recrystallization if performed at the wrong temperatures. Changes in the crystal structure greatly alter the stiffness of PE : shock cooling leaves the material soft and very slow cooling leaves it brittle provided the spherulitic structure is allowed to grow and is not affected by factors such as 'seeding'. Pelagatti and Baretta (84) found that changing cooling rates and annealing temperatures produced only very small changes in the amount of material in the crystalline state and they therefore concluded that this was not an important result of different conditioning procedures.

Because conditioning procedures affect the modulus of PE there must be quantitative differences in the results of ESC tests. The bent strip test results of De Coste et al. (22), Howard & Gilroy (54) and Pelagatti and Baretta (84) show that quenched specimens with their fine crystal structure and low modulus have the longest times to failure. Pelagatti and Baretta found that the slower the cooling rate the shorter the cracking time, but Howard & Gilroy found crack resistance increased again at very long cooling times. All three groups found that the effects of quenching were temporary and disappeared after 35 days in low MW materials (22) but were more permanent for higher MW, although all the conditioning effects were much less marked for low MFI materials. Conditioning at 50^oC (84) and 70^oC (54) both greatly reduced failure times but the conditioning at 50^oC was considered to be an acceleration of the effect which long periods at 20^oC would have on the metastable quenched material, whereas the 70^oC conditioning effect was said to be the result of a secondary recrystallization.

The results of quenching specimens before constant load tests are in some doubt. Isaksen et al. (61) and Larsen (68) found that quenched specimens gave better results than those cooled at slightly slower rates, whereas Hittmair and Ullman (46) found that failure times increased continuously for specimens cooled at a range of speeds from quenching at -80^oC to slow cooling at 6^oC/ hr. Herman and Biesenberger (44) testing shock-cooled and annealed materials with different MWDs found that the narrow MWD materials cracked more readily after quenching, whilst the broader distribution materials were more resistant in the quenched state. There was one exception, which was a polymer of lower density than the others but with a very narrow MWD ; for this material there was no significant difference between the two conditionings.

The only general conclusions which can be drawn from the results of constant load tests is that the effect of quenching is not very significant and is probably overridden by other polymer variables. There is however agreement (46, 61, 68) that very slow cooling is advantageous and greatly increases failure times for constant load conditions.

2.3.4. Orientation

Molecular orientation of PE seriously alters its susceptibility to cracking. A specimen stressed along the direction of orientation will require much higher stresses to cause cracking than a similar specimen stressed across the orientation. This is one area of study in which the method of testing does not really alter the conclusions, since it is effectively the softer material which cracks more readily in both cases. This effect provides evidence for the theory of critical strain dependence of ESC rather than critical stress.

In the extreme case, when yielding occurs during a tensile test, environmental failure does not affect the yielded zone but the lower strain regions (54). Doll and Plajer (25) related this to the effects of orientation caused by processing. In an unoriented polymer, cracking occurs at right angles to the stress direction but when the material has been processed in such a manner as to cause orientation, the cracking tends to take place in the direction of orientation, provided elongation takes place at an angle to that direction.

2.4. EXTERNAL VARIABLES

2.4.1. Temperature

2.4.1.1. Moderate Temperature Increases

Times to failure are shortened drastically by moderate increases in temperature because both initiation time and cracking time are reduced. The magnitude of the temperature effect has been demonstrated by De Coste et al. (22) who found that increases in test temperature from 50^0C to 97^0C reduced failure times by factors of 150 and 80 for materials of density 950 and 960 kg/m^3 respectively. Similarly O'Connor and Turner (79) showed cracking times were reduced by a factor of about 40 when temperature was increased from 30^0C to 50^0C.

Although this is extremely useful for shortening the time of tests it leads to difficulties in obtaining reproducible results. After comparing the results of a series of 'round robins' for the ASTM, Larsen (68) recommended that test temperatures should be controlled to $\pm$ 0.5^0C if the effects of temperature changes were to be ignored.

Opinionsas to the exact relationship between times to failure and test temperature are variable. The existence of a linear relationship has been advocated by Doll and Plajer (25) who put forward a simple expression for calculating times to failure at temperatures lower than those used in tests. Fulmer (33, 34) found Arrhenius plots showed the linearity of the data from bent strip and stress relaxation tests but Suezawa et al. (99) found their data did not give linear plots for tests on tubes in tension and torsion. Finally, and perhaps most important to the present work, Hittmair and Ullman (46) showed that their results for tests at 50^0C and 60^0C became very similar when allowance was made for the ultimate tensile strength of the material at the two test temperatures.

2.4.1.2. Excessive Temperature Increases

When considering testing at high temperatures in order simply to accelerate the testing, although it is not relevant to conditions of end use, great care must be taken to ensure that no changes in mode of failure occur. Fulmer (33, 34) justified the use of temperatures up to 97^{o}C for materials with densities 950 and 960 kg/m^3 but found a change in mode of failure at 110^{o}C for 960 kg/m^3 density PE. With lower density materials it is likely that the temperature at which this change occurs will be lower because the lower end of the melting range of the polymer is probably the important factor in high temperature tests.

2.4.2. Environment

2.4.2.1. Types of Cracking Agent

Many environments adversely affect PE ; Peters (85) gives a comprehensive table comparing the effects of 320 environments upon 55 plastics, including PE, and Howard (49) compares the effects of a number of environments upon a PE in bent strip tests. Richards' (90) original description of cracking environments as being mobile polar liquids has been shown to be rather lacking and numerous environments, including nitrogen, air and water, have been found to cause cracking (35, 49) although high temperature air tests have been associated with oxidation.

Cracking agents are known to have very little effect upon the unstressed polymer and are separated from solvent cracking agents by the lack of weight increase during immersion tests. Hittmair and

Ullman (46) found absorption tests with Igepal CO 630 gave equivocal results but when molten polymer and Igepal were mixed and then the polymer allowed to solidify, IR spectroscopy showed no Igepal in the PE, which meant the actual concentration would be less than 0.01%. This slightly contradicts the work of Isaksen et al. (61) who found cracking environments were absorbed, but only in very small quantities, and De Coste et al. (22) who measured the absorption of Igepal in PE and found it to be 0.08% at 25^{o}C and 0.30% at 60^{o}C, by weight. For ethanol Richards (90) measured the absorption as 0.002 cc/gm of PE.

There is more agreement in this respect when test results are considered. Tung (100) showed that there was no effect upon the creep properties of PE in a 25% Igepal solution until cracking initiated. O'Connor and Turner (79) showed that cracking stopped when the environment, silicone oil, was removed and Marshall et al. (71) found no effect from pre-soaking in alcohols.

If there is a slight absorption of detergents, alcohols and other cracking agents, the quantity absorbed and the rate of absorption will be increased by stressing the PE in the environment (46, 111). J.L. Williams and Peterlin (111) have shown that drawn PE absorbs less benzene than undrawn unless the sheet is drawn in the benzene when there is a two-fold increase in sorption and a 70-fold increase in the diffusion constant compared with the undrawn sheet. They observed large numbers of microcracks in the opaque sheet, drawn in the benzene, which might account for the observed properties. These findings demonstrate that cracking is not limited to unabsorbed environments. Although many authors have shown that only yielding occurs in the presence of absorbed liquids, Carey (17) found toluene to be a very aggressive cracking agent for specimens pulled on a tensile testing machine. This is probably because Carey found the right combination of testing speed, PE and environment to give cracking before large scale absorption and softening could occur.

2.4.2.2. Properties of Environments

The main generalisation which has been applied to cracking environments is that they are adsorbed on to the surface of PE and that it is this adsorption which in some way facilitates cracking. Siemiya et al. (95) showed that, as with absorption, stressing the specimen increased the adsorption and caused cracking which in turn further increased adsorption. Working with LDPE and PE/PVA copolymer it was found that there was more adsorption by the homopolymer in bent strip tests but no significant difference for tensile specimens. The effect of absorption has been suggested as being to lower the cohesive bond strength around the interfaces of a microfissure as observed in other environmental crack growth phenomena (see for example Rehbinder (88, 89)) and to institute a spreading pressure at the apex of the fissure causing it to grow (61). If this is true it would be expected that surface tensions would play an important role in failure speed, but Hittmair and Ullman (46) showed that there was no such effect. To accompany their tests on different environments Hittmair and Ullman used dilutions of Igepal and found that the more concentrated solutions gave shorter times to fail than the dilute solutions and 100% Igepal was the most aggressive of all. They concluded that the surface tension was not the controlling factor in this case because it was lower for the very dilute solutions. McFedries et al. (76) found that results for 100% Igepal and dilutions to 3% all gave the same results in biaxial tension tests and that more dilute solutions required longer failure times. They regarded this as an effect of interfacial tension which they found to be constant from 100% to 3% Igepal. Larsen (68) also reports little effect of strength of Igepal. Another opinion on dilutions came from Pelagatti and Baretta (84) who found for bent strip tests that for two polymers and a range of MFIs a 10% solution of Igepal was more aggressive than the anhydrous detergent.

The surface tensions of methanol and ethanol are effectively identical but Isaksen et al.(61) and Marshall et al. (71) found ethanol was a more aggressive cracking agent than methanol. However, since methanol is the smaller molecule, it might be expected to cause more rapid cracking. Isaksen also showed that wettability on PE was not a controlling factor. Bergen (11) took the opposite view when he found that those environments which had low contact angles on PE tended to cause cracking more readily as did environments with small molecules.

There are few, if any, conclusions which can be drawn from the conflicting reports, only the importance of adsorption is not contradicted.

2.5. MECHANISM OF FAILURE

2.5.1. Structure of Polyethylene

Polyethylene molecules consist of a main chain with side branches, the number and length of the side branches and the length of the main chain depending upon the polymerisation process. During crystallisation the long chains fold to form platelets or lamellae, which grow usually from an impurity, which acts as the centre of crystallisation. The growing lamellae radiate from the centre forming a spherulite. The crystallisation process is very selective with chains of about the same molecular weight going together to form a lamella and leaving 'impurities' out of the crystalline structure (61, 63). These impurities which include low MW material and possibly parts of long chain branches, are pushed into the regions between the lamellae and between the spherulites. The impurities constitute the amorphous weak links in the system although there are interlamella tie molecules, particularly in high MW polymers, which cross the amorphous regions and give added strength to the bulk material.

2.5.2. Microscopic Failure Studies

Studies of stressed spherulites in LDPE by Reding and Brown (86) have shown that cracks grow radially through the spherulites. This work was extended (87) to show that the cracks ran between the crystalline regions. Hittmair and Ullman (46) observed crack growth in their Carey-type specimens and found the cracks grew radially through the spherulites from the stress-raiser hole. When there was no Igepal present, cracking occurred at higher stresses and was accompanied by cold drawing. The broken edges of the polymer had a different appearance from those of the environmental stress cracked material. Isaksen et al. (61) studied thin ESC tensile specimens which were notched in order to locate the point at which cracking would occur. They found that 'fissures' grew through interspherulitic regions as readily as interlamella regions. These fissures, or elliptical shaped microzones of cold drawing, developed in advance of the razor cut. In water, the drawn area grew by interconnection of the fissures but the drawn material remained mainly unbroken. In an active environment, the development of the fissures was similar but the drawn zones suffered rupture between the drawn and the undrawn material. It is thought that these results may be affected by the plane stress loading. Haas and MacRae (40) have extended these studies to biaxial strain. As with Reding & Brown it was found that the majority of the cracks emanated from the centres of spherulites, although occasionally there was cracking at boundaries. The detergent was found to have no effect upon the strain at which cracks occurred nor upon their appearance, but the small cracks coalesced more readily in the presence of the detergent. It appears that the yielding found in uniaxial tension tests was suppressed. It was noted that some drawing occurred when a crack traversed the diameter of a spherulite.

2.5.3. Role of Environment

The precise mechanism of ESC failure is unknown and this is largely because the role of the environment is in doubt. Two ideas have been put forward which have been accepted as the most likely explanations. These are :-

a) The environment reduces the stress required for cracking by reducing the energy of surface formation (this includes energy for plastic drawing not just surface energy)

b) The environment contributes a stress over a microscopically small area which, when added to the applied stress, exceeds that required for crack propagation.

Although the latter was considered to be the more likely at one time, the reduced surface energy hypothesis has become more widely accepted. The microscopic observations in the previous section make the second suggestion extremely unlikely, as a spreading pressure inside a crack will be effectively the same as an externally applied stress and there seems no reason why this should not cause yielding in the same way as increased applied stress with a water or air environment.

The relative lack of absorption of environments has been discussed earlier but it is worth noting that the characteristics of absorption, as specified by Richards (90), bear certain similarities to ESC. Absorption takes place in the amorphous regions of the polymer and is greatest in low MW materials, particularly those with broad MWDs, and the presence of very short chain material also increases absorption. It is perhaps relevant that there are these similarities since it is not absolutely proved that no absorption occurs in PE under stress.

2.5.4. Role of Material Structure

The crystallisation process in PE which rejects low molecular weight and highly branched species, leaving them between lamellae or between spherulites, concentrates all the weak material in spots where it can seriously impair the strength of the whole polymer. The strength of the amorphous material and its ability to stop microcracks will depend upon the covalently bonded interlamella tie molecules and the less strongly bonded 'rejected' material. The few strong bonds are likely to be the main crack arrestors (40). If this is a correct assumption a number of the molecular structural findings of ESC can be explained.

Tie molecules are more common in high MW material, there being a much greater likelihood that a long molecule will be involved in crystallisation from more than one centre, so this idea is consistent with the conclusion that high MW materials are more resistant to cracking. If the structure could be held together by more primary bonds, with the low MW fractions either included or bridged across, then cracking should be reduced. This has been found to be the effect of cross-linking (4) which can make a PE immune to ESC. Similar structural changes can be obtained by shock cooling which slightly increases crack resistance. The results in this case are much less marked and they are confused by the fact that the smaller spherulites give shorter paths for cracks to grow along before reaching a crystalline region.

If the strength of the numerous secondary bonds and the physical entanglement of the amorphous region were of primary importance, density would be expected to have a marked effect because the very large increases in the thickness of the amorphous regions with reducing density would give more crack initiation points and more paths of weakness through the regions. As only a slight density effect is found under constant load conditions, it is likely that the tie molecules, which will not greatly alter in number, are the controlling factor.

Tie molecules are not the only important features of crack resistant polymers. Reding and Walter (87) have considered the role of spherulite size and the importance of restricting the growth of a perfect crystalline structure, leaving long amorphous regions uninterrupted by crystalline regions. Shock cooling and seeding are the most obvious ways of restricting spherulite growth and both possibly give increased crack resistance although the effect of quenching, as discussed earlier, is not very significant. Reding and Walter say similar effects cause improved performance in PE containing additives such as rubbers.

A third factor which could affect crack resistance is internal stress, caused during the crystallisation process or general thermal contraction. This should make shock cooled material more prone to cracking which it does not. The reason for this could be either that other factors prevail or that on a microscopic scale internal stresses may be relieved by the formation of micro-cracks, which would simply add to those caused by an applied stress and have little effect, since it is the propagation or arrest of microvoids which is important rather than their formation. Alternatively internal stresses could act to disguise the increased crack resistance which should be provided by the small spherulites. On a macroscopic scale internal stresses can cause failure without any external stress being applied. This factor provides what is probably the only use of ESC which is as a test of quality of mouldings (7, 9).

The effect of copolymerisation is unexplained by the above hypothesis. Copolymerisation with other olefins causes a reduction in density and accompanying reduction in upper yield point and ultimate tensile strength. The reduction in density is caused by chain branching and therefore less crystallinity, in a manner very similar to the branching effect in the homopolymer. The changes in physical properties are exactly the same as those found by reducing the density of the homopolymer (31) but the ESC resistance is greatly increased by copolymerisation.

2.6. TEST METHODS

2.6.1. Constant Strain and Constant Load Tests

Throughout this review reference has been made to the differences in results obtained from different test methods. As an introduction to the method employed in this work some of the more important procedures which have been developed must be considered.

The primary constant strain test is the ASTM bent strip test (2) which consists of immersing a rectangular specimen, with a longitudinal razor notch, bent through 180° in a tube containing Igepal CO 630 at 50°C. The definition of failure of a specimen is the appearance of a crack and the time to fail is the average for the 20 specimens used. The first problem with this type of test was gaining inter-laboratory reproducibility. Kaufmann (62) and Rudin and Birks (91),who found scatter so great that tests at 40°C failed more readily than those at 30°C, suggested modifications to the accepted method to reduce scatter. The real improvements to reliability came as the result of the ASTM 'round robins' and Larsen (68), who found it necessary to carefully control thermal history of specimens and to control test temperature to ±0.5°C.

Because the method is based upon applying a constant and large strain, the dominant factor affecting failure times was the material density. Although this factor may be relevant to cable sheathing, as a general test for comparing materials, it is of little use. The ASTM have accepted the recommendation of McTigue (77) that specimens of high density material should be thinner, but this does not really solve the problem, it merely makes the test applicable to constant strain applications for high density material. The ASTM say : 'Information from this test is not intended to be used for direct application to engineering problems'.

The constant load test adopted by the ASTM (3) consists of applying a load to each of about 20 dumbell specimens immersed in Igepal CO 630 at 50°C. Again the average failure time is calculated but failure is defined as total fracture. This type of test stems from the constant strain rate tests of Carey (17), who found it

necessary to have a hole through the specimen, but the actual test employed was that of Lander (67). Larsen (68) has published the results of the ASTM 'round robins' which were conducted to enable the realisation of maximum reproducibility, but the results depend upon the applied stress selected and, at present, can only be used for type III PEs. The ASTM are more confident of the applicability of this method saying :
'Results obtained under the conditions specified in this method do not necessarily relate to the performance of the plastic in a particular end use. However, by evaluating the material over a suitable range of initial stresses or temperatures, or both, using this method, information useful for predicting end use performance may be obtained'.

There are a number of test methods which have involved biaxial stressing (40, 47, 76). These have been developed because of the suspected importance of the stressing mode in reducing times to failure which may serve to show that other test methods are lacking, but does not really provide information suitable for design purposes. A similar criticism can be applied to the tension and torsion tests on tubes performed by Suezawa et al. (98, 99). These served the purpose of showing the importance of tensile stress as opposed to torsion.

The aim of the constant load type tests is generally to define a critical stress below which failure will not occur, at a given temperature in a given environment, but there is a lot of scatter on results in spite of strict control of specimen production, both thermal history and method of cutting specimens. The importance of specimen surface finish was mentioned earlier when reference was made to the effects of flame polishing. Carey (17) recognised the importance of surface defects and attempted to 'nick' specimens with a razor blade but found that this could not be performed with sufficient consistency to improve results, so he drilled circular holes through specimens to provide a stress raiser. This did not however solve the problem as the surface inside the hole became an important factor (46) and a return has been made to razor notching techniques (36, 61).

The time dependence of critical stresses led to the hypothesis of a critical failure strain which would be almost independent of time, requiring only a short period to enable the environment to bring about failure. The test methods used to confirm this were primarily either on individual specimens strained upon a jig which gave different strains along the length of the specimen or on a number of identical specimens each strained to a different level upon a jig. Numerous verifications of the hypothesis have been made (10,11, 23, 25, 79, 92, 100) and they have led to correlations being made between creep tests in air, rapid jig tests in cracking environments and long term strength in the environments.

Whilst accepting the critical strain criterion O'Connor and Turner (79) point out that the relationship between overall strain and local conditions is obscure, which implies that the same scatter on results as the constant load tests is likely because of surface finish. It was also noted in constant strain tests that the mode of failure depended upon the stress level. Bergen (11, see also 7) noted a similar finding and also that the critical strain decreased with increasing stress at high stress levels. At lower stresses he found that the failure strain-stress relationship levelled off and so accepted, for practical purposes, that there was a critical strain.

2.6.2. Application of Fracture Mechanics

The lack of reproducibility of results from the standard tests for ESC and the differences in results obtained with the different types of test mean that, for engineering purposes, there is too much guess work required when choosing a material for a particular end use, where ESC could be a problem. Manufacturers can produce grades of PE which are very difficult to crack (impossible in some tests), but these are expensive so it is important for many applications that the grade of material can be selected which will serve its purpose without being too expensive or too difficult to process. For the more important load bearing applications of PE, such as gas pipes, expense is not the main criterion of material choice. What is important is the ability of the designer to predict the effect which any environment will have during the fifty year design life. Both these criteria require a better test method than those presently available.

CHAPTER 3

FRACTURE MECHANICS

Fracture mechanics are normally used to predict the conditions under which a structure, loaded to well below its general yield stress, will fail by rapid propagation of an existing crack. There are many reviews of fracture mechanics theories in the published literature and for full details reference should be made for instance to Berry (13), Irwin and Paris (60), Knauss (65) and Paris and Sih (83). The following history is intended to serve only as a background to the following work.

3.1. GRIFFITH'S THEORY

The study of fracture originated from the work of Griffith (39) who explained the differences between the theoretical and actual strength of materials in terms of the differences in strain energy stored in cracked and uncracked plates under stress. By assuming a crack had an elliptical profile and applying the stress equations of Inglis, Griffith calculated the strain energy at the tip of a crack and equated this to the theoretical energy required for the formation of two new surfaces in the material, thus defining the critical condition for crack growth. The critical applied stress was found to be dependent upon material properties and inversely proportional to the square root of the crack length, which was verified experimentally. Griffith's original equations for critical stress were found to be wrong but after modification they became :-

$$\sigma_c = \sqrt{\frac{2\,E\gamma}{\pi\quad c}} \qquad \text{for plane stress} \qquad 3.1$$

and

$$\sigma_c = \sqrt{\frac{2E\gamma}{\pi(1-\nu^2)c}} \qquad \text{for plane strain} \qquad 3.2$$

3.2. STRAIN ENERGY RELEASE RATE

Further verifications of the analysis followed and the theory was effectively extended, by Irwin (55) and Orowan (81), to include the energy irreversibly consumed by plastic flow, by replacing the surface energy with an energy term which was orders of magnitude larger.

Irwin defined a strain energy release rate (G) which included all contributions to the energy dissipated as the crack advanced including (as shown by Paris and Sih (83)) those which were not related directly to that required for the formation of new surfaces. In the critical case (Gc) the strain energy release rate is similar to the Griffith surface energy inasmuch as it is the energy to form two new surfaces.

3.3. STRESS INTENSITY FACTOR

Irwin (57) used the work of Westergaard (105) to obtain equations for the two-dimensional stress distribution in the vicinity of a crack tip. These equations may be summarised by :-

$$\sigma_{ij} = K(2\pi r)^{-\frac{1}{2}} f_{ij}(\Theta) \qquad 3.3$$

where r and Θ are polar co-ordinates with the origin at the crack tip and K is the stress intensity factor. The equations are for opening mode stressing (mode 1), K therefore is called K_1.

Irwin (57) also considered analytically the work required to close a segment of a crack by applying forces perpendicular to the crack surfaces. The results of these calculations were that the strain energy release rate, or crack extension force, was found to be related to the stress intensity factor by the equations

$$G = \frac{\pi K_1^2}{E} \quad \text{for plane stress} \qquad 3.5$$

$$G = \frac{\pi K_1^2(1-\nu^2)}{E} \quad \text{for plane strain} \qquad 3.6$$

From these equations it is obvious that if there is a critical value of G (Gc) then there is a corresponding critical value of K_1 (K_{1c}), at which fracture will occur. By substituting G for 2γ in equations 3.1 and 3.2 it is found that K_1 is a function of applied stress and crack length only. The generally accepted equation for K_1 does not fit the equations thus calculated ; they must be multiplied by a factor of $\sqrt{\pi}$ to give

$$K_1 = \sigma \sqrt{\pi a} \qquad 3.7$$

The K_1 defined by the above equation is applicable to an infinitely wide, centrally notched plate but making the equation applicable to any geometry is only a matter of suitable mathematical adjustment to allow for the stress field. The equations for K_1 used in this work for finite specimens with single edge notches (SEN) and centre notches (CN) are those of Brown and Srawley (16) and are :-

$$K_1^{\,2} \quad = \quad Y^2 \sigma^2 a \qquad 3.8$$

$$\text{where } Y = 1.99 - 0.41\,(a/w) + 18.70\,(a/w)^2 - 38.48\,(a/w)^3 + 53.85\,(a/w)^4 \qquad 3.8a$$

for SEN and

$$Y = 1.77 + 0.227\,(2a/w) - 0.51\,(2a/w)^2 + 2.7\,(2a/w)^3 \qquad 3.8b$$

for CN.

3.4. PLASTIC ZONE

The preceding analyses are based upon linear elastic stress analysis and so are not really applicable to the many circumstances in which G and K_1 have been found to work reasonably well. Without performing a full elastic-plastic stress analysis, methods have been devised to define a fracture criterion. Irwin (58) studied the relationship between an esimate of the plastic zone size at the tip of a crack and plate thickness and the effect of this relationship upon the ductile-brittle failure mode transition. Later (56) he used the same plastic zone radius (r_y) to reduce crack length effects on fracture results in aluminium. The modification made to the elastic analysis was simply to assume that the crack tip was effectively at the centre of the plastic zone, so the crack length was increased by the plastic zone radius given by the equation :-

$$r_y = \frac{1}{2\pi}\left(\frac{K_1}{\sigma_y}\right)^2 \qquad 3.9$$

where σ_y is the yield stress of the material under test.

3.5. CRACK OPENING DISPLACEMENT

An alternative criterion of fracture was suggested by Wells (104). This criterion was a critical opening of the faces of a crack in the vicinity of its tip. There are two assumptions in this crack opening displacement (COD) criterion. They are that failure is essentially the result of a critical strain induced in the locality of the flaw and that the opening of the flaw near its tip is a measure of this strain. In order to use the COD criterion, it is necessary to relate it to the loading and geometry of a body and this is often done by employing the analysis of Dugdale (27). Dugdale considered an internal slit of length 2a in an infinite elastic plate (and equally an edge crack of length a in a semi-infinite plate) under uniaxial tension (σ). He also considered the slit to consist of an unstressed section, of length 2ℓ, and two near tip sections, of length s, under surface tractions (Y). By superimposing the two stress distributions to eliminate the stress singularity at the end of the slit (slit half-length = a = ℓ + s) Dugdale calculated the ratio of s to a. The physical interpretation of this analysis is the elimination of the stress singularity by the formation of a line plastic zone of length s along which the material is at its, constant, yield stress (σ_y) and the linear elastic crack length (2a) is related to the actual crack length (2ℓ) by the equation :-

$$\frac{\sigma}{\sigma_y} = \frac{2}{\pi} \cos^{-1}\left(\frac{L}{a}\right) \qquad 3.10$$

For a fuller explanation of this approach reference should be made to Hayes (42).

The Dugdale results also fit well the analysis of Barenblatt (6) who mathematically removed the stress singularity at a crack tip by applying opposing forces to reduce the stresses to the level defined by the 'cohesion modulus' of the material.

3.6. APPLICATION TO SLOW SPEED CRACKING

The fracture mechanics concept has been based upon the definition of a critical parameter giving the conditions under which an existing crack will start to grow in an unstable manner. The concepts discussed above have successfully been used as fracture criteria for a large range of materials, including plastics, but more recently the same criteria have been related to crack speed both analytically and experimentally. There are two aspects of this relationship applying to slow and rapid propagation, the former being successfully applied to fracture in environments.

The reasons for fracture speed being dependent upon K_1 are two-fold :-

a) For fracture, which is not necessarily induced by an environment in a material whose strength properties are time dependent (e.g. non-linear visoelastic as in the case of PE), it is reasonable to assume that the strength of the crack tip material, which is being stressed to failure, will be dependent upon the rate at which it is being stressed. This in turn will be dependent upon the crack speed. Conversely, if the material requires a greater energy to cause failure at a higher strain rate, then a higher K_1 must be applied, and more strain energy made available at the crack tip region to cause fracture at a higher strain rate, i.e. a higher crack speed.

b) For environmentally induced failure the rate of penetration of the environment into the crack tip region will determine crack speed. This penetration rate will be dependent upon the available free volume through which the environment can flow and this in turn is a function of COD and probably K_1.

In neither of these cases is it suggested that the K_1 - crack speed relationship is simple.

Relationships between K_1 and crack speed have been found for the fracture of PMMA and LDPE by Marshall et al. (69, 70, 71, 72), for Glass by Weidmann (103) and aluminium by D.P. Williams (106). The work on LDPE (71), which was performed using alcohols, served as the lead to the present study in which only materials particularly resistant to ESC were used.

CHAPTER 4

EXPERIMENTAL - FRACTURE TESTING

4.1. INTRODUCTION

4.1.1. Aims

The Literature Survey refers to the successful applications of fracture mechanics to the cracking of polymers. Reference is also made to the correlations between stress intensity and crack speed. The work of Marshall et al. (69, 71) demonstrated that LDPEs with MFIs 7 and 20 could be made to crack readily in ethanol and methanol, but this work has been criticised because the materials were known to be very easy to crack.

The present work was begun with the intention of extending the work on cracking of PE to materials which were known to be extremely difficult to stress-crack. The initial aim was simply to see if PEs selected for their crack resistance could be made to crack and, if so, whether the crack growth could be measured. The real aims of the project were to find whether the test method which had been employed by Marshall (69) was applicable to polymers in which ESC resistance is important and, if applicable, to develop it to a stage where it might be used commercially. The importance of developing a test method is shown by the contradictions in the literature on ESC and the ultimate requirement of this work was to define a parameter by which the stress crack resistance of all materials could be compared. This parameter would then be used to consider some of the variables which other workers have considered. Most important was the intention to define a parameter which could be used in design work to define safe conditions for components in adverse environments.

4.1.2. Materials

The materials used for all the tests in this work are listed in Table 3

TABLE 3 MATERIALS TESTED

	Material	Nominal* MFI (gm/10mins)	Nominal Density (Kg/m^3)	
PE-A	BP Rigidex 002/60	0.2	960	Homopolymer
PE-B	" " 002/55	0.2	955	Copolymer
PE-C	" " 002/47	0.2	947	Copolymer
PE-D	" " 002/40	0.2	940	Copolymer (yellow)
PE-E	" " 2000	0.2	954	Copolymer
PE-F	ICI 0585 2242	0.2	935	Homopolymer (yellow)
PE-G	" " 2211	0.2	935	Homopolymer (yellow)
PE-H	Du Pont Aldyl A	1.9	944	Copolymer (yellow)

* All the MFIs were measured using a load of 2.16 kg.

The majority of the tests were performed using the series of BP materials, which were Phillips polyethylenes. PE-A is the basic homopolymer, and the other materials have increasing amounts of comonomer in the polymerisation causing the reduction in density. PE-E is a copolymer similar to PE-B but it has undergone different copolymerisation and formulation procedures. It is noted that two batches of PE-E were used in this work and they had slightly different formulations.

All the yellow materials included were, at the time, prospective gas pipe materials. PE-F and PE-G were the same except for their pigments and were included for comparison with the other materials as well as to find whether the two pigments would have any effect upon the cracking resistance. PE-H, in its tan coloured American produced form, had been used for natural gas pipes in the U.S. for more than twelve years without any reported ESC problems and was included for comparison with the other materials.

All the materials were received in the form of compression moulded sheets having been slow cooled.

4.1.3. Environments

The primary environment for ESC tests is Igepal CO630 which is an alkylphenol polyoxyethylene ethanol, a non-ionic detergent. For the tests in this work Adinol CO630 was used. This is a detergent made to the same specifications as Igepal but by another manufacturer. All the elevated temperature tests and many of the 20^{o}C tests were performed using concentrated Adinol but a series of dilutions of 10% v/v and less in distilled water were also used in order to investigate the discrepancies in results obtained by other workers, as described in section 2.4.2.2. Higher dilutions were not used because they turned to gels which could only be liquified by addition of alkali which would possibly invalidate the tests. The tests indicated 'trace of Adinol' were performed in tanks as shown in figure 9. The tanks having contained Adinol were washed and soaked for 24 hours before being used for tests in distilled water. The conclusion from comparison with other tests in water, performed in tanks whose components had never been used for detergent tests, is that the Adinol had not been totally removed.

The other environments used were the commerical detergent Teepol and the three alcohols methanol, ethanol and butan-1-ol. Both detergents and alcohols are recognised cracking agents, the constituents of neither group being absorbed by PE to an easily measurable extent (alcohols are used to precipitate PE).

To expand the work beyond testing with the worst possible environments and make the results more relevant to normal working environments for PE, tests were also performed in water and air. Air is recognised as an oxidative stress cracking agent when causing cracking at elevated temperatures and has been found to cause chemical changes in the material but this factor has not been considered in this work.

4.1.4. Notching

It was considered important that different notching techniques be used to show whether the initial notch affected the crack growth. The initial notch is a factor of primary importance in fracture tests to determine the criteria controlling the onset of rapid propagation. The failure criterion found will be dependent upon the shape of the critical initial defect and tests are useless if they do not represent the worst case which can occur in the structure to be designed.

For slow propagation tests the initial notch is not likely to be as important because the initiation condition is not considered, and once crack growth has started the crack forms its own leading edge configuration which is likely to be consistent. There is, however, the possibility that the initial notch will in some way influence the notch which grows from it and that this inherited characteristic will remain with the crack and invalidate the results. For this reason the effects of notching technique were considered.

The initial tests were on SEN specimens, see figure 3, and it was on these that notching techniques were tried. The first method was to make a saw cut in the edge of a specimen and sharpen it with a new razor blade. The notch thus formed went no deeper than the razor blade and no real crack was formed. When loaded, the notch appeared blunt and a sharp crack grew from it. As the growth of the sharp crack was the important factor, the notching was thought satisfactory.

However, some scatter on results (see also section 6.8.) led to the belief that the first few millimetres of cracking might be influenced by the notching, so three other techniques were employed. The first was pre-notching at a higher K and allowing the specimen to recover before testing. The second was impact notching using a razor blade and holder, falling under gravity and being stopped when the blade had entered the specimen by 3mm - 6mm. The third method was the same as the second but with part of the specimen cooled with liquid nitrogen. In these cases brittle cracks propagated from the end of the razor and these were restrained by tightly clamping the faces of the specimens.

The different notching techniques were found not to change the results so the first method was readopted and similar methods were used for the CN specimens using part of a scalpel blade and for the surface notched (SN) and pipe specimens using the curve of a scalpel blade.

4.2. CONSTANT LOAD TESTS

4.2.1. Introduction

From the outset of this work it was realised that if crack resistant PEs could be made to crack, and the cracks observed, the tests would have to be of long duration. Long term testing poses a number of difficulties, the first being the determination of the conditions under which to perform tests. When loading the initial test specimens only guesses at the conditions under which cracking will occur can be made. Too high a load will lead to yielding either in the bulk of the specimen or at the crack tip and perhaps the yielding will not occur until after a considerable test time. The other extreme comes with low loads when the time required to cause initiation becomes very long and perhaps so long that the test has to be given up with a consequential delay on results. The two extremes in the case of ESC testing are not very far apart and finding the zone from which useful results come is difficult. Even when this zone is found its realisation takes a considerable time because of the long initiation periods.

The second problem posed by long testing times is deciding which variables to study. Only a limited number of variables can be considered so it is important that these are the ones most likely to give informative results. Finally, in order to consider as many variables as possible only the minimum number of tests must be performed when justifying any conclusion or comparing any variables.

4.2.2. Experimental

The majority of this work is based upon tests performed upon constant load rigs. The rigs consisted of a rigid frame supporting a lever loading mechanism in which lever arms of ten to one were normally used. The lever arms were pivoted in bearings to reduce the friction to a negligible level. The loads on the specimens were applied either through chains or pivoted, threaded bars both of which would permit a small amount of misalignment without applying a torque to the specimen. The specimen clamps were attached to the lever arm connection and the base of the rig by pins at right angles. These ensured freedom of movement to eliminate bending stresses in both directions.

The specimens were immersed in tanks of environment. The design of the most successful tank which was made of brass is given in figure 4. Tank sealing with 'Neoprene' or nitrile rubbers was found to be successful but other rubbers were either attacked by the detergent environment or they contaminated the environment.

The first tests were on 1.5 mm thick SEN specimens in methanol at 20°C. A number of tests were attempted using different loads on similarly shaped specimens but no crack growth was observed. High loads gave yielding and lower loads gave a dark zone at the crack tip which was assumed to be yielding on a smaller scale. Because of this lack of success, detergent was used as the cracking agent and only low loads were applied. On some of the tests thin dark lines were observed at the ends of the notches. These lines gradually extended for a few millimetres and then stopped. When a specimen was sectioned through this line it was found that there had been some crack growth through the middle of the specimen's thickness but that the two edges had yielded. It was assumed that this yielded material had stopped the crack proceeding by supporting the applied load. This effect, which was observed at some stage on every specimen, was described as crack tunnelling.

The presence of the yielded material invalidated any crack speed measurements so it had to be eliminated. The first steps towards eliminating the yielding were based upon the assumption that it was caused by the plane stress field at the edge of the specimen and that the loading was still too high. So specimens of 6 mm thickness were tested with lower initial stress intensity factors than used on the earlier specimens.

The first reasonably successful tests were on PE-E in Teepol. The low applied Ks meant test times of a month or more were required but the width of the specimen which failed in a macroscopically brittle manner was greater than the yielded material at the specimen edges. During these tests the crack lengths were measured, using a travelling microscope, and times were recorded.

The cracks obtained during these tests were still not totally satisfactory, for there was still a visible amount of yielded material at the edges of the specimens, as can be seen from the fracture surface photographed in figure 5. As the width of the yielded material increased with crack length, and therefore K, it was thought that the loads were still too high. In successive tests the loads were reduced until long lengths of macroscopically brittle fracture surface were obtained and tunnelling was limited to the last stages of crack growth, see figure 6. These Ks have meant that the majority of the tests at 20^oC have taken about two months to complete and some have taken six months.

As well as altering the loadings to improve test results the environment was changed to Adinol CO630 during the early development stages. Apart from being the most widely used cracking agent its advantages over other detergents are :-

a) It is chemically simpler than most commercial detergents which are blends of soaps and detergents with water, colouring and other additives.

b) It does not contain colouring and therefore cracks are more easily observed.

c) Being a concentrated detergent, it does not evaporate significantly even at elevated temperatures.

An experimental detail which it is thought should be included concerns the visible crack tip. Figure 7 shows a normal crack and from the photograph the position of the tip is obvious, but in the early tests, where side yielding was prevalent, the open crack tip was preceded by a dark zone (lighting from the back of the specimen). As the experimental technique was improved this dark zone was greatly reduced, but in many tests a small dark zone appeared. The position of the crack tip was always taken as the tip of this dark zone because it was considered that this point indicated either, the tip of a slightly curved crack front, or the tip of a craze-like zone, either of which should be regarded as the true crack tip.

Having found that cracks could be observed growing through crack resistant, low MFI, PE the next step was to determine whether the K_I-crack speed approach was valid. The measurements of crack length and time were converted to K_I and crack speed and plotted as explained in the results section. The repeatability of the results obtained from tests on SEN specimens was not sufficient to justify the approach. The validity and the importance of the use of a critical, or a crack speed dependent, K_1 is that it is independent of geometry. Because of this it is applicable to any practical situation and by using this factor the validity of the approach can be justified by comparison of results for tests on different specimen geometries.

The specimen geometry changes made were :-

a) the variation of the initial crack length and the specimen thickness and width using SEN specimens

b) the testing of double edge notched (DEN) and centre notched (CN) plates and tapered cleavage specimens, see figure 3.

The study of crack growth through specimens with different geometries was sufficiently successful, as will be discussed later, to justify the application of fracture mechanics to ESC so the testing was extended. The first factor considered was increased temperature. Raising the test temperature causes drastic reductions in test times, which are necessary to make the tests at present in common use practical. The elevated temperature tests were all in Adinol and the temperatures used were 60°C and 40°C. The apparatus used for the tests is shown in figure 8. The tanks of detergent were heated by pumping hot water, from the Churchill water heater shown, through copper pipes which passed through the tanks of detergent. An initial intention to have each tank thermostatically controlled was found unnecessary as the temperature variations between tanks and within each tank were negligible with only the water temperature regulated.

Another variable considered was the cracking environment and the environments used were described in section 4.1.3. Tests were performed in Adinol and 10%, 5%, 1% and 0.1% v/v Adinol/water mixtures as well as the alcohols, water and air at 20°C.

It was found to be impossible to remove Adinol from the test tanks so other methods of immersion were tried. A simple either disposable or easily cleaned tank was required to facilitate frequent changes of environment without risk of contamination. The chosen design was based upon glass slides sealed to the specimen but no sealing compound could be found which would not allow detergent to seep between itself and the PE after a few days. Only two methods of sealing were found. These were to use epoxy resin to attach the tank or to use the tank shown in figure 9. The seal is made using a nitrile or 'Neoprene' rubber 'o' ring and the glass slides are held on with rubber bands. The first tanks suffered ESC of the rubber bands but with the environment kept on the inside the tanks proved very successful and were used for the majority of the 20°C CN tests.

4.2.3. Results and Discussion

4.2.3.1. Analysis

The results of the SEN experiments were in the form of crack length-time date. These were plotted and crack speeds calculated by taking slopes at various points along the curves. Appendix 1 details some curve fitting techniques which were considered but, because of the form of the curve and the scatter on the results, the slope measuring method of finding crack speeds has been used for all the data. The values of crack length corresponding to the slope measurements were used in the equation for K_1 and a plot of K_1 versus crack speed made.

4.2.3.2. Specimen Geometry

The tests on the effects of specimen geometry were performed to show whether the application of fracture mechanics to ESC is justified. The results obtained from these tests were independent of geometry showing that crack speed is related to K_1, as given by the Brown and Srawley (16) equations.

The results of the tests on specimens with different widths are shown in figure 10. As would be expected of a valid fracture analysis, there is no significant difference between the data for 30 mm wide dumbell specimens and 100 mm wide straight sided specimens, each being over 2½ times as long as they were wide.

The initial notch length was also found to have no significant effect on the K_1 versus crack speed curves. This is shown in figures 11 and 12 for both SEN and CN specimens but it is important to all the graphs because no attempt was made to standardise initial notch length.

The specimen thickness was the one geometric factor expected to have an effect upon results because the change from well developed plane strain conditions is, according to the Brown and Srawley calculations, around 4 mm for the tests considered here (assuming this analysis is applicable to PE). The equation for predominantly plane strain conditions is :-

$$t = \frac{2.5\ K_1{}^2}{\sigma y^2} \qquad 4.1$$

Taking the yield stress (σy) of PE as 12 MN/m^2, then for a K_1 of 0.5 MN/m$^{3/2}$ the required plate thickness (t) is 4.34 mm.

Figure 16 shows that PE-E specimens from 1.5 mm to 12 mm thick give the same results but the narrowest specimen tends to crack more slowly at high K_1s. Figure 13 shows this slowing of cracking in 1.5 mm plaques quite clearly. For PE-C at 60°C curves for both 3 mm and 6 mm specimens are the same, as shown in figure 18. For PE-A there is a speed reduction for 3 mm specimens at high K_1 when compared with 6 mm thick material but this is less significant than that for the 1.5 mm PE-E. At low K_1s the curves for thin specimens merge with those for thick specimens in all cases, which is consistent with a stress field effect.

The success of tests on different geometries was variable. The DEN specimens proved to be unstable, in the sense that one crack tended to grow without the other and the specimen became asymmetrical. The tapered cleavage tests were also failures - owing to the low modulus of PE the specimens twisted at the load time. When the twisting was restrained by using side plates, or by making specimens of 25 mm thick material, the ends deformed and cracks grew through the arms of the specimens at right angles to the intended direction.

The CN specimens were successful and proved very stable. Even if one crack appeared to initiate first, with the exception of a few disregarded tests, the cracks grew symmetrically. The CN results were treated in a similar way to the SEN and are indicated on figures 11 and 12. The majority of the K_I versus crack speed graphs include SEN and CN test results but they are not differentiated, for clarity.

CN specimens were important to the practical aspect of the work, as well as the analytical, because of the lack of bending induced. Whilst the bending of SEN specimens is taken into account by the equation for

K_1, there are difficulties involved in the measurement of crack length. A long crack opens into a vee and the difference between the horizontal distance from the crack tip to the edge of the specimen and the crack length along the crack surface becomes significant. Also CN specimens give the average crack speed of two growing cracks and halve test times for the same size specimen.

The absence of any effects of specimen width or notch length and the equality of results from SEN and CN specimens demonstrates that the K_1-crack speed approach to the analysis of ESC is valid. In demonstrating the validity of the analysis the tests show that there is one K_1-crack speed relationship given by each material for one environment and temperature. Within the limits of experimental error, which are considered fairly small by the standards of both fracture and ESC testing, and providing plane strain conditions predominate, changes in specimen geometry can be accounted for simply by using the appropriate stress intensity factor. This means that although the theoretical relevance of K_1, based upon linear elastic analysis, to the microscopically ductile fracture of a non-linear viscoelastic solid, is difficult to see, there is still a unique relationship between K_1 and fracture. This is providing the viscoelastic properties of the PE are taken into account by incorporation of crack speed in the data. Some of the scatter on the results will probably be caused by the lack of allowance for the viscoelastic nature of the bulk material and this will be discussed in a later section.

4.2.3.3. Notching and Crack Initiation

In order to fully justify the use of an experimentally based fracture analysis the notching must either have no effect or the sharpest attainable notch must be used in the experiments. The tests on the effect of initial notch show that the methods of forming a sharp notch did not have any effect upon the K_1 versus crack speed curves.

The major drawback with any crack growth type of analysis is that there must be an initial notch from which the crack will grow. Whilst this reduces the scatter on results, compared with tests in which failure is initiated at random flaws, the random flaws are an intrinsic part of the finished product. This is of course only true if failure in a test specimen initiates from a surface which is similar to the relevant finished product ; if crack growth is from a face which has been cut to form the specimen then the failure time is likely to be misleading.

Having accepted that the initial notch may not be representative of the intrinsic flaw, the tests with different types of notch show that this is not important in crack growth tests as long as the front of the notch is initially straight. The majority of the results are from specimens notched at 20°C with either a razor or scalpel. Figures 13 and 14 show that prenotched specimens give results within the scatter band of the razor notched specimens. Impact notched specimen results, figure 15, also show no significant difference. As PE is not very sensitive to impact at 20°C it was considered that the material might adopt the shape of the razor tip in exactly the same way as the slower razor notching, so further impact notching was performed soon after the specimen had been immersed in liquid nitrogen. The notches produced by this technique were sharp but, after conditioning for at least 30 days at 20°C, the results of testing showed that the sharp notches did not affect the K_1 versus crack speed curves, figures 12 and 15.

The reason for the lack of initial notch effect is thought to be the formation of a consistent environmental crack from the major defect in the specimen no matter how that defect is formed. This was further justified by observation of specimens loaded to give high initial K_1s in which a yielded zone formed at the tip of the notch before the environmental crack initiated. Once initiated, the environmental crack grew through the yielded material and on through the specimen. The factor which is likely to be affected by the initial notch is crack initiation time.

It is considered that the study of crack initiation is a major piece of work in itself, but it was thought useful to compare the crack initiation times for some of the present specimens without any attempt to further develop a notching technique, or reduce the very large scatter on results. As crack initiation is difficult to observe and because the specimens were not monitored continuously, the crack initiation time was taken as the intersection on the crack length versus time curve of the two parts made up of the pre-initiation period, when the crack length was constant or very slightly decreasing due to creep, and the crack growth curve. It is important that the crack growth was not forced through the stationary crack data as this would give a false measured speed reduction at the lower end of the data. The times of intersection of the two parts of the crack length versus time curves are shown as the ordinates of figures 19 and 20 with the initial stress intensity factor K_0 as the abscissa. The scatter denies any real interpretation of the results but a trend is just evident. In figure 19, for the $20^{\circ}C$ tests, PE-E appears more resistant to crack initiation than PE-A and PE-F. Figure 20 for 60°C tests shows that PE-F is the most readily cracked material, followed by PE-A, then PE-B and PE-E which are similar, and PE-C which is just the most crack resistant. Inasmuch as this trend is observable it shows that the materials which are the most resistant to crack growth are also the most resistant to crack initiation.

4.2.3.4. Temperature

The increases in crack speed caused by increasing test temperature are shown for almost all the materials in figures 11, 14, 21, 22 and 28. All these tests were performed in Adinol and the temperatures used were 20°C, 40°C and 60°C.

The shape of the K_1 versus crack speed curve is not altered by the temperature changes but there is a shift in the curve. As well as the speed increase there is also a shift of K_1 requiring a lower K_1 to cause cracking at increased temperatures. Another factor relevant to these results and the application of test results in general to practical situations is that the temperature shift is not constant even for similar materials. In figure 23 PE-A, PE-B and PE-C curves are compared at 20°C and in figure 24 the same polymers and PE-D are compared at 60°C. Allowing for the different crack speed scales it is obvious that the curves are further apart on figure 23 and do not overlap as they do in figure 24. This shows that the higher density materials are less affected by the increase in temperature than the lower density materials. These observations will be discussed in section 6.5. where the K_1 versus crack speed curves are split into two sections and different explanations are given for the parts of the curves.

Because the properties of plastics change with time particularly at elevated temperatures, PE-F was used to determine the effect of conditioning time at 60°C. The time taken for a 6 mm thick specimen to reach temperature was found to be about 15 minutes by sealing a thermocouple in the centre of a specimen and immersing it in a 60°C bath. A conditioning period of one hour was therefore considered sufficient. The importance of conditioning referred to in the literature and the knowledge that conditioning time at temperature slightly affected creep results in PE-F made a study worthwhile. The resulting K_1-speed curves for specimens conditioned for up to 100 hours are shown in figure 15 and it is obvious that whatever effect there is falls within the experimental scatter. This means that the one hour conditioning time is sufficient and, more important, that the specimen will not change during the test when the testing time is long, compared with the conditioning time.

4.2.3.5. Material Variables

The majority of the tests for this work used Adinol as the cracking agent and were performed to enable a comparison to be made between the PEs tested. Many of the K_1 versus crack speed graphs can be compared in order to determine the relative ESC resistance of the materials concerned. Figures 23 and 24 are specifically for this purpose, and show the relative merits of PE-A, B, C and D. Figure 25 is included to show the data for PE-H at 60°C. The most obvious conclusion which can be drawn from the results is that copolymerisation leads to increased crack resistance. This is a well known fact but has been difficult to study with the normal ESC test methods because the PE copolymers are so crack resistant that they do not fail in the tests. Because of the limited available test data on copolymers and their practical importance the main objective of the material study in this work is the comparison of copolymers.

The series of 'Phillips' materials, PE-A, B, C and D were directly comparable in respect of material variables but the other two copolymers were produced using different processes. In spite of these differences, the K_1s required to give particular crack speeds for all of the materials are shown in figures 26 and 27 plotted against the average density of a number of specimens of each material. Figure 27 for 60°C tests shows points for PE-D, H, C, E, B and A in order of increasing density and figure 26 for 20°C shows PE-C, E, B and A. Both graphs show, within the bounds of experimental scatter, that for all the data there is a linear relationship between the K_1 required to cause crack growth, at a specified speed, and the density of the copolymer.

The PEs used for this ESC work contain different comonomers and PE-E is a blend copolymer, so it might be expected that the results would not show a simple relationship. There is some justification for saying that PE-E does not fit the linear relationship particularly well, but the results for this material show a lot of scatter, probably because two slightly different formulations were used, and the average points recorded on these graphs are not very far removed from the lines shown, particularly at 60°C.

Copolymerisation is the only material variable which has been looked at in detail but the homopolymers which do not feature in the density relationships have been used to look at other effects. Comparison of the K_1s required to cause cracking in these materials, with the K_1s required to give the same crack speed in any of the copolymers confirms the inferior resistance of the homopolymers, showing that the density relationship is applicable only to copolymers. The reason for testing both of these materials was to find out whether the pigments had any effect upon crack growth. The importance of some additives has been shown in the literature but the effect of pigments has not been considered. Pigments are generally chosen because of their cost and permanence - in the case of buried pipes resistance to colour changes in the presence of sulphide reducing mico-organisms is of prime importance. The ability of pigment particles to act as crack arrestors was thought worthy of consideration because of the vast differences which could be made by some additives, but it was found that there was no difference between the two types of pigmented material at 20^oC, 40^oC or 60^oC. The results are shown in figure 28.

4.2.3.6. Environments

The environments used are described in section 4.1.3. ; all the tests for comparison of these environments were at 20^oC. A comparison of the K_1 versus crack speed curves for the tests on PE-E and PE-A in dilutions of Adinol and water are shown in figures 29 and 30. Both graphs show the relative aggressiveness of the 5% v/v solution and figure 30 shows the fall off as either concentration or dilution is increased.

The effects of other environments are shown in figures 29 and 31. Cracking in air is, as expected, considerably slower than in detergent (figure 29). Figure 31 compares the cracking speed in alcohols with that in Adinol and, contrary to the preliminary tests in this work, methanol is found to be as aggressive as Adinol. Ethanol is found to give less rapid cracking than methanol with speeds similar to those obtained during tests in water. This result is surprising since ethanol is an acknowledged cracking agent and water was not thought to be aggressive, and is not aggressive compared with detergent. The least aggressive of the three alcohols tested is butan-1-ol.

The relevance of surface tension to ESC has been considered in the literature but the conclusions drawn from test results are inconsistent. The surface tensions of the environments used in this work are given in Table 4.

TABLE 4 SURFACE TENSIONS OF ENVIRONMENTS

Environment	Surface Tension (mN/m)
Adinol	34.3
10% Adinol	30.1
5% Adinol	31.5
1% Adinol	30.3
0.1% Adinol	32.3
Water	72.3
Methanol	22.6
Ethanol	22.8

The surface tensions of the Adinol environments were measured using maximum bubble pressure, the result being taken in each case from four readings at different depths. The surface tensions of water and alcohols were taken from handbooks. Figure 32 shows the K_1s required to cause cracking in PE-A at 2×10^{-9} m/s ($20^{o}C$) for each of these environments plotted against the surface tension. It is obvious from the graph that there is no overall relationship between K_1 and surface tension although, allowing for experimental scatter, there might be a connection for the Adinol solutions. The surface energy of PE is approximately 32 mN/m so if reduction of surface energy is important to ESC the liquids with surface tensions greater than 32 mN/m should not cause cracking. This idea is based on the assumption that PE is homogeneous (the crystalline phase) which is not correct and it is likely that if surface tension is important it will be because of effects on high surface energy regions, impurities and perhaps the amorphous polymer.

4.3. CONSTANT STRAIN TESTS

4.3.1. Introduction

One of the greatest anomalies resulting from the test methods normally used for ESC comes from the conclusions drawn from tests on materials with different densities. These results are completely contradictory as regards the effect of density.

The bent strip test, being a constant strain test, gives better results with low density, low modulus materials, whereas the Lander test, being a constant load test, gives longer lives for high density materials. The differences have been accredited to the effects of the different stresses induced at constant strain in materials with different moduli. It is accepted that specimens of different thickness be used in the bent strip test, to allow for differences in stiffness.

The Lander test cannot be used to predict lifetimes or accurately compare materials with different stress relaxation rates when the loading to be applied contains an applied strain. However, by assessing the applied stresses, a better comparison of materials for constant strain conditions may be made using this test than can be made for constant load conditions using the bent strip test. The designer of a plastic product, having ESC data available, will be able to gain some idea of the merits of different materials if the end use can be reasonably assessed as constant load or constant strain of a similar magnitude to that used in the bent strip test. In the situation where both stresses and strains are present, the only recourse would be to the Lander test with an estimated total stress, and this would not necessarily be justified because loads on the strained part would fall due to both relaxation and crack growth and there is no way they could be compared when only the time to fail of a test specimen is known.

Apart from the practical problems of interpreting the effects of density, many effects of other variables are masked by density or stress relaxation effects. It is therefore important that these effects can be excluded from the results of a good test method.

4.3.2. Experimental

4.3.2.1. Apparatus

One station of the high temperature test constant loading rig, shown in figure 8, was converted to form a constant strain station, figure 33. The handle at the bottom of the photograph was connected, through bevel gears and a screw through a pivoted threaded block, to the lever arm to replace the loading mechanism. The rigidity of the system was much greater than that of the specimen, so applied strains remained constant. The load on the specimen was measured using a strain gauged ring above the specimen, see figure 34, the strain gauges being attached to a Peekel bridge.

4.3.2.2. Method of Testing

The strain gauged ring was calibrated by loading and unloading with knownweights, both off the rig and on the rig using the 10 : 1 lever arm. The rigidity of the system was checked by loading a steel specimen to determine whether there was any fall-off in load with time.

The experimental procedure was similar to that used in constant load tests. CN specimens of PE-A were strained on the rig until the applied stress was about 50% higher than that used in a comparable constant load test. At regular intervals the crack length and the bridge readings were recorded and plots were made of crack length and load against time. The stress intensities were then worked out using the crack length and load pertaining to one time.

4.3.3. Results and Discussion

The K_1 versus crack speed curve for constant strain tests is shown in figure 21 and compared with constant load test results for the same PE, environment and temperature. The graph shows no significant difference between the results for the two stress situations.

These results prove that modulus alone will explain many of the differences found in tests by other methods. In showing this the results also show that the K_1-crack speed analysis is independent of density and stress relaxation effects. This makes the test method far better than either the bent strip or the Lander test for comparing materials and for research into the factors affecting ESC because results will not be complicated by unwanted factors.

These results also reveal the importance of this type of analysis for the assessment of materials for practical applications. Any group of materials can be compared using this method without recourse to making the test or specimen similar to the final usage, as long as the appropriate stress relaxation curve is known. Alternatively loads, which might reasonably be calculated for practical purposes, could be found which would enable materials to be suited to an end use by studying only constant load test results. It is reasonable to assume that a combination of applied strain and stress could equally be considered in this manner and that materials could be compared for any end use by using test data for crack growth and modulus. These results therefore confirm that the K_1-crack speed approach is the most useful for both research and practical applications.

4.4. SURFACE NOTCHED PLATES

4.4.1. Introduction

The most commonly encountered crack configurations in service failures are surface cracks and embedded cracks. An analysis of slow crack growth is particularly relevant to these two crack shapes because they are generally the weak points which grow slowly until they become critical and lead to rapid failure. Where non-absorbed environments are the cause of fracture, embedded cracks are immune from growth and only surface cracks, in contact with the environment, will grow. Given that a gas pipe might contain surface scratches, as a result of processing or handling operations, or notches at joints, and an environment which would be slightly aggressive, the relevance of this type of failure to gas pipes and fittings needs little explanation. This is, in fact, the only slow crack growth which could be problematical. All the earlier results on the analysis of ESC must therefore be relevant to surface cracks, and they should be if the K_1-crack speed analysis used is truly valid.

A surface crack is best approximated by a semi-elliptical crack, in order that a three dimensional elastic analysis can be made and this has been done, notably by Irwin (59). The original Irwin analysis was modified in order to make it correspond with other fracture analyses and to include the Irwin plastic zone, by Brown & Srawley (16). This analysis is based upon the solution of Green & Sneddon (37) for an elliptical crack in an infinite solid under uniaxial tension (σ), from which Irwin derived the stress intensity factors around the edge. The estimate of stress intensity factor for a semi-elliptical surface crack in an elastic plate is found by increasing the infinite solid solution by a factor 1.1 to account for the effects of the two free surfaces. This correction factor is considered valid only when the crack depth is less than half the material thickness and when the gross stress is less than the materials yield strength. Although this analysis is not valid for deep flaws, and there are other corrections which attempt to improve the predictions, see for example Shah & Kobayashi (96) and figure 35, these have not been used here because the difference between a deep flaw and a through crack is considered negligible in terms of service life. The one correction referred to, Shah & Kobayashi, gives values from 1.1 to 1.2 for cracks up to 80% of the material thickness which further demonstrates the lack of necessity to change the correction factor of Irwin.

4.4.2. Analysis

The first problem when using the Irwin analysis for calculation of K_1s for surface notches in PE was that the crack depth could not be measured. The analysis had therefore to be used to predict the crack depth from the measurable geometric factors. This was done by modifying the substitution for the increase in strain energy (dU) for a small increase in the size of the ellipse (f)

$$dU = \frac{\pi E c f \eta_o^2 \Phi}{(1 - \nu^2)} \qquad 4.2$$

where

$$\Phi = \int_0^{\pi/2} \left[\sin^2 \theta + \left(\frac{a}{c}\right)^2 \cos^2 \theta \right]^{1/2} d\theta \qquad 4.3$$

The strain energy change is also half the stress (σ) multiplied by the change in crack volume

$$dU = 2\pi \sigma a c f \eta_o \qquad 4.4$$

By substituting for a in equations 4.2 and 4.4 (Irwin substitutes for η_o) we get

$$dU = \frac{\pi E c f \eta_o^2 \Phi}{(1 - \nu^2)} = 2 \pi \sigma a c f \eta_o$$

$$a = \frac{E \eta_o \Phi}{2 \sigma (1 - \nu^2)} \qquad 4.5$$

Equation 4.5 can be solved by iteration, since Φ is a function of crack depth, and thus the crack depth can be found. The crack depth, once calculated, can be substituted into the equation for K_1 from Brown & Srawley

$$K_1^2 = \frac{1.2\,\pi\,\sigma^2 a}{\Phi^2 - 0.212\,\frac{\sigma^2}{\sigma_y^2}} \times \frac{A_{gross}}{A_{net}} \qquad 4.6$$

This equation includes the plastic zone correction which was not included in the through crack analyses. This is because the calculated crack depths would not include the plastic material at the crack tip which was considered included in the measured crack lengths. The plastic zone lengths, for all the cracks, were also calculated using this K_1 in the formula

$$r_y = \frac{1}{2\pi}\left(\frac{K_1^2}{\sigma_{ys}^2}\right) \qquad 4.7$$

and these were added to the calculated crack lengths. It was considered important to add these because they constituted significant parts of the crack lengths being in the range 0.027 mm to 0.9 mm for cracks ranging from 1 mm to 5 mm.

The above analysis would, it is believed, be satisfactory for measuring crack depths in elastic materials, or any material to which linear elastic fracture mechanics can be applied and a modulus and poissons ratio can be defined.

For PE neither modulus nor poissons ratio can be readily defined but, as explained below, only modulus is needed in order to perform the analysis required here. The two difficulties of defining the modulus are that it is dependent upon the strain at which it is measured, ranging from the tangent to the yield modulus, and it is also time dependent. The time dependence of the modulus can be found by employing the constant strain rate modulus tests (see section 5.1.) on this material at $60^{0}C$, which not only give the time dependence of the modulus of the material, but also show that it does not change greatly for the moduli measured at different strains.

The strain at which the modulus should be measured is that prevalent in the bulk of the specimen since this controls the opening of the crack faces. However, this opening will be affected by the larger elastic and plastic around the crack tip which will permit the crack faces to open more than expected. This means that the effective strain, i.e. that at which the modulus should be calculated, is higher than that in the bulk of the specimen. There was no direct way to assess this effective strain, but the modulus at this strain was calculated by reversing the crack depth analysis.

Five tests were stopped well before the crack had grown through the thickness of the plate. The crack opening and test time were recorded just before the tests were terminated. The specimens were sectioned and the crack depth measured. Then using this crack depth with the crack opening and test time, the modulus was calculated. This was done by substituting in equation 4.5 to give modulus for a poissons ratio of 0.5. The moduli found in these tests were then reduced to the one second moduli using the relation :-

$$E = E_o t^{-0.1}$$

which is considered a sufficiently accurate representation of the power law relationship shown by the constant strain rate tests. The results of these calculations are given in Table 5.

TABLE 5 SN TESTS - MODULUS DATA

Test No.	Crack Depth (mm)	Crack opening (mm)	Modulus (MN/m^2)	Time (sec)	One second modulus (MN/m^2)
4	6.50	.300	97.1	24,120	266
5	4.13	.160	98.6	17,220	261
6	3.88	.160	89.1	20,700	270
18	4.79	.171	77.9	57,600	233
19	5.55	.310	106.5	8,400	263

It was considered that these calculated moduli were sufficiently similar for their average to be used in the crack depth calculations,

$$E = 259t^{-0.1} \quad MN/m^2$$

The value of poissons ratio was unimportant, as the same value was used in the reserve, crack depth, calculations and the values cancelled. The only reason for changing this value, which was probably too high for so rigid a plastic, Ogorkiewicz (80), would arise if it was required to define the modulus used in terms of the strain at which it was measured. Reduction of the 2% and yield moduli from constant strain rate tests to time dependent moduli and division by 1.1, to allow for the lower stress required to cause the same strain at a given time in a constant stress situation, see J.G. Williams (108), give moduli following the equations

$$E_{2\%} \quad = \quad 394t^{-0.1005} \quad MN/m^2$$

and

$$E_{yield} \quad = \quad 126t^{-0.1018} \quad MN/m^2$$

It thus appears that the modulus calculated for these tests is both reasonable, and placed between these two moduli which were found by a more conventional method.

4.4.3. Experimental

4.4.3.1. Specimens and Procedure

The basic specimens were the same as for the majority of tests and were all nominally 6 mm thick. The initial notch was put in with a scalpel blade using only that part which formed a regular arc. All the tests were at 60^{o}C in Adinol. During the first seven tests the crack opening and width were measured using a travelling microscope. It was found, however, that the crack did not widen until it was virtually through the thickness. This meant that only the crack opening need be measured during a test, since the initial crack was easily identified when a test was complete and the specimen split in two. This change in testing requirements meant that a Robot camera could be used, at reasonably high magnification, to record accurate crack opening measurements at regular time intervals, figure 8.

4.4.3.2. Analysis

The crack openings were used with specimen dimensions, load and yield stress to calculate crack depth and K_1 using a computer program which performed the required iterations, using the complete elliptic integral subroutine (CEL2) provided in the IBM Scientific Subroutine package. The crack depths were used in the standard way to give crack speed and a plot of K_1 versus crack speed made, figure 36, for comparison with the through crack results.

4.4.4. Results and Discussion

The results are shown in the K_1 versus crack speed curve, figure 36. There is a considerable amount of scatter on these results which, it is reasonable to assume, is the result of general scatter on all these and other fracture results made worse by the dependence upon a simple modulus and constant poissons ratio. The shape of the crack was not semi-elliptical although it did tend to this shape. The dimension being measured was small, and as difficult to observe as the other crack measurements, so the inaccuracies were increased although the errors in individual measurements were overcome to a certain extent by taking a large number of readings from which the crack length versus time plot was made.

Examination of the fracture surfaces using a light microscope showed the same characteristics as the other fracture surfaces and the K_1 versus crack speed graph shows that the surface notch results fall on the same line as all the through crack results. It is important that the slope of these results fits the slope of the SEN and CN results because it further shows that there was no geometrical effect and that K_1-crack speed can provide a unique assessment of fracture resistance.

These part-through cracks must be growing under conditions of plane strain, so the agreement with the through crack results further shows that these specimens were sufficiently wide for well developed plane strain.

4.5. PIPE TESTS

4.5.1. Introduction

The fracture testing of pipes, as an extension of the surface crack work, is considered to be the final requirement to tie in all the work on plate specimens with a practical situation. The K_1-crack speed approach to the ESC of PE is justified by the different tests described above, but the relationship between these and pipe failure requires further consideration. If tests of plate specimens can be used to define a lower limit of K_1 or internal pressure, below which a crack in a pipe will either not initiate or will grow a negligible distance during the design life, then design against ESC in PE will be two stages advanced from the present state. Not only will tests on materials be directly comparable for all load situations, but there will be figures available to put into design calculations.

4.5.2. Analysis

The analysis for the measurement of a crack growing from the inside of a pipe is based upon the surface notch work on plate specimens. A basic change in the analysis came from the necessity to find the correct stress. It was considered that there were four components to the stress acting at the crack :-

a) The hoop stress in the pipe wall caused by the internal pressure

b) The longitudinal stress in the pipe wall

c) The pressure acting on the surface of the crack

d) The resistance of the pipe to being opened.

The hoop stress in the wall was taken as the average Lamé stress over the crack depth. This was considered a sufficiently good approximation to a full stress displacement analysis over the elliptical crack, because this is itself an approximation. The longitudinal stress was taken into account in the crack depth calculations by assuming that the opening would be reduced by a factor $\nu \sigma_l$, but the stress used in the stress intensity factor calculations did not include this term since a stress acting parallel to a crack causes no singularity or contribution to the stress intensity factor according to Paris & Sih (83). Also in the course of the present work, tests on plate specimens stressed parallel to the surface cracks showed no signs of crack growth.

The pressure acting upon the faces of the cracks was taken into account by equating a crack having a uniform pressure on the faces with one loaded with the same stress at infinity with no stresses on the crack faces (see for example J.G. Williams (108)). The effect of the pipe being a ring which resists opening, was considered negligible in terms of the stresses induced by the small openings considered here (see Appendix 2).

Using these assumptions the stress required to analyse the cracking in pipes was derived as follows :-

Lamé circumferential stress at the pipe bore

$$\sigma_{h_{r=r_i}} = \frac{P r_i^2}{(r_o^2 - r_i^2)} \left(1 + \frac{r_o^2}{r_i^2} \right)$$

Circumferential stress at tip of crack

$$\sigma h_{r=r_i+a} = \frac{P r_i^2}{(r_o^2 - r_i^2)} \left(1 + \frac{r_o^2}{(r_i + a)^2}\right)$$

Therefore the average circumferential stress

$$\sigma_h = \frac{P r_i^2}{2(r_o^2 - r_i^2)} \left(2 + \frac{r_o^2}{r_i^2} + \frac{r_o^2}{(r_i + a)^2}\right)$$

Adding to this the pressure acting upon the crack face, we obtain

$$\sigma h_{Total} = \frac{P r_i^2}{2(r_o^2 - r_i^2)} \left(\frac{r_o^2}{(r_i + a)^2} + \frac{3 r_o^2}{r_i^2}\right) \qquad 4.8$$

This analysis is similar to that of Underwood et al. (101) who calculated K_1s for long part-through cracks inside pipes. Figure 37 shows a comparison, on a crack depth basis, of their experimental results and the K_1s for their tests calculated using equation 4.8 and

$$K_1 = 1.12 \, \sigma_{h_{Total}} \sqrt{\pi a} \qquad 4.9$$

Equation 4.9 is the approximate solution for K_1 assuming the calculated stress makes the cracked pipe similar to a single edge notched plate specimen. The full ASTM SEN solution was considered inappropriate here because it is calculated to account for bending stresses in the specimen and the pipe section being a complete circle will be constrained.

It is considered that the above analysis gives a better representation of the average stress acting along the length of the crack than does the analysis of Underwood et al. This is because the Underwood analysis is based upon the stress at the crack tip only. As the stresses in the material surrounding the crack will influence the crack opening, equation 4.8 has been used to calculate the crack depth, in conjunction with equation 4.5. It is not however considered sufficiently close to the experimental K_1s and analysis of Underwood et al, or the analysis of Bowie & Freese (14), to be used for the K_1 calculations. As the simple calculation of Underwood was found to fit the experimental results for short cracks better than their second analysis, and as the constraint caused by the shape of the pipe was found to be negligible in this case, the stress used in the K_1 calculation was

$$\sigma_{h_K} = P\left(\frac{(r_o/r_i)^2 + 1}{(r_o/r_i)^2 - 1} + 1\right) \qquad 4.10$$

taken from

$$K_1 = 1.12\,\sigma_h\sqrt{\pi a} + 1.13P\sqrt{\pi a}$$

$$\sigma_h = P\left(\frac{(r_o/r_i)^2 + 1}{(r_o/r_i)^2 - 1}\right) \qquad \text{at the inner wall}$$

$$K_1 = 1.12\,\sigma_{h_K}\sqrt{\pi a}$$

The error caused by dropping $0.01P\sqrt{\pi a}$ (about 0.2%)is negligible. By using the maximum hoop stress, allowance is made for the stress at the tip of the crack being higher than it would be at the same depth in an uncracked pipe.

From the two equations for stress, 4.8 and 4.10, the relationships between crack opening and K_1 for semi-elliptical cracks on the insides of pipes can be found by using the equations derived for the surface notch analysis. The only difference is that the measured crack openings must be increased by multiplying by a factor b, given by

$$b = 1 + \frac{\nu \sigma_l}{\sigma_{h_{Total}}}$$

to allow for the closure due to the longitudinal stress. Also the stress for the crack opening calculations was included in the iteration from which crack length was found.

4.5.3. Experimental

The pressurising rig used for testing pipe specimens, which is shown in figure 38, was basically that referred to by J.G. Williams & Ewing (110) and used nitrogen from a gas bottle to pressurise a cylinder containing distilled water, the water being used to fill and pressurise the pipe. Flexible hoses were connected to and from one end cap in the pipe, because the tests were performed with the pipe horizontal, but it had to be vertical for bleeding the system. The end caps were brass inserts, as shown in figure 39. They were slightly larger than the pipe internal diameter and were pushed into chamfered ends of the pipes and hose clips fixed around the outside to aid sealing. One end cap contained fittings for both input and output, the other was fitted with a periscope for observation of the inside of the pipe.

4.5.4. Specimens

The specimens were of PE-B material (from the same batch as the plate specimens) extruded to approximately British Gas Corporation specifications for 2" PE pipe by BP. Each specimen was 350 mm long. The inside at the centre was painted with printers ink for PE and a scalpel notch put into it approximately half way along at a distance appropriate to the periscope. The printers ink served as a dark background through which the scalpel blade cut to make a clearly visible notch. The end caps were then inserted and the pipe set up on the test rig with the crack uppermost.

Observation of the crack was made via a closed circuit television system using light from a fibre optic light source to eliminate any localised heating, see figure 40. The crack was put uppermost to enable easy access for the light and to make its image vertical on the T.V. monitor, to eliminate errors from the line scanning, see figure 41. Measurements of the crack width were made with and without water in the pipe and also at regular intervals when the pipe was pressurised.

The T.V. system was considered more accurate than the photographic method because of the high magnification readily obtained and the ease with which this magnification could be determined. The method could be used in this instance because printers ink stayed on the PE in water at 20^{o}C whilst it did not at 60^{o}C in detergent, even on a flame polished specimen. It could not therefore be used on the SN plates. The initial crack opening was measured and subtracted from subsequent readings. It did not matter whether the ink defined the exact outline of the crack since any deformations of the material on either side of the crack faces would be very small as these are low stress regions.

The pressure in the pipe had to be topped up regularly so crack opening readings could be taken at the same time. All tests were started during a morning to allow frequent topping up while the pipe was creeping and it was found that by the end of the first day the pressure drop would be less than 0.15 MN/m^2 overnight.

The crack lengths and thus the K_1 versus crack speed curves were worked out in a similar manner to the SN plates.

4.5.5. Results

It was found that the pipes cracked quite readily in distilled water at a pressure of 1.72 MN/m^2 and tests, although at quite high K_1, could be performed in one week. The cracking was found to be influenced by the longitudinal stress when the crack was deep. Unlike the plate specimens the crack widened significantly before going right through the wall of the pipe. In these calculations this provided a further reason for excluding data for deep cracks so no points have been included where the crack plus plastic zone was 5 mm or more (wall thicknesses being from 5.92 mm to 7.60 mm).

The modulus found in the same way as for plates was taken to be

$$536t^{-0.0877} \text{ MN/m}^2$$

from averaging moduli of 499, 540, 572 using a time dependence from constant strain rate data. It is noted that by multiplying the ratio of 20^oC modulus to 60^oC modulus, from the constant strain rate tests, to the modulus used in the plate work a one second modulus of 588 MN/m^2 is obtained. This is slightly higher than that calculated from the pipe tests but this would be expected because the pipe will be oriented in the longitudinal direction and therefore will have a higher modulus in this direction and a lower modulus in the hoop direction.

The crack opening and time measurements from the tests were read into a computer program which was essentially similar to the program for calculation of crack length and K_1 from the SN data. In this case the area used is defined as specimen thickness times 250 mm, being length of pipe between the end caps. Values of crack length and time were used to give the K_1 versus crack speed curve, figure 42.

4.5.6. Discussion

There are two main differences between the pipe material and the plates : (a) the pipe is oriented along its length and (b) its material was fast cooled giving, probably, a smaller spherulite size particularly at the outer wall. These two effects could act on the ESC resistance in opposite ways. The second factor would be expected to have a much smaller effect than the first. This is particularly true of this material because it has small spherulites anyway. Also the storage of all materials at 20^oC and 50% RH for at least two months would reduce the effect of fast cooling, but the small spherulites could make the pipe more difficult to crack than the plates. The orientation, however, is in the worst direction for slowing a longitudinal crack and thus the pipe would be expected to crack more readily than a plate. With these factors taken into account, the results of these pipe tests show a reasonable correlation with those of the plate tests.

There is more scatter on these results than on the others ; some of the reasons are the same as for the SN plate results given in subsection 4.4.4. Although the method of measuring the crack opening was an improvement upon that used for the SN plates the experimental errors were increased by the changes in pressure during testing. The analysis contains more approximations than any of the other analyses and, possibly partly because of this, there was more variation on the calculated modulus. The differential effect of rapid cooling will also cause scatter by producing a crack length dependence which has been shown to be absent from other tests.

Taking all the above factors into account it is considered that the results of the pipe tests compared with those of plate tests show a good correlation with those expected for an oriented form of PE-B.

CHAPTER 5

EXPERIMENTAL - MATERIAL TESTING

5.1. DETERMINATION OF MODULUS

5.1.1. Introduction

Both the SN analysis and the COD analysis, given in section 6.5.1., required a knowledge of the strain rate or time dependence of the modulus of the materials. For calculation of CODs the strain rate dependence was of primary importance and it was necessary for the moduli to be found at the same temperatures as the tests. The method selected for finding the modulus was a constant strain rate pull on a tensile testing machine.

5.1.2. Apparatus

The apparatus is shown in figure 43. Dumbell specimens were pulled on an Instron testing machine and strains were measured by driving the chart with an Instron extensometer capable of measuring up to 50% strain. For tests at $40^{o}C$ and $60^{o}C$ the specimens and extensometer were enclosed in a box containing thermostatically controlled heaters.

5.1.3. Experimental

The specimens were pulled at a number of strain rates, at each of the required temperatures, and the load-extension curves recorded on the Instron chart. The strain rate over the gauge length, defined by the extensometer, was measured by marking the chart at regular intervals and calculating the average strain rate to the strain being considered. The loads recorded at 2% strain and at the maximum yield point (stationary point on the curve) were recorded along with the yield strain.

5.1.4. Results

The recorded yield strains were found to have no significant strain rate dependence, partly because the scatter was large and any strain rate dependence small. The lines defined by least squares fit on the log yield strain versus log strain rate data are given in Table 6 where the line is defined by

$$\epsilon_y = \text{antilog } a_0 \dot{\epsilon}^{a_1}$$

TABLE 6 YIELD STRAIN DATA

Material	Temperature	a_0	a_1	Regression coefficient
PE-A	20°C	- 1.154	- 0.0727	- 0.628
	60°C	- 0.916	- 0.0260	- 0.376
PE-B	20°C	- 1.149	- 0.0715	- 0.687
	40°C	- 0.986	- 0.0188	- 0.503
	60°C	- 0.855	0.00678	+ 0.168

The yield strain was therefore taken as constant and the average value for each material at each temperature was used to calculate the yield modulus. Also the 2% modulus was calculated.

Graphs of the moduli plotted against strain rate on a log-log basis are shown in figures 44 and 45 and the linear regression lines are given in Table 7, where

$$E = \text{antilog } a_0 \dot{\epsilon}^{a_1} \text{ MN/m}^2$$

TABLE 7 MODULUS DATA

Material	Temperature	Modulus	a_0	antilog a_0	a_1	Regression coefficient
PE-A	20°C	Yield	2.592	391	0.0845	0.959
	20°C	2%	3.312	2050	0.1090	0.956
	60°C	Yield	2.212	163	0.0935	0.966
	60°C	2%	2.945	900	0.1357	0.957
PE-B	20°C	Yield	2.500	316	0.0805	0.986
	20°C	2%	3.163	1460	0.0877	0.970
	40°C	Yield	2.415	260	0.1014	0.993
	40°C	2%	3.045	1110	0.1094	0.973
	60°C	Yield	2.228	169	0.1018	0.994
	60°C	2%	2.945	641	0.1005	0.965

5.2. DETERGENT ABSORPTION TESTS

5.2.1. Introduction

Studies of the absorption and adsorption of detergent by PE have been referenced in the literature survey and, although the conclusions of the survey writers, such as Howard, are that there is no absorption, there is some evidence that very small quantities are absorbed. The work of J.L. Williams and Peterlin (111) on absorption of benzene in PE showed that absorption was increased and absorption rate very greatly increased when the PE was drawn in the environment. Also Siemiya et al. (95) showed that adsorption was increased by stressing. In spite of these results the detergent absorption tests have been on unstressed material, so it is possible that there is absorption into the stressed material.

Some simple absorption tests on thin specimens immersed in Adinol at $20^{o}C$ or $60^{o}C$ were performed as part of this work but no significant weight increases were recorded. It was considered worth-while doing some absorption tests on stressed specimens to determine both weight increases and changes in material properties. In order to detect any weight changes if they occurred it was necessary to use very thin specimens and to stop cracking it was necessary to perform the tests in a significantly shorter time than was used for the ESC tests.

5.2.2. Test Method

Tensile test specimens were made by microtoming a block of PE-B approximately 20 mm x 10 mm to give sections approximately 0.2 mm thick. A steel knifed freezing microtome was used to give slices of this size and the thickness was chosen because of the difficulty of obtaining full size flat sections with a smaller thickness. The microtomed sections were uncurled by gentle warming in glycerol. The flattened sections were razor cut into dumbel shaped specimens using a metal template having a central width of 6 mm.

The specimens were split into two groups at random and the specimens of one group, for testing in Adinol, were weighed. The specimens were all pulled on an Instron testing machine at a constant strain rate of 0.1 mm/min ; half were tested in air and the other half in Adinol. The yield loads for each specimen were recorded, and after testing, the Adinol immersed specimens were carefully wiped and re-weighed.

5.2.3. Results

The average stresses calculated for the two groups were

22.0 MN/m^2 (range 20.0 to 23.3) for the air tests and 23.0 MN/m^2 (range 19.5 to 25.7) for the tests in Adinol. The weights of the specimens after testing in Adinol were found to have increased by typically 0.0003 gm (less than 1%).

5.2.4. Discussion

The large scatter on these results was probably due mainly to variations in specimen thickness. The thickness was measured at four points on each specimen, i.e. each edge at two positions along the length. The average was taken of the two readings at each position and the smaller of these two averages was used in the stress calculations. Allowing for the experimental error there was no significant difference between the two average yield stresses.

The small increase in the weight of the specimens was attributed to Adinol which had not been removed from the surfaces so it was assumed that there was no significant weight increase.

In order to extend this work to give more accurate results it would be necessary to go to a more complicated technique because any results from this method must always be suspect, owing to the possibility of cracking occurring. The simplest method of making any absorption more obvious is to increase the time of the test, but this also increases the likelihood of cracking. If cracks appeared they would (a) appear to reduce the yield strength of the material by reducing the cross sectional area of the specimen, and (b) increase the weight of the specimen after test by filling with environment.

The only methods which it is thought could really be used to show whether absorption occurs are methods which are sufficiently sensitive to tell the difference between adsorption and absorption. Autoradiography using a traceable cracking agent is the most obvious method. When the results of the above tests are considered, along with the work of J.L. Williams and Peterlin (111), who found cracks in the solvent-drawn PE which had the very high absorption rate, it is debatable whether any conclusive results are likely to come from further testing. So the development of an autoradiographic testing technique was not considered worth-while at the time of this work, but it may be necessary if future work suggests that useful results might be produced.

CHAPTER 6

DISCUSSION

6.1. THE APPLICATION OF THE K-CRACK SPEED APPROACH TO ESC

The feasibility of the study of the growth of stress cracks in ESC resistant PEs, using notched specimens under constant load, was the first factor which had to be established at the beginning of this work. Having done this, and developed the technique to the extent of being able to make the whole thickness of specimens crack in a macroscopically brittle manner, it was necessary to define the critical criteria of cracking. The K_1-crack speed approach was the first method used because of its applicability to the cracking of LDPE in alcohols (Marshall et al. (71)) and its relevance to practical situations. The use of K_1 provides a criterion which can be applied to any loading and geometry without the knowledge of modulus over long periods, as is required by surface energy methods.

The constant load tests on through-wall cracked specimens were used as the basis upon which the validity of this approach to ESC analysis was considered. In order to test the applicability of fracture mechanics the geometric factors, which might affect cracking, were examined, because the importance of K_1 is that it is a material variable, independent of geometry. As only specimen thickness had any effect upon the results it was concluded that fracture mechanics could be applied to ESC to give a unique relationship between K_1 and crack speed for each PE, environment and temperature. The validity of this relationship was further justified by the results of the constant strain tests on PE-A. These showed that the K_1 versus crack speed curves were the same when the load was relaxing and when it was constant, as long as the instantaneous load was used in the equation for K_1.

The final proof that there is a unique relationship between K_1 and crack speed must come from the part-through crack results. The discussions relevant to the specific results are given after the results, but the broader relevance of the work is only outlined. One of the reasons for starting these tests was to determine more precisely the effects of the stress field and its relation to crack speed. The tests on specimens of different thickness had revealed a stress field effect in the higher K_1, higher crack speed, part of the curves and, although this thickness effect was found to be overcome at 6 mm or less, it was thought worth doing tests on specimens in which plane strain conditions were known to predominate. There was still the possibility that crack speed in the upper part of the K_1 versus crack speed curve was controlled by a changing stress field. At the commencement of these tests no relationship had been found to explain the crack speed controlling factors for fast cracking but the importance of polymer relaxation to the slow speed cracking was realised. If the relaxation controlled cracking could be shown to extend to higher speeds, a criterion of failure would more readily be defined and one of the differences between this work and that of Marshall et al. (71) would be removed.

The excellent correlation between the results of the SN plate tests and the through-wall cracked plate tests justifies the application of the technique to what is probably the most important practical situation. Having extended the work in this direction the next stage, bearing in mind the end use of the materials tested and the pipe failure shown in figure 1, was to study the growth of part through-wall cracks in pipes.

The results of these tests show the same trends as all the other results and are considered directly comparable with the cracks in the gas pipe.

As a design tool, the present work is incomplete because all results are based upon crack growth. Although this is not really a great handicap, because designs using this data would always have a factor of safety incorporated, it is possible that extrapolating the crack growth curve to limit growth to a negligible length in 50 years would mean over-designing since a crack would never initiate at the predicted K_1. If fracture mechanics can be used to define crack initiation time as well as crack growth rate, it is a complete design tool and can be used to predict component lifetimes and ensure safe structures, given an assessment of the worst flaw which will occur. This problem applies to all fracture mechanics work and although it can be difficult to solve it is not always so. Within the gas industry the major flaws which are likely to occur in plastic pipe systems are relatively easy to identify, because they occur at the joints and are very large compared with the intrinsic flaws in the components of the systems. Stress analyses have therefore been performed at these flaws and fracture mechanics-crack growth criteria are being adopted for system safety considerations.

Whilst the latter parts of the above justification of the use of fracture mechanics for definition of ESC were in progress, through-cracked plates were being used to study the variables affecting ESC. The main criteria which have been suggested as critical in ESC are stress and strain, the former having been superseded by the latter. Critical strain has been reasonably well accepted, in spite of certain anomalies which were indicated in the literature survey. The present work has shown that there is an extremely good relationship between cracking and stress intensity factor, when the time dependence of the material is taken into account by using crack speed as a basis for comparison. It was stated earlier that the scatter on the K_1-crack speed results is far less than would normally be found during ESC or fracture testing. This is in spite of the lack of control of the thermal history of the specimens, which is carefully controlled in order to increase reproducability in other tests.

It is suggested that the results, which have been used to define critical strain as the controlling factor, are totally dependent upon the manufacture of the specimens and the surface defects caused during this process. The critical strains therefore bear little relation to the serviceability of the material when used commercially. Fracture mechanics not only provides a method which is directly applicable to the end use of the material, but also can be used to accurately compare materials. By studying crack growth and crack growth rate this method is far more sensitive than any other because it can be used to detect changes in the failure criterion or mode which occur with changing crack length for one specimen. It was thought at the outset that some of the contradictory results from tests with different environments were caused by the measurement of only time to fail for what could be a multi-stage failure process. When the present results are compared with the K_1 versus crack length curve for a 'Lander' specimen having a full thickness crack, figure 46, it is not surprising that results are inadequate. The K_1s at which cracking traverses most of the specimen are too high and the specimen is much too small for plane strain conditions to predominate. Attempts have therefore been made to analyse failure results on a K_1-crack speed basis and these are discussed below.

6.2. IMPORTANCE OF THE STRESS FIELD

Whilst ESC was thought to occur only under conditions of plane strain there is sufficient literature available to confirm that cracking will occur in very thin specimens, under plane stress conditions (see for example 61). The early tests in this work were not successful because of the development of yielding at the edges of specimens, in front of the crack tip. As the test technique was improved more cracking was obtained and failed specimens were as shown in figure 5. It can be seen that yielding of the sides of the specimen occurs along most of the crack length. This side yielding must slow the rate of crack growth and so invalidate the results. In order to determine whether there was a 'skin' on specimens, caused by the moulding processes, and this 'skin' was more resistant to cracking than the bulk material, a number of specimens were machined, using a milling cutter, to remove the surface from one side of the specimen. The outcome of these tests was symmetrically yielded specimens, which showed that whatever 'skin' there was would not seriously affect results and that the stress field at the edges of specimens was the major factor affecting the failure mode in these regions.

When the testing technique was further perfected the yielding was reduced to a level at which it could be considered negligible. This is shown both by the photograph of the crack in figure 6 and by the micrographs showing a traverse of crack surface, figure 64. The great reduction in the size of the yielded area made the crack speed measurements meaningful but also showed that ESC will occur in the plane stress regions, at the sides of a specimen, when the stress is sufficiently low. The exact definition of sufficiently low is not simple. The crack length at which yielding, visible under a magnification of 20 x, commenced was measured on a group of early specimens and found not to occur at a constant K_1 but apparently, as shown in figure 47, the onset of yielding is time dependent.

The effects of specimen thickness are also the result of the different stress fields developed in specimens. The comparisons show that once a certain thickness has been reached the K_1 versus crack speed curves are those for plane strain failure mode, but for thin specimens at high K_1 cracking is slower, showing that even in the absence of visible yielding there is a different failure criterion for plane stress.

Combining these two aspects, it can be concluded that ESC failure occurs in plane strain and plane stress but not necessarily at the same speed nor at the same K_1. The yielding constraint of plane strain makes cracking the predominant failure mode up to higher K_1s. At low K_1s the crack speeds are the same but as the K_1 increases yielding predominates in plane stress, the change-over point being dependent upon the time which the specimen has been under load.

6.3. MATERIAL VARIABLES

The materials tested in this work were those plastics relevant to one end use along with some associated materials. One of the original criteria upon which these materials were selected was their resistance to ESC, which is why most of the materials tested are copolymers with a MFI of 0.2. It was thought that the most useful new information could be obtained from this work by studying the changes in ESC susceptibility with copolymerisation, which is why many of the tests were on the series of PEs produced by the same catalytic process but having different quantities of comonomer. The other material variables, which are important to ESC and were discussed in the literature survey, were not thought to be as worthy of study as copolymerisation because the modifications which can be made to materials, as used in commercial products, are not very great owing to the prohibitive cost of major changes to production processes. The exception to this is modification of MW or MWD, although lowering MFI makes material more difficult to process, the gains in ESC resistance may make the additional cost worth-while. The reason for not studying MW effects was that the available background information is far greater than that on copolymerisation. Copolymers have proved difficult to crack using the previously developed methods ; the very crack resistant materials are often reported as having failure times greater than the length of the test, which is of no use for comparison with each other.

It has been found that crack growth tests, in originally notched samples, can be used to give observable crack growth in the most crack resistant materials, so comparisons have been made between the different copolymers. These comparisons were made on a density basis (figures 26 and 27) and for given crack speeds it was found that crack speed was related to density. In the literature survey the discussion of the general effects of density led to complicated conclusions particularly regarding crystalline texture. It is accepted that many factors will affect any relationship between cracking and density and that homopolymers and copolymers may not be comparable because copolymers will crack less readily than homopolymers and the general density effect for homopolymers will be the opposite of that for copolymers. As there are so many variables associated with density, the relationship shown in the graphs leads to the conclusion that the copolymerisation branching effect is the controlling factor. The branching will cause the reduction in density. Folt (31) found that the reduction in density caused by copolymerisation with 1-olefins is dependent upon the mole fraction of the 1-olefin. This is for true copolymers, but a similar effect was obtained by adding larger quantities of 1-olefin using a blending process.

This linear correlation between density and quantity of comonomer makes the relationship between density and ESC more readily explainable. It means that for true copolymers the ESC resistance is dependent upon the mole fraction of comonomer, all other factors being equal. As this relationship between density and ESC includes a blend copolymer it may be concluded that those morphological factors which affect density are essentially the same as those which affect ESC resistance.

The practical importance of this relationship could easily be realised when deciding polymerisation requirements to produce a material for a specific end use. The quantities of monomers and the procedures required to give desired end products are well documented but the definition of desired end product can only be made by reference to a correlation between end use and the molecular features of the material.

6.4. TEMPERATURE

The effects of test temperature on the K_1-crack speed curves are shown in a number of graphs. Changing the temperature does not alter the shape of the curves but displaces them, giving faster cracking at high temperatures. The slower cracking parts of these curves are considered in the section on COD and temperature effects are explained in terms of changes in modulus of the PE.

Comparing the higher speed parts of the curves it is noticeable that, although the ordering in terms of ESC resistance is unaltered, their relative positions are changed. Relative to PE-B, PE-A is more difficult to crack at high temperature than at lower temperature. The relative positions of all the materials suggests that a higher density leads to better relative performance as temperature is increased.

Fulmer (33, 34) used Arrhenius plots to compare failure times at different temperatures and found that straight lines could be drawn through the data points. Figure 48 is an Arrhenius plot of log crack speed against 1/T (where T is temperature in ^{o}K) for PE-A, B, C, E and F and it shows for each of PE-A, B, E and F that the three points lie in a straight line. The crack speeds were the average of the data at each temperature for a particular K_1, which was within the upper part of the data and was most convenient in terms of available results. It made little difference where, in the upper part of the curves, the data was taken.

Although the Arrhenius plots are good they are not necessarily more correct than plots of log crack speed against temperature, such are the temperatures used. The slopes of the lines are given in Table 8 along with the densities of the PEs.

TABLE 8 TEMPERATURE EFFECT - ARRHENIUS PLOTS

Material	Slopes ($x - 10^{-3}$)	Density (Kg/m^3)
PE-A	5.22	960
PE-B	5.75	955
PE-C	6.89	947
PE-E	5.95	954
PE-F	6.86	935

The table shows that there is a relationship between the slopes and density. The changes with temperature in the moduli for PE-A and PE-B, given in Table 7, show ratios which are not the same for the 2% and yield moduli. They are 1.40 and 0.87 respectively. Because of this variation it is difficult to identify any relationship between these ratios and the ratio of the slopes from Table 8, 0.91.

The increases in crack speed going from 20°C to 60°C are about 100 times and only one factor of 10 can be explained by environmental viscosity changes, see Table 9, and section 6.5.2. Modulus changes are greater than two but combining these two factors will obviously not explain the changes in crack speed. There is therefore a further unidentified factor, influencing crack speed, which is dependent upon density and varies greatly with temperature.

TABLE 9 TEMPERATURE EFFECT - VISCOSITY OF ADINOL

Temperature °C	Viscosity of Adinol (mNs/m^2)
20	350
40	99
60	40

6.5. CRACK SPEED ANALYSIS

6.5.1. Slow Speed Cracking

There are a number of theories for the rate dependence of slow speed cracking of linear viscoelastic materials. One general conclusion is that the crack speed will be controlled by the relaxation processes in the material (see for example Frankiewicz et al. (32), Knauss (65), Knauss and Dietmann (66) and Wnuk (113)). Some of the K_1-crack speed relationships obtained in this work are shown in figures 49-52, plotted on log-log scales, and it can be seen that within the experimental error a straight line with slope 0.1 fits the data for the slower cracking speeds. This suggests that, for slow speeds, cracking is relaxation controlled. These parts of the K_1 versus crack speed curves are considered in relation to material moduli.

The above references essentially come to the same conclusion, that K_1^2 is proportional to the creep compliance and this controls the crack speed. As this relationship does not fit the observed results they were considered in terms of a COD analysis. The applicability of this type of analysis to crack growth in other polymers has been shown by J.G. Williams (107) and Ferguson (30). In this work it has been shown that there is a unique relationship between K_1 and crack speed and this permits the use of the analysis employed by J.G. Williams for assessment of COD. This method, which is outlined below, does not attempt to define the actual COD but to give a value related to the COD which can be used for comparison with other data calculated using the same technique.

By calculating the strain rate at the crack tip from elastic analysis for a given crack speed and using this to find the appropriate modulus, a value of COD can be calculated if certain assumptions are made. The strain rate is calculated by differentiating the elastic strain a short distance ahead of the crack, with respect to crack speed, and is given by :-

$$\dot{\epsilon} = \pi \epsilon^3 \left(\frac{E}{K}\right)^2 \dot{a} + \epsilon\left(\frac{\dot{K}}{K} - \frac{\dot{E}}{E}\right) \qquad 6.1$$

where ϵ is strain and the dots denote differentiation with respect to time. The second term is typically nearly three orders of magnitude smaller than the first for the data used here and it is considered negligible. The strain which is considered important is that at which crazing occurs, but this is undefined for PE so the yield strain has been used and this has been taken as constant over the range of strain rates employed. The modulus used is therefore that for yield so the COD (δ) is calculated by iteration using the equations

$$E = f(\dot{\epsilon})$$

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

$$\epsilon = \frac{\pi \epsilon_y^2 \dot{a}}{\delta}$$

The results of applying this analysis to the mean K_1-crack speed data for PE-A and PE-B are shown in figures 53 and 54. These graphs show that the COD tends to a constant value for slow speed cracking as would be expected for relaxation controlled cracking but far more important than this is the effect of temperature. The curves for each material at different temperatures all tend to the same COD. This shows that the material's time dependent properties not only control the rate of change of crack speed but override all the effects of changes in the environment such as viscosity changes. The practical importance of this point is that it can be used to relate relatively rapid high temperature laboratory tests to the slow speed failures which might be experienced at lower temperatures. And for practical purposes it is this slow speed end of the data which is important, rather than that in which the COD is increasing.

In the literature survey reference is made to the results of Hittmair and Ullman (46) and their realisation that, when allowance was made for the ultimate tensile strengths of their PE at 50°C and 60°C, the results of the two tests at these temperatures gave similar results. These tests would have been affected by their dependence on an unmeasured intrinsic flaw and by more than one part of the failure mechanism being involved in the failure. That is why the results are only similar when allowance is made for tensile strength changes. It is therefore considered that these findings can be explained by the COD relationship identified using the K_1-crack speed analysis.

6.5.2. Faster Crack Speeds

For higher crack speeds the relaxation controlled cracking hypothesis does not fit. The slopes of the log K_1-log crack speed curves are nearer 0.5. A linear K^2-crack speed relationship which this slope represents, fits the results of Marshall et al. (72) for fluid flow controlled crazing. Their relationship, between initial K_1 and craze growth speed, was for PMMA in methanol where the flow was through the end of the craze rather than the sides. J.G. Williams (109) has correlated this and environmental fracture speeds in other polymers and non-polymers to those parts of K_1 versus crack speed curves where the fluid flow to the crack tip to reduce the material strength is the controlling factor.

If cracking is controlled by the flow of the environment it would be expected that viscosity would have a very important effect upon crack speed. The data on dilutions of Adinol do not really show a viscosity crack speed relationship, but one may be assumed for the alcohol environments. Comparing the two types of environment gives no viscosity relationship at all, see section 6.6.

It is possible that other environmental properties override the effect of viscosity when comparisons are made between different environments. The dilutions of detergent may be seriously affected by micelle formation and the alcohols by molecular size.

In order to try and explain this K_I-crack speed relationship some crack speed analyses are discussed below. Marshall et al. (71) used a modification of an Irwin analysis for effective rate of stressing around a crack tip to develop an equation for crack speed which was related to K^2. This equation, 6.2, also included yield stress (σ_y) and time of test (t_{test})

$$\dot{a} = \left(\frac{K}{\sigma_y} \right)^2 \quad \frac{1}{\sqrt{2\pi}\, t_{test}} \qquad 6.2$$

It is the time factor which really makes this equation inapplicable to the present work, being much less important than the equation suggests. The reason for the discrepancy between the two sets of ESC data is probably that the LDPE tests were of considerably shorter duration than those considered here and the effect of having t_{test} in the equations only shows up at very long times.

Another speed analysis which gives a crack speed related to K^2 is that of Cherepanov (18). Based upon the Maxwell element, which is considered applicable to plane strain, the equation for crack growth time is :-

$$t_{test} - t_o + \frac{\eta}{\mu} \ln\left(\frac{K}{K_o}\right) = - \frac{2}{\pi}\eta\gamma \frac{K^2 - K_o{}^2}{K^2K_o{}^2} \qquad 6.3$$

where :- μ = shear modulus

η = viscosity coefficient

γ = surface energy

and the Maxwell model is defined by

$$\dot{\epsilon} = (3\mu)^{-1}\dot{\sigma} + (3\eta)^{-1}\sigma$$

If this equation is used to consider a small crack growth of length $\triangle a$ in time $\triangle t$ it gives

$$\triangle t = \frac{-2}{\pi}\eta\gamma \frac{\triangle a}{K^2 a_o}$$

Therefore $$\dot{a} = \frac{-\pi K^2 a_o}{2\eta\gamma}$$

In order to do this it is assumed that

$$\frac{a - a_o}{t_{test} - t_o} = \frac{\triangle a}{\triangle t} = \dot{a}$$

$$\frac{K}{K_o} = 1$$

and that a crack in an infinite plate is being considered although the error caused by not making this final assumption is considered small.

For small $\triangle a$, a_o is essentially the present crack length, therefore the analysis gives a speed proportional to the crack length. This was shown earlier to be untrue and was part of the justification for the K_1-crack speed approach, but some results are shown plotted in the form K^2a against crack speed in figures 55 and 56 and it is obvious that these do not show any relationship.

M.L. Williams (112) considered the other classical visoelastic model, the Voigt element, to develop a crack speed relationship for slow cracking. This is really more applicable to the plane stress case and gives the relation

$$\dot{a} = \left[(\sigma_o / E_v) \sqrt{b \delta_w} \right] / \left[\tau \epsilon^* 2(\sqrt{2} - 1) \right] \qquad 6.4$$

which gives, for an infinite plate,

$$\dot{a} = \left[(K / E_v) \sqrt{\delta_w / \pi} \right] / \left[\tau \epsilon^* 0.828 \right]$$

The substitutions made into this equation were $E_v = 268$ MN/m^2 and $\tau = 1.5$ seconds to define the Voigt element for PE-A at 60^{o}C (from 2% modulus versus strain rate data), $\delta_W = 10^{-5}$ m being the size of an element taken from the microscopy data and $\epsilon^* = 6$ being the failure strain, a figure approximately applicable to the bulk. The K_1-crack speed relationship given by this analysis, see figure 57, is not that observed although the crack speeds calculated are not unacceptably far removed from the experimental results for the higher K_1s.

6.6. VISCOSITY

The upper parts of the K_1 versus crack speed curves have been tentatively related to the viscosity of the cracking agent and flow controlled crack speeds. There are three groups of data which might be used to show the validity of this suggestion.

a) The tests in alcohols provide the data which are least likely to be complicated by other factors, because the differences between members of the alcohol series are far simpler than those between a detergent and its dilutions. The viscosities are shown in Table 10. Comparison of viscosity with crack speed is made in figure 58 which shows K_1 plotted against crack speed multiplied by viscosity. A relationship between crack speed and viscosity is easily realised from this graph and thus the concept of flow controlled cracking may be justified.

The three sets of available data with their scatter are not sufficient in themselves to prove the correlation with viscosity is correct, but when the slope of the data is taken into account as well as the relative positions, viscosity is the only single explanation.

TABLE 10 VISCOSITIES OF ALCOHOLS

	Methanol	Ethanol	Butan-1-ol
Viscosity (mNs/m^2)	0.597	1.20	2.95

b) Changing the test temperature alters the viscosity of Adinol as shown in Table 9. It also varies other environmental properties and the physical properties of the PE being tested. The observation of a relationship between crack speeds and Adinol viscosities is therefore difficult. It is obvious from figures 23 and 24 and the Adinol viscosities that there is not an exclusive relationship between viscosity and crack speed at constant K_1. Figures 51 and 52 show that even when the changes in material stiffness are taken into account and comparison is made on a constant COD basis the viscosity changes do not account for the increases in crack speed.

The very large increases in crack speed with increasing temperature may be explained to a considerable extent by the changes in viscosity. These results do not rule out the importance of flow rate, but they show that there must be at least one other very important but undefined factor relating crack speed changes to temperature changes.

c) The final group of results in which viscosity effects might be observed are the tests in concentrated and dilute Adinol and water. The viscosities of the Adinol solutions and water are all very similar, that of 10% being slightly higher than the others. These viscosities are less than one twentieth of the viscosity of the concentrated detergent and therefore cannot explain the crack speeds observed. As Adinol concentration is reduced from 100% to 5% the crack speed increases, but not in proportion to the viscosity. As the concentration is further decreased the cracking speed slows down although the viscosity is virtually constant. There are other features of detergent dilutions which could override any viscosity effect and these are discussed in section 6.7.

6.7. DETERGENCY

Most liquids capable of detergency have a strong tendency to become adsorbed at most phase boundaries, regardless of the chemical nature of the bordering phase. Adsorption at the air or vapour interface is responsible for the low surface tensions of detergent solutions. When considering PE in solutions of detergents such as Adinol the amphipathic character of the detergent molecules enables them to lower the interfacial free energy by being adsorbed from the aqueous solution on to the PE surface. The molecules tend to become oriented in the adsorbed layer, with the polar ends towards the polar phase and the non-polar ends towards the non-polar phase. For the non-ionic detergent solution - PE combination considered here, the likely molecular configuration is one with the polyoxyethylene molecules attracted to the hydrophobic PE surface and the hydrophilic alcohol groups displaced towards the water.

There are various chemical descriptions of Adinol CO 630 (or Igepal CO 630, Antarox CO 630, Hostapal CO 630) ; the ASTM call it a nonylphenoxy poly(ethyleneoxy)-ethanol. It is manufactured by condensation of nonylphenol with ethyleneoxide until the hydrophobe, the ethylene oxide chain, reaches a length of 8-12 molecules when optimum detergency is obtained (for further details see for example Davidsohn and Milwidsky (20) and Milwidsky (78)). The condensation reaction is such that the precise number of ethylene oxide molecules cannot be controlled, so there will be a range of different molecular lengths in any sample of detergent. In the present work three separate samples were used and no differences in the results were found but some care was taken to ensure that all three samples came from the same plant. The operating conditions of the plant are the controlling factors in this polymerisation process and, although the products listed above are all nominally the same, it was considered inadvisable to change products.

The reason for the use of concentrated detergent in this work is for comparison with ASTM tests and because the concentrate can be heated relatively simply. Dilutions of non-ionic detergent solutions dissociate at elevated temperature ; also evaporation of water leaves a surface skin similar to the gel formed when Adinol is diluted in the range 20% to near 100% in the absence of alkali. There are, however, reasons for using very dilute solutions. They are more common and therefore of greater practical importance, they are less viscous, cause more rapid cracking and are chemically simpler.

The last point above refers to the ability of surfactant molecules to associate into soluble micelles when the solution reaches a certain concentration (see for example Schwartz (94)). The critical micelle concentration (CMC) is dependent upon the species, so for a commercial detergent, it is virtually indefinable because of the range of species present. Micelles are an important feature of detergency in general but they make ESC work difficult to analyse because the amount of detergent available for adsorption on to surfaces, to reduce surface energy, is not proportional to the concentration. The form taken by micelles is dependent upon the surfactant and their structure changes in a discontinuous manner as concentration increases. The micelles first formed are roughly spherical and may contain 50 to 500 molecules. They are arranged with the hydrophobic 'tails' tucked together in the interior of the structure and the polar 'heads' in the exterior, adjacent to the aqueous molecules.

The chemically complicated nature of detergent solutions makes visualisation of their effects on crack growth difficult. Flow into craze-like regions at crack tips would probably be inhibited by large micellar structures but whether these would be broken down in the vicinity of the PE is unknown. It is considered likely that the lack of a simple explanation for different cracking speeds in detergent solutions is closely linked with these structural complications.

The possibility of a link between detergency and ESC is very likely since the breaking of cohesive and adhesive bonds will be effected by similar external influences. The detergent effects of chemicals, other than synthetic detergents and soaps, often does not come about in the manner outlined above. If simple reduction of surface tension was the only controlling factor short chain alcohols would cause more rapid cracking, at the same viscosity, than detergent solutions. This is not the case as can be seen from figure 32 or the data compiled by Howard (49). It is possible, however, to see in figure 32 that surface tension might influence the results of the tests in detergent solutions. These data unfortunately cannot be supported by the literature in which only Pelagatti and Baretta (84) agree that the 10% solution is more aggressive than the anhydrous detergent. Larsen (68) and McFedries (76) say that there is little or no effect of dilution and Hittmair and Ullman (46) found increasing concentration reduced crack times.

Ignoring these contradictory ESC results from the literature, it is suggested that if more information was available on the very general field of relative effect of detergent materials, it could prove important in the analysis of ESC.

6.8. SCATTER ON RESULTS

By the standards of other ESC tests the amount of scatter observed on the results in this work is considered very acceptable. One great advantage over the Lander (3) or Carey (17) tests, which are considered the closest comparable tests, is the removal of the random initial stress raiser. The hole in the Carey specimen does not remove this random effect but adds a further stress raiser to ensure that failure will occur from a particular region. The observation of only crack growth, and not initiation, is a limitation on the present work but it could be extended to fully cover both areas.

The relatively small scatter on results is only relative to other fracture tests and in real terms is quite large, especially on time. Some of the reasons are factors which must be considered in all testing of plastics. The material for each specimen although from one batch will be slightly different, primarily because of its heat treatment. During each test the bulk material will change to an extent dependent upon the test time and temperature and the applied stress. The bulk material is also likely to undergo some recrystallisation changes which will be very slight but perhaps add a little to the scatter.

The environments will also change with time. Most of the environments used for this work are regarded as hygroscopic and, although they were replaced between most of the tests, if any composition changes occurred during a test they had to be accepted. Temperature changes would also cause scatter which is why ASTM require control to $\pm 0.5^{\circ}C$ during ESC tests. The control generally possible during this work was $20^{+0.5}_{-1.0}\,^{\circ}C$ and $\pm 0.5^{\circ}C$ at higher temperatures and many tests were discarded when equipment malfunctions allowed greater temperature fluctuations, but it is still thought that some scatter will have been caused by temperature changes.

The above comments are all fairly general but there is one particular factor which is specific to these tests and was apparently the greatest source of scatter. The overall K_1-crack speed curves have been shown to consist of two distinct parts with different slopes and it was found that many of the individual specimens gave two part K_1-crack speed curves. This not only occurred where the K_1 was very low and relaxation controlled cracking could be regarded as the cause, but also at higher initial K_1s where there was, on some specimens, a slowing of the crack speed for a short length of cracking. The different notching techniques showed that notching was not responsible for this effect but that something happened to the material whilst on test.

There are two explanations for the slowing of initial cracking :-

a) If ESC is effected in a plastic zone or craze at the tip of the crack and the environment is required to have penetrated this region, the initial part of the crack will deform, when loaded, too quickly to accept the environment. Having deformed, the polymer will be much less receptive to the environment (see J.L. Williams and Peterlin (111)).

b) The second possibility is that a plastic zone forms while the crack is stationary, which is much larger than that formed in front of a running crack and that this zone slows cracking down because it is oriented material stretched across the crack tip. This type of deformation has been observed by Bergkvist and Andersson (12) and a similar phenomenon can readily be identified when PE specimens are loaded to give an initial stress intensity of more than 1 $MN/m^{3/2}$. A rounded crack tip forms in a large plastic zone before cracking starts but when the crack initiates and grows through this region it is sharp.

Apart from being a main inhibition to reproducibility this type of scatter could have more far reaching effects than the other types because the overall shape of the curve obtained for one specimen resembles that for a whole family and it may be wrongly interpreted as representative of the family. It might be concluded from one test result that the low K_1 relaxation controlled cracking region had been reached. The only way to distinguish the real K_1-crack speed curve is from a number of tests or from the size of the apparent relaxation controlled region. The length of cracking which was apparently in the relaxation region, but was subsequently found to be at higher K_1, was restricted to the first 1.5 mm of crack growth. The true relaxation controlled crack length is related only to the range of applied K_1 and for the present work extended up to 9 mm.

6.9. FRACTURE SURFACES

6.9.1. SEM Study

The surfaces of many of the specimens have been photographed and studied using a scanning electron microscope (SEM). The specimens were all plated with gold and secondary reflected electrons used. The primary advantage of this method, over visible light studies, was the increased depth of field which was needed to see the rough fracture surfaces ; the secondary advantage of higher magnification was useful in some cases. For each photograph the exact position on the specimen was calculated and recorded to allow the comparison of surface appearances with relation to K_1 and crack speed.

6.9.2. Results

Some of the photographs taken in this study are shown in figures

59 - 64. Figure 59 shows surfaces of two PE-A specimens tested in Adinol at 20°C, a comparison being made on a crack speed basis. Figure 60 shows the surface of the same material tested in methanol which gave cracking at the same speed for the same K_1. Another comparison of the effect of changing the environment is given in figure 61 - in these four photographs the surfaces of PE-F are shown fractured in concentrated Adinol and a 5% dilution. Figure 62 shows the surfaces of PE-C tested at 60°C in Adinol and this can be compared with figure 63 which shows surfaces cracked in air, two specimens being used for the air photographs. Finally figure 64 shows the significance of the plane stress zone present at the edge of all specimens. For one of the specimens tested in air these photographs show the difference in the appearance of the surface at the edge of the specimen relative to the rest for a constant K_1 of 0.366 MN/m$^{3/2}$.

6.9.3. Discussion

The first conclusion which can be made from study of the micrographs is one that has been made before, and is that ESC failure is microscopically ductile. The surfaces show fibrils which have been drawn from the surface and broken by excessive extension. Before final failure occurred there must have been a craze-like structure formed but it was not as stable as a craze and the void content increased as final failure approached. This type of failure surface gives half the explanation for a critical COD failure criterion since the controlling factor will be the failure strain of the material. The other requirement for critical COD is that the same thickness of material be drawn to failure at the crack tip at the beginning of each failure process. The second criterion above is unlikely to be completely true since each series of micrographs shows an increase in the size of the drawn fibrils as the crack speed increases, but the micrographs of surfaces cracked at high speed will fit the increasing COD data.

The effect of changing the environments is rather difficult to analyse as regards the fracture surfaces. The 5% Adinol, which gives more rapid cracking than concentrated Adinol, at the same K_1, gives a similar type of fracture surface to the concentrate, but there is more drawn material, figure 61. The two comparisons made in these micrographs are for the same speed so it might be expected that the surfaces would either be similar or that there would be less drawn material on the lower K_1 fractured surfaces - those cracked in the dilution. It is reasonable to assume that the nature of the surface is not only a function of crack speed but also environment and this point is well proven by the other micrographs.

The surfaces formed at 60^oC in Adinol and air show very little relationship at all. The Adinol surface is similar to all the surfaces formed in Adinol at 20^oC, but the air surface shows a totally different type of drawing, very long thin 'rod-like' fibrils being formed with a much less obvious failure mode than the surfaces which resemble normal drawing type failure. A certain quantity of the 'rod-like' fibrils can be seen in some of the Adinol failures at 20^oC but none at 60^oC. ESC failure at 60^oC in air might be expected to give anomalous results but the fracture surface is very similar to that caused by methanol at 20^oC. The difference between the surfaces of methanol and Adinol specimens implies that the failure mechanism of ESC is extremely complicated and that a number of environmental variables are important since these two both give the same results in terms of K_1-crack speed relationship.

The final consideration here is the effect of the stress field and it can be seen from the micrograph taken at the edge of a specimen, figure 64, that drawing is not restricted in the same way as at the centre. This effect however is not very significant since the micrograph covering the zone from approximately 200 to 300 microns from the edge of the specimen is exactly the same as that taken at 1 mm from the edge and that taken at the centre, shown in figure 63.

6.10. MECHANISM OF FAILURE

The mechanism of ESC has been shown by the microscopic studies of other workers to be the formation of microvoids, mainly from the centres of spherulites, and their coalescence to form a complete crack. The studies of Haas and MacRae (40) showed that there was no difference between the levels of biaxial strain at which the first microcracks appeared whether the environment was detergent or air. They found that the difference between the two environments came during the second stage of growth, when the detergent caused more rapid coalescence. These results suggest that the mechanism of failure is not related to the lowering of the surface energy of the PE, since the formation of the initial microvoids would be affected.

If the microscopic drawing of the material is the process which is affected by the environment, then the tensile tests on thin specimens might have given a good quantitative indication of the effect caused by Adinol. As no effect was revealed the best assumption which can be made is that the magnitudes of the components used were wrong and, whilst the reasons for not pursuing this particular line of work are given in an earlier discussion, it is suggested that work on the scale of that by Haas and MacRae could give the sort of quantitative strength reduction information required by engineers.

The fracture surface studies in this work show one factor which may be regarded as similar to those found by Haas and MacRae. The fracture surfaces of specimens tested in air show more drawing, in the yielded zone, than those tested in Adinol. It is reasonable to assume that this drawing took longer in the air tests, both because there was a greater amount and because the rate of crack growth was less for the same stress condition. This means that the coalescence, which is the rate controlling feature, is probably similar in the microscopic and macroscopic studies and justifies in part the use of thin biaxially stressed sheets for detailed study. The difference between the two fractures is in the brittle regions. Whilst initial cracks were found, in microscopic studies, growing mainly radially through what was probably interlamella amorphous material, there is little evidence of brittle crack regions on the fracture surface micrographs. On some micrographs there are apparently flat regions which could be interpreted as brittle initial cracks, but in most cases the surface appears to be only a series of fibrils. If there are brittle regions they would be expected to relate to size of the spherulites which for PE-A were less than one micron. The spherulites could not be determined using microtomed or ultramicrotomed sections under cross polars at a magnification of 800 x although some ordered structure could be detected. Brittle regions covering a fraction of this spherulite size could well be hidden by the drawn material but they could not cover a large proportion of the fracture surface and so are unlikely to be a controlling factor in the mechanism.

CHAPTER 7

CONCLUSIONS

The environmental stress cracking of polyethylene is the failure in a macroscopically brittle manner of stressed PE material and is a slow crack growth phenomenon. The present study has shown that even the most crack resistant PE copolymers can be made to crack under appropriate loading conditions and that fracture mechanics can be used to quantify the conditions under which failure will occur. Taking the time dependence of the PE into account, by comparing stress intensity factors on a crack speed basis, it has been shown that there are no specimen geometry effects which cannot be taken into account by the application of fracture mechanics analysis. This geometry independence extends, not only to the use of different crack lengths and different specimen sizes, but also to the comparison of single edge notched plates with centre notch plates and these through-wall cracks with semi-elliptical surface cracks.

Having shown that the application of fracture mechanics to ESC was valid, and found in the process that the experimental scatter was less than that normally associated with ESC testing, the method was used to consider some of the variables which affect cracking. The main material parameter considered was the effect of copolymerisation because there was little documentation on this factor,possibly because of the difficulty in cracking many copolymers using the ASTM methods, particularly the more common 'bent strip test'. Comparison of a series of four similar materials, one homopolymer and three copolymers polymerised using the same process, with a blended copolymer and a copolymer from another manufacturer showed that there was a linear relationship between K_1 and density for each crack speed. It is thought that this simple relationship may not be universally true because variables other than comonomer type and quantity will affect results. But it must be concluded from the present results that the effect of copolymerisation will override the effect of the other variables to a considerable extent and that the factors in copolymerisation which reduce density are either the same as, or bear a linear relationship to, those which increase stress cracking resistance.

Before continuing with the conclusions drawn about the external variables it is necessary to consider the K_1-crack speed relationships found. For the first time two parts have been identified in the cracking process. The first part, for slower cracking, has been associated with the relaxation properties of the polymer, initially because the log K_1-log crack speed data gave straight lines of slope approximately 0.1. The second part having a log-log slope of approximately 0.5 was associated with the flow of the environment to the crack front. The importance of these two parts of the K_1-crack speed curves are considered with the conclusions on temperature and environmental effect respectively.

The environments used in these tests were Adinol CO 630, a non-ionic detergent and its dilutions, alcohols, water, Teepol and air. The rate of crack growth in different environments varied considerably. For the Adinol-water mixtures it was found that crack speeds, at the same K_1, increased with the quantity of Adinol up to about 5% but for 10% and 100% the cracking slowed again. The tests in alcohols confirmed the importance of flow of environment by showing a relationship, for the faster cracking, between viscosity and crack speed. The three alcohols are chemically very similar and have virtually the same surface tensions so it was possible that any viscosity effect could be shown up with these environments without being hidden by other factors. The crack speeds obtained in alcohol environments varied by a factor of approximately 6, at constant K_1, and this speed variation bore a linear relationship to the viscosity of the alcohols thereby permitting the production of a master curve for K_1 against crack speed times viscosity.

The K_1-crack speed relationship for slow speed cracking shows that the relaxation characteristic of the material is the controlling factor. By considering the loading state of specimens in terms of crack opening displacement it has been shown that there is a constant value of COD throughout the range of slow crack speeds. This critical COD is dependent upon material, being greater for the more crack resistant materials, and the environment, but it is independent of temperature. This means that for slow speed crack growth, which is of the greater practical significance, the COD at which cracking will occur at operating temperatures may be determined from high temperature testing. From knowledge of this COD and the ratio of modulus at operating temperature to modulus at test temperature, the K_1 for slow crack growth can be determined.

The overall effect of temperature is to greatly increase crack speeds, and therefore reduce testing times, without altering the shape of the K_1-crack speed curves. All the curves are displaced towards faster crack speeds and lower K_1s as the temperature is increased, but they are not all displaced by the same amount. This shows that the higher speed cracking is not totally controlled by the flow rate and other properties of the environment. The speed increases, observed at either constant K_1 or constant COD, with temperature increase were greater than could be explained by changes in the fluid viscosity. The magnitude of the displacement is dependent upon the density of the polymer. Higher density materials are less affected by the temperature increase than the lower density materials, although the PE-F curves do not show as large a displacement as might be expected for such a low density polymer. The average crack speeds measured at constant K_1 can be compared by using an Arrhenius plot or a log crack speed against temperature plot and in both cases, within the limits of experimental scatter, a linear relationship is obtained.

An investigation of the failure mechanism which causes ESC can really only be obtained from microscopic studies of crack growth. Whilst such studies have not been the objective of this work, some factors affecting the failure mechanism have been investigated. It was found that there were no significant differences between the yield stresses of microtome-section tensile specimens when tested in Adinol and air at a slow constant strain rate, nor were there any significant weight increases in the Adinol specimens. There were, however, differences between the fracture surfaces in the different environments. The mode of failure, as has been observed by other authors, is macroscopically brittle but shows drawing under moderate magnifications. The fracture surface studies revealed increases in the quantity of drawn material and the cross-sectional area of the drawn fibrils, with increasing crack speed. Also there were differences in the type and quantity of drawing which occurred in the different environments. The quantity of drawn material was increased in the less aggressive environments and the strains which the polymer withstood before tearing were also increased.

The conclusion from the SEM fracture surface studies is that the aggressive environments increased failure speed by reducing the amount of drawing which took place.

The fracture surface micrographs also showed how little of the yielded material there was at the edge of a specimen. Once the testing technique had been perfected the extra drawing which occurred in the plane stress regions, at the edges of a specimen, was so small that it could only be seen under a microscope. It was therefore virtually the same as the other drawn material, showing that ESC can occur in plane stress provided the stress intensity is sufficiently low that it does not cause preferential yielding. This conclusion is an extension of that which can be made from the tests on specimens of different thickness, in which it was found that the changing stress field affected results from specimens of about 5 mm thickness or less, but failure could be induced in all the thicknesses.

For the final conclusion from this work reference must again be made to the available test methods for ESC. The ASTM 'bent strip' test is not suitable for more than a very limited application and can then only be used to define an order for crack susceptibility of polymers. The 'Lander' test is dependent upon an unmeasured initial surface defect which is likely to be representative of the test specimen rather than a finished product. In comparison with these tests, the K_1-crack speed approach provides a method for comparing materials under any loading conditions and accounts for the intrinsic flaws which will be present. The success of the application of this method shows the importance of the notches present in a quantitative manner and thus proves the lack of fundamental validity of the critical stress and critical strain criteria which have previously been put forward in spite of some anomalous results. The application of fracture mechanics to ESC provides a sensitive and universally applicable method of determining the critical conditions under which cracks will grow.

This method not only provides a way in which materials may be compared but also produces a design criterion which could be used to design components more economically or, in cases such as the gas industry, ensure safe operation over a long design life. Finally, it is a research tool which can be used to more accurately define the variables associated with ESC, particularly those concerning environments. The present work has revealed two K_1-crack speed relationships with different controlling factors showing that only by this type of approach can the crack affecting parameters be determined and used to give the data which will eventually lead to an explanation of ESC.

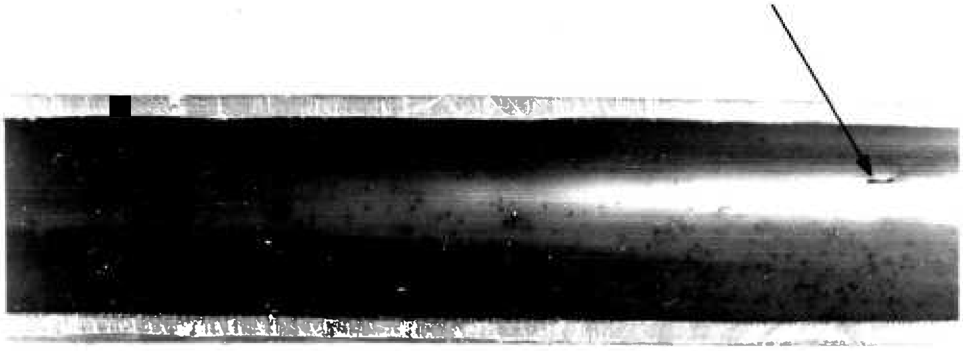


FIGURE 1 CRACKED GAS PIPE SPECIMEN

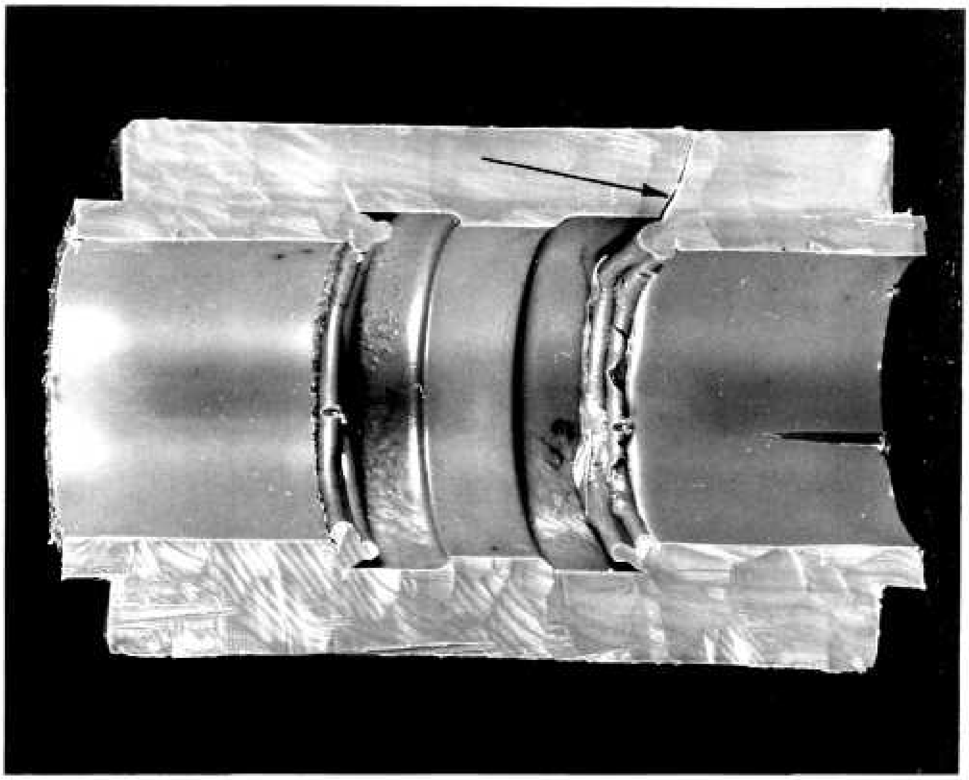
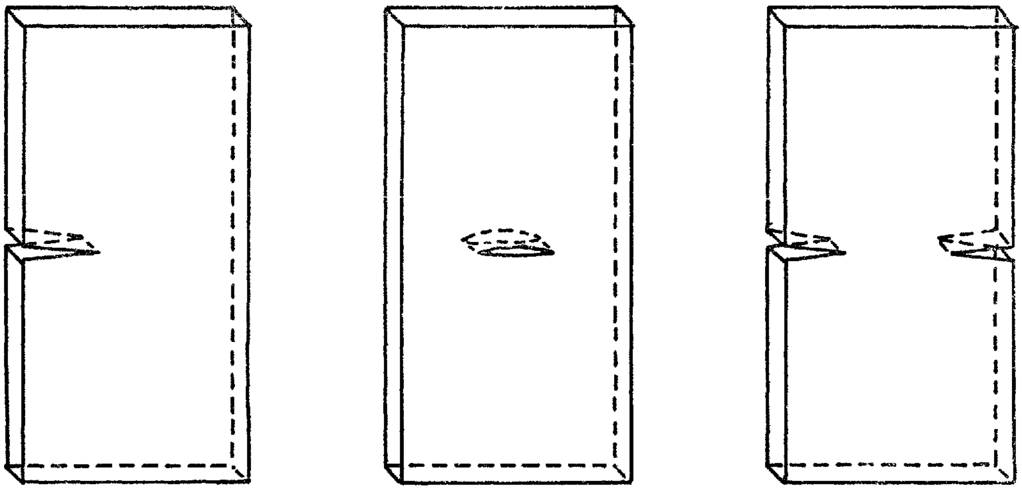
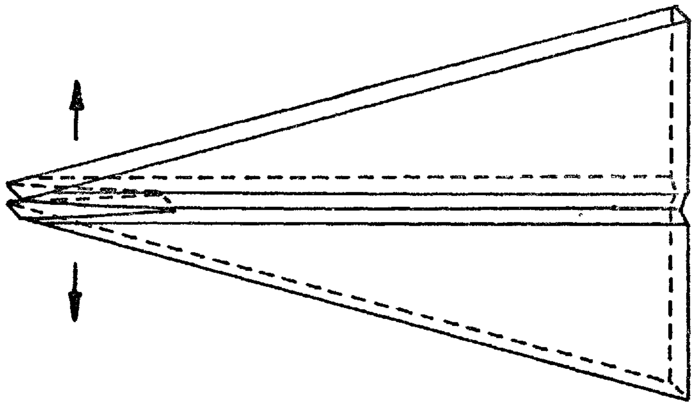


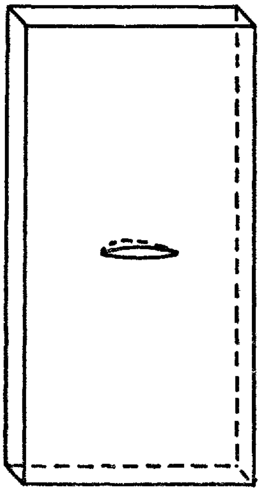
FIGURE 2 CRACKED STRAIGHT COUPLER



SEN CN DEN



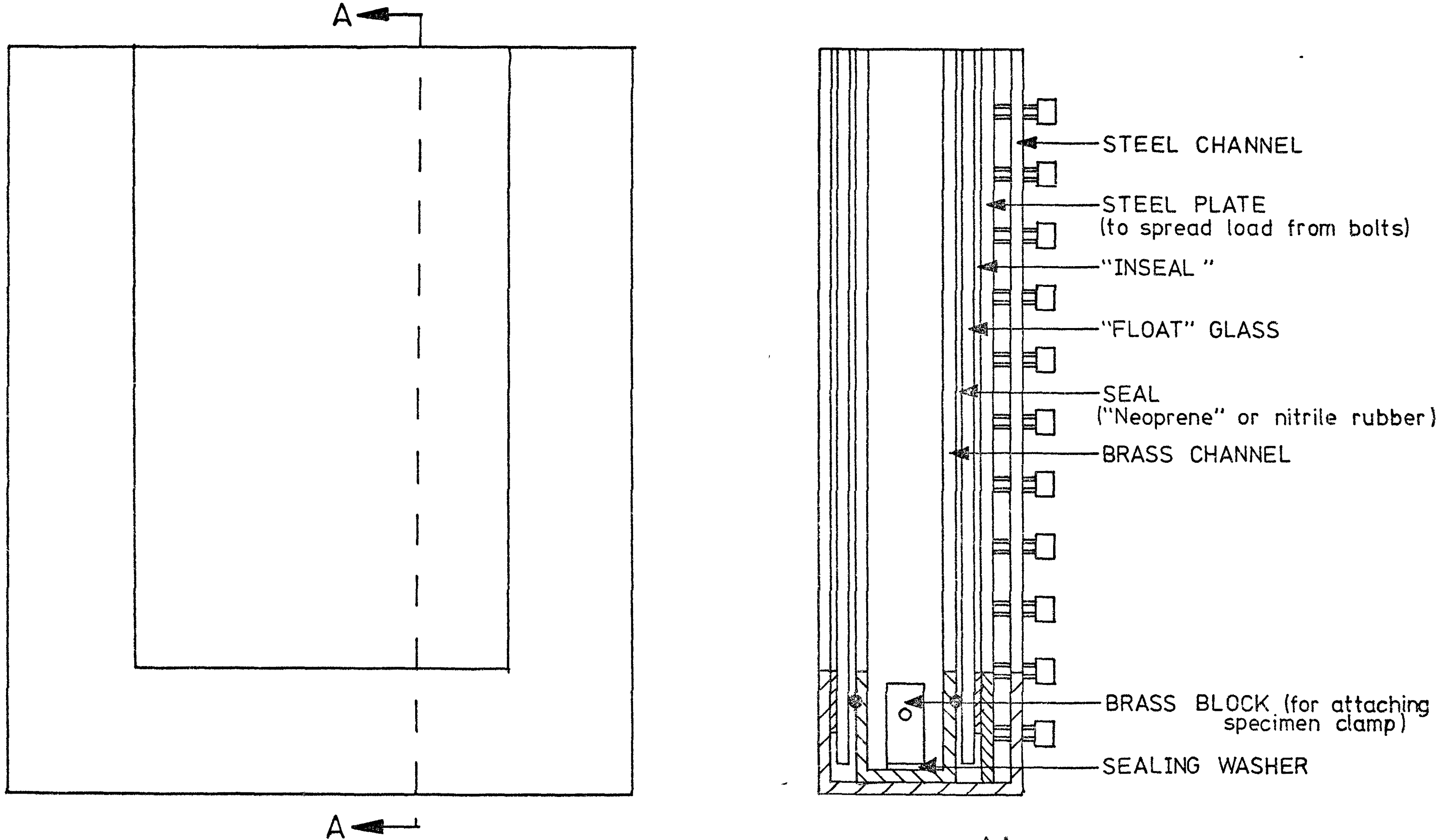
Tapered Cleavage



Surface Notch

SPECIMEN GEOMETRIES

FIGURE 3



SECTION ON AA

TANK FOR ENVIRONMENT FIGURE 4

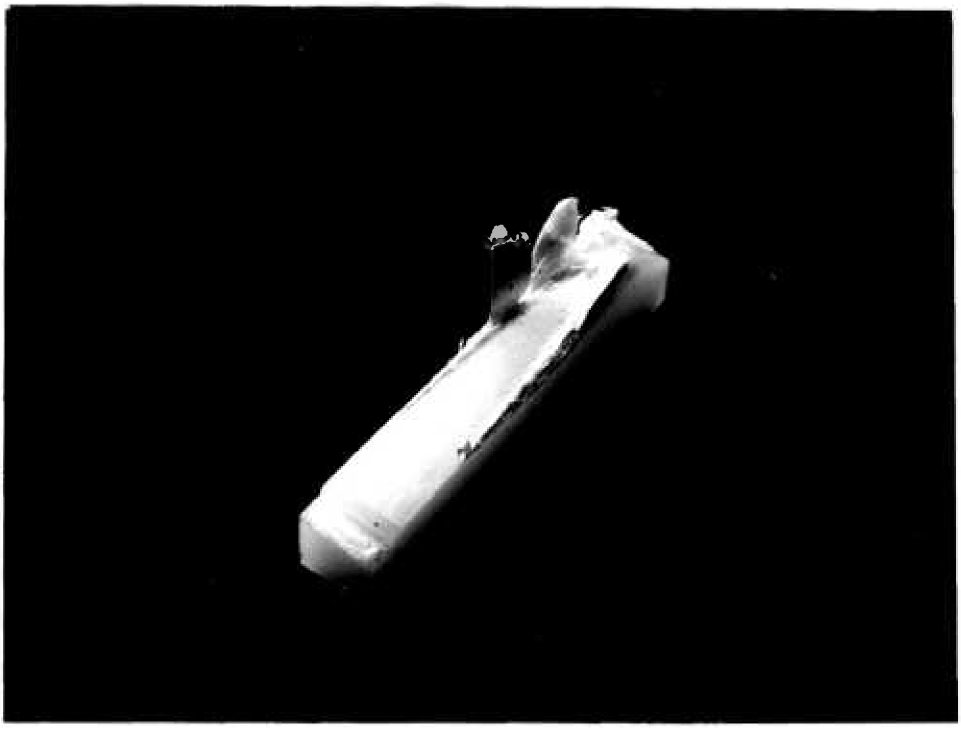


FIGURE 5 FRACTURE SURFACE OF EARLY SPECIMEN SHOWING SIDE YIELDING

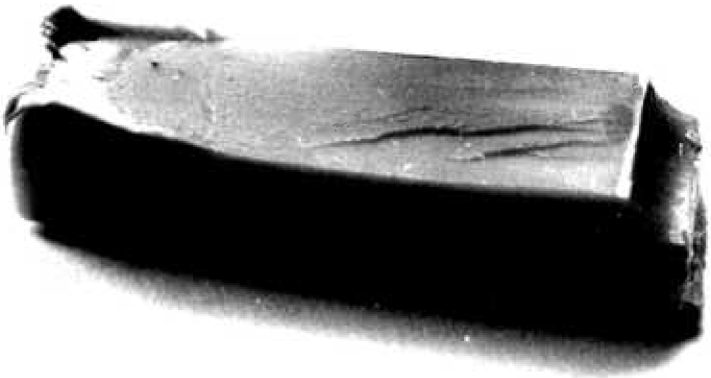


FIGURE 6 FRACTURE SURFACE - SIDE YIELDING ELIMINATED

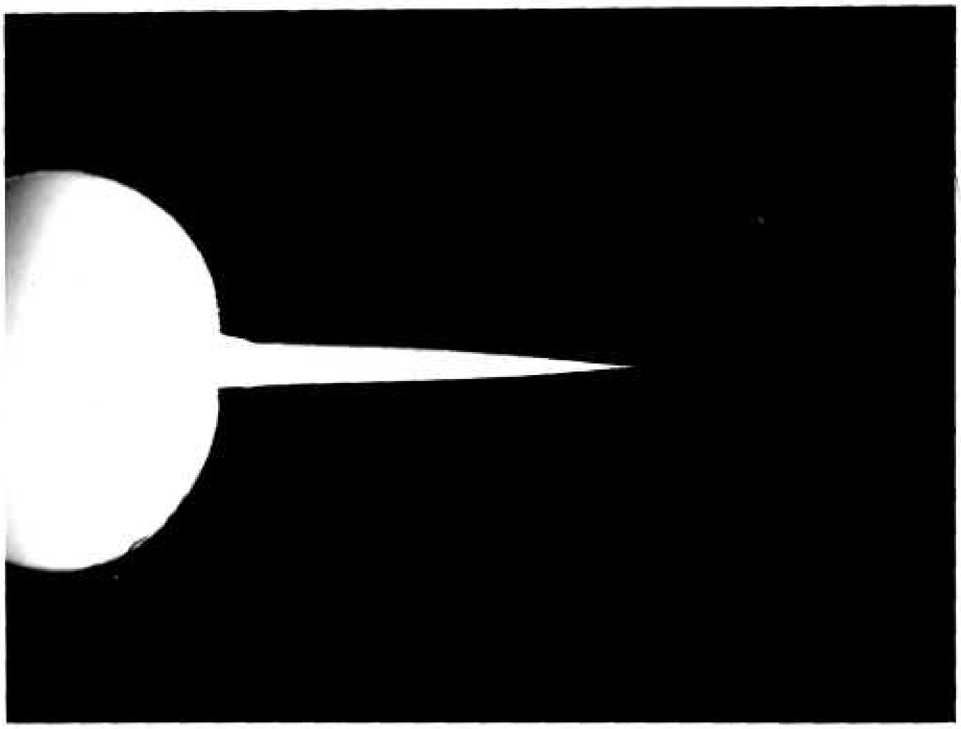


FIGURE 7 VISIBLE CRACK TIP

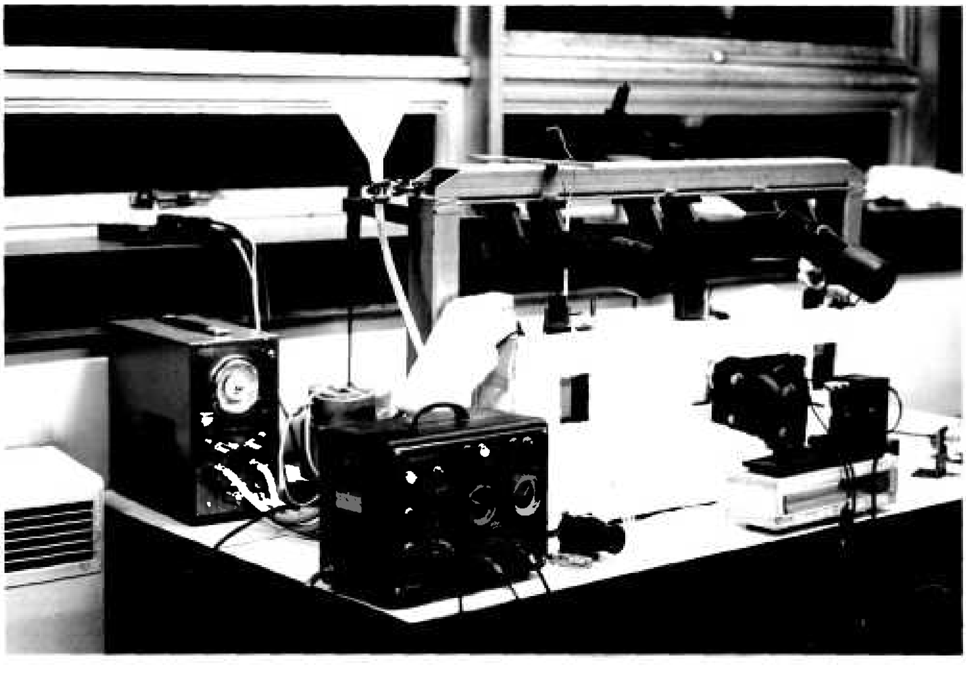


FIGURE 8 CONSTANT LOAD RIG FOR ELEVATED TEMPERATURE TESTS
SHOWING ROBOT CAMERA

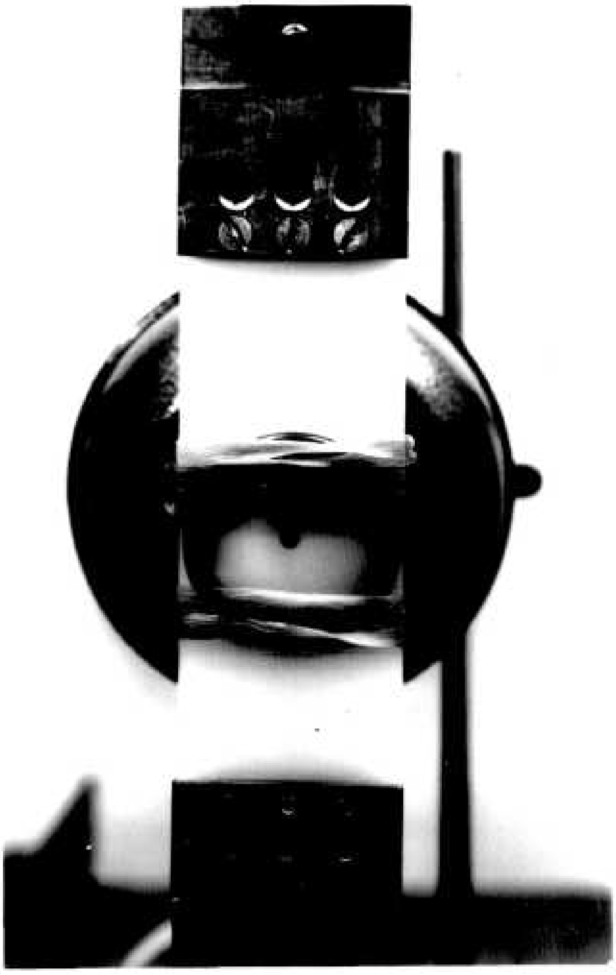
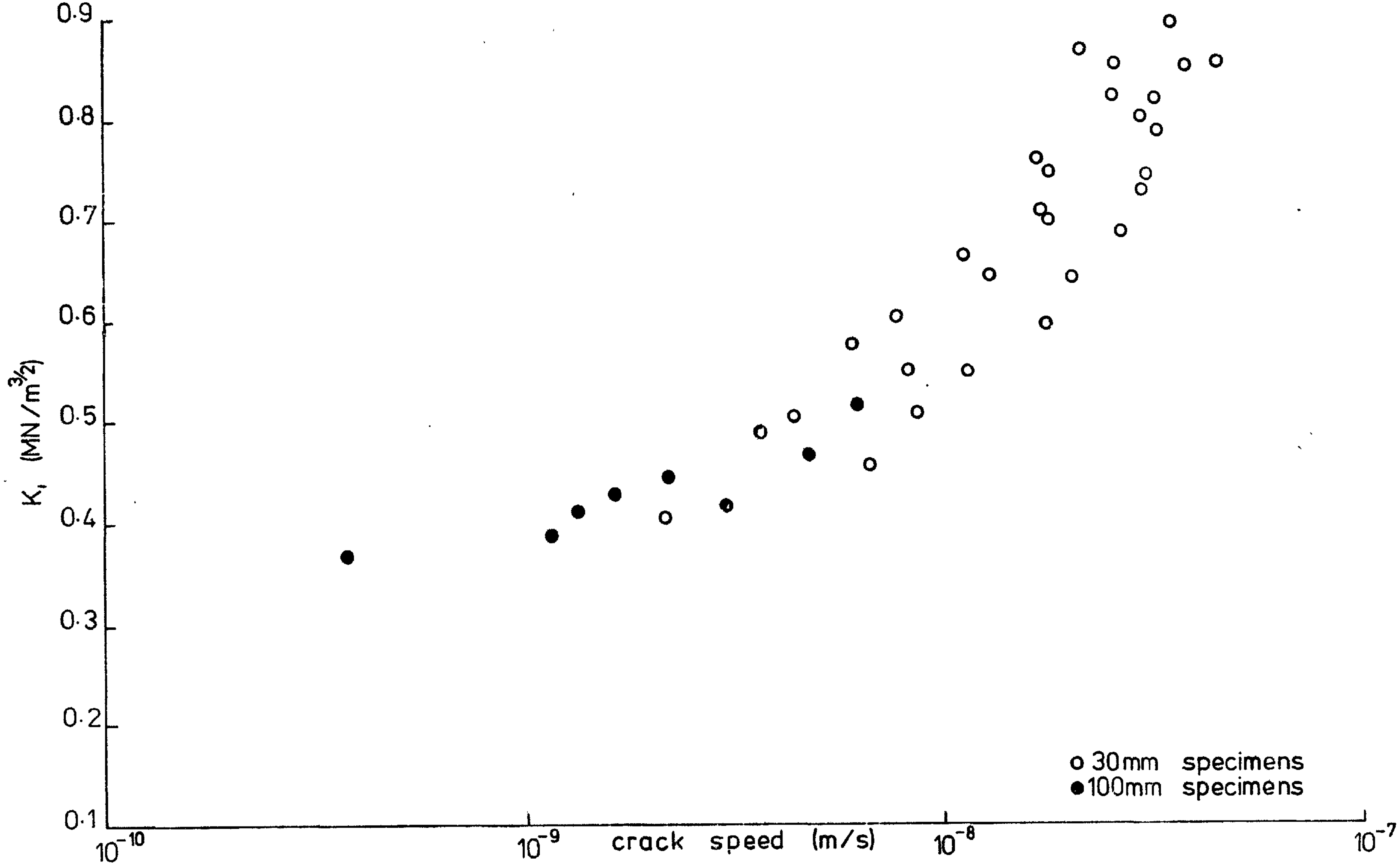
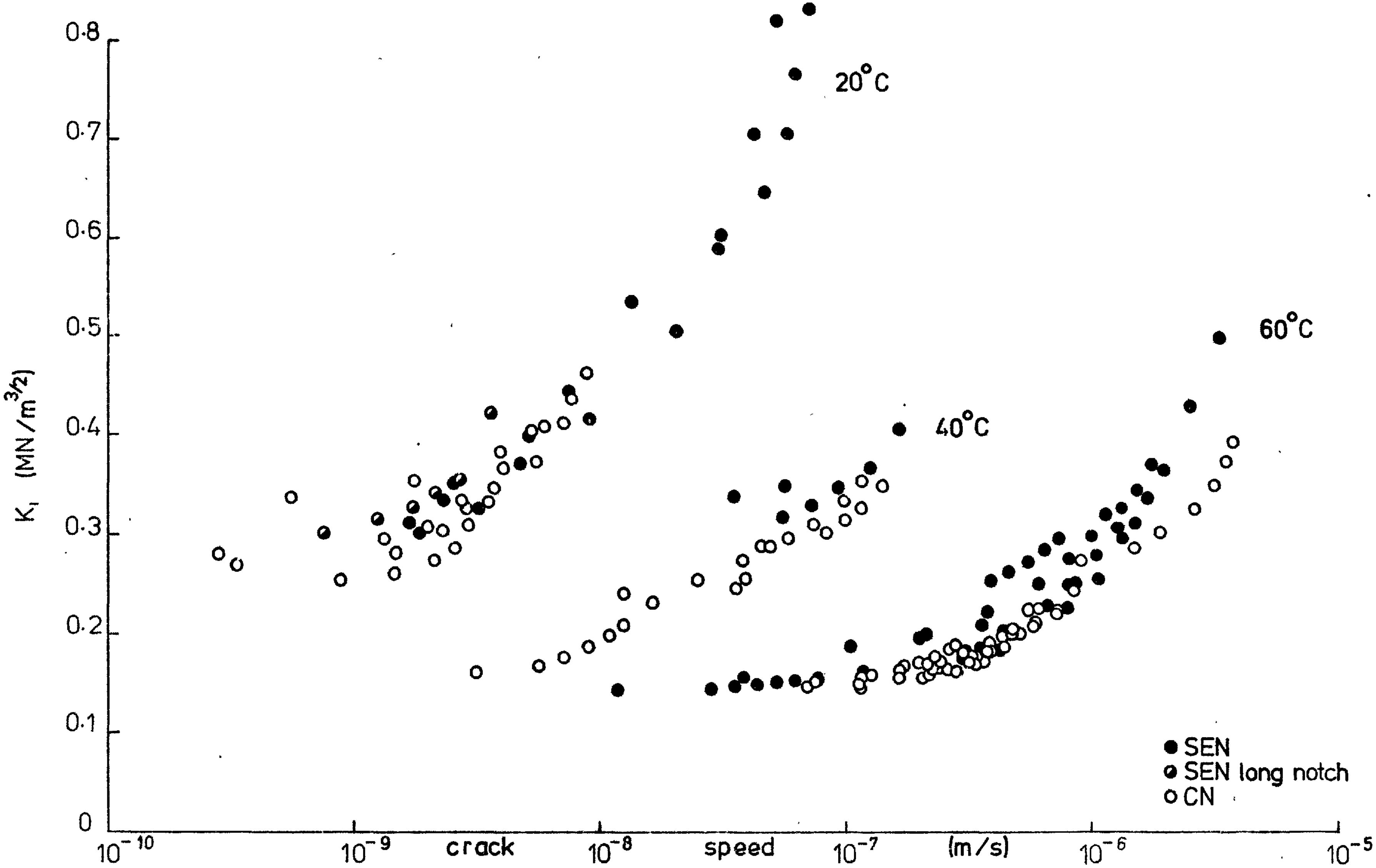


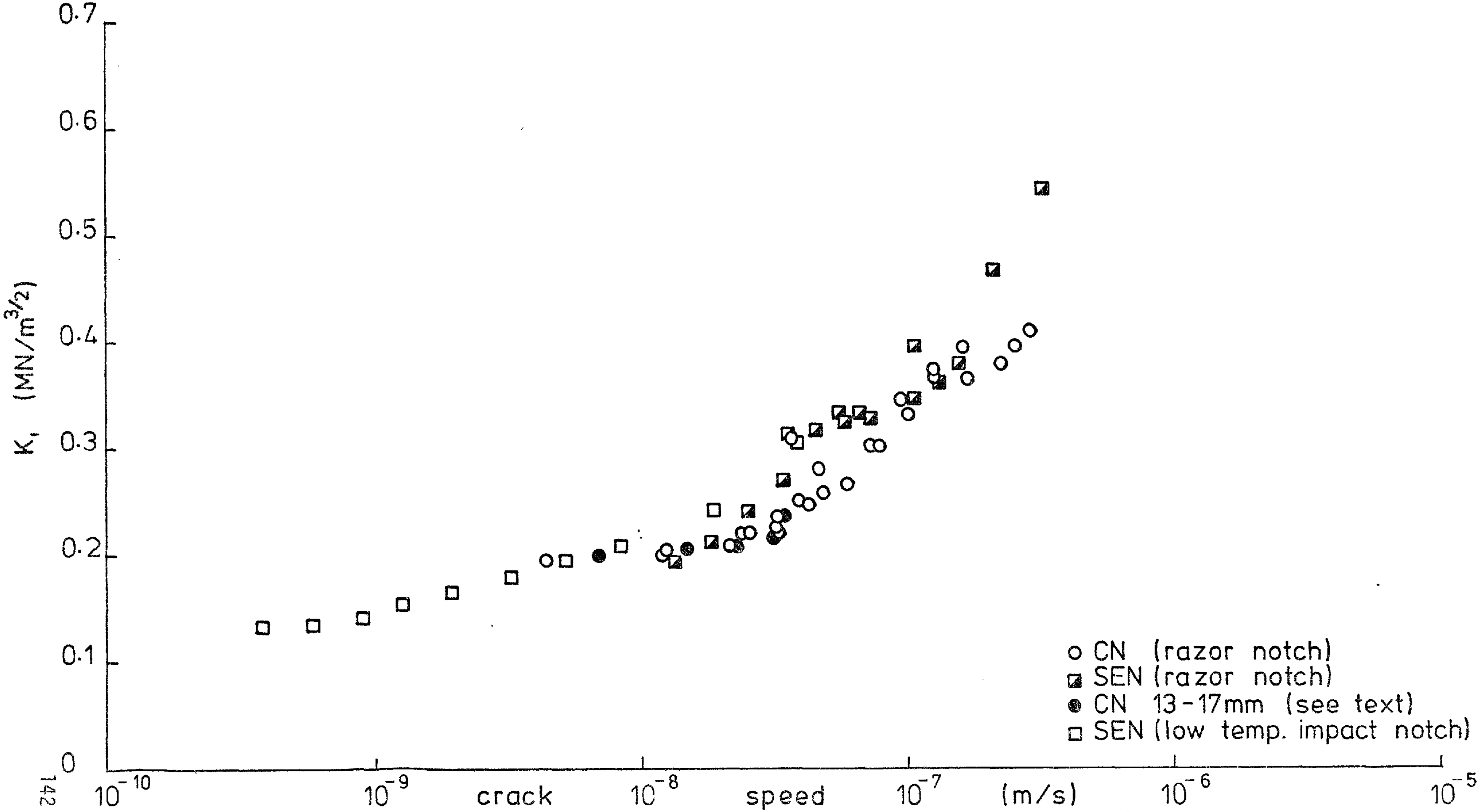
FIGURE 9 SIMPLE TANK DESIGN



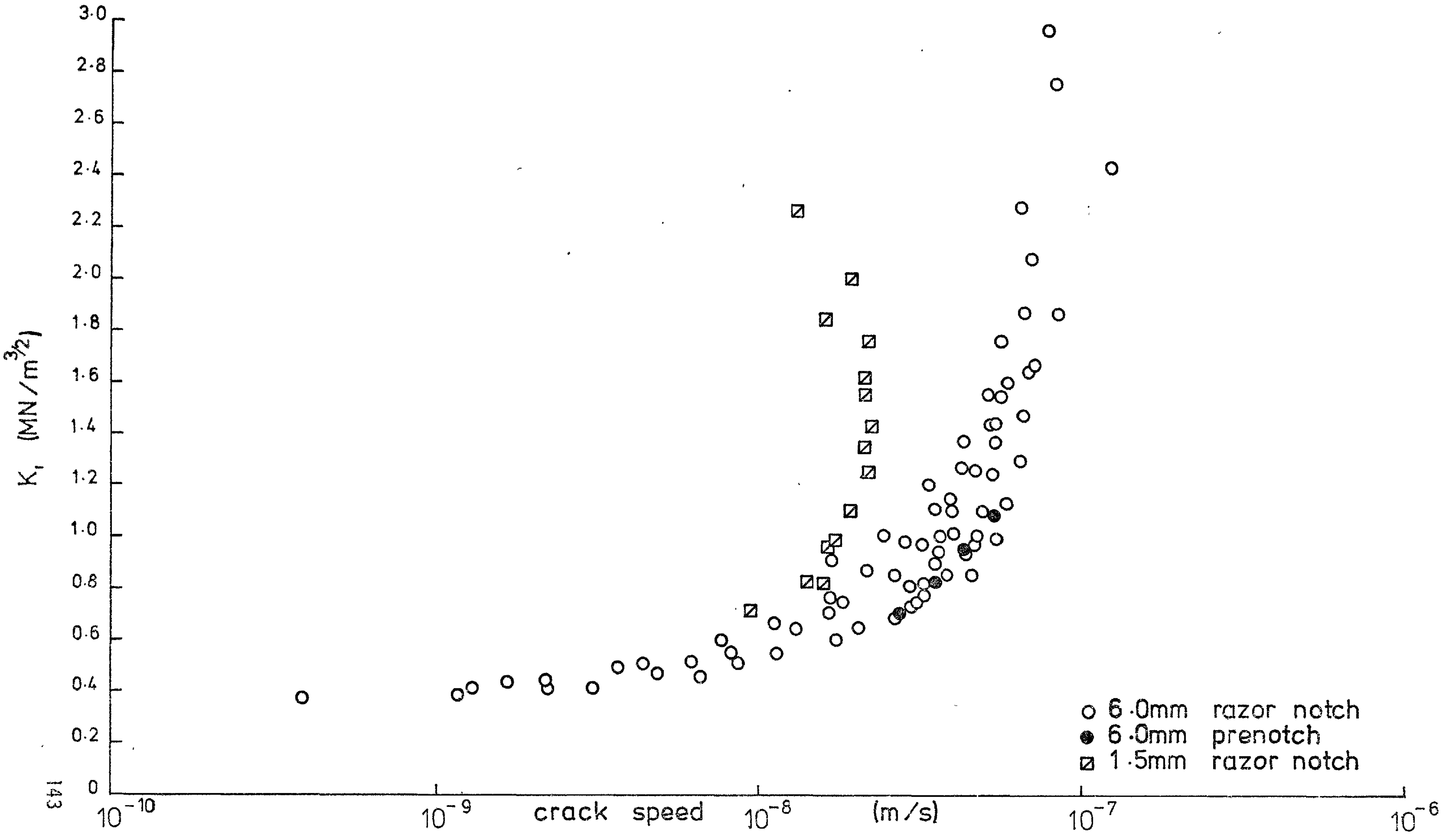
EFFECT OF SPECIMEN WIDTH PE–E 20°C in TEEPOL FIGURE 10



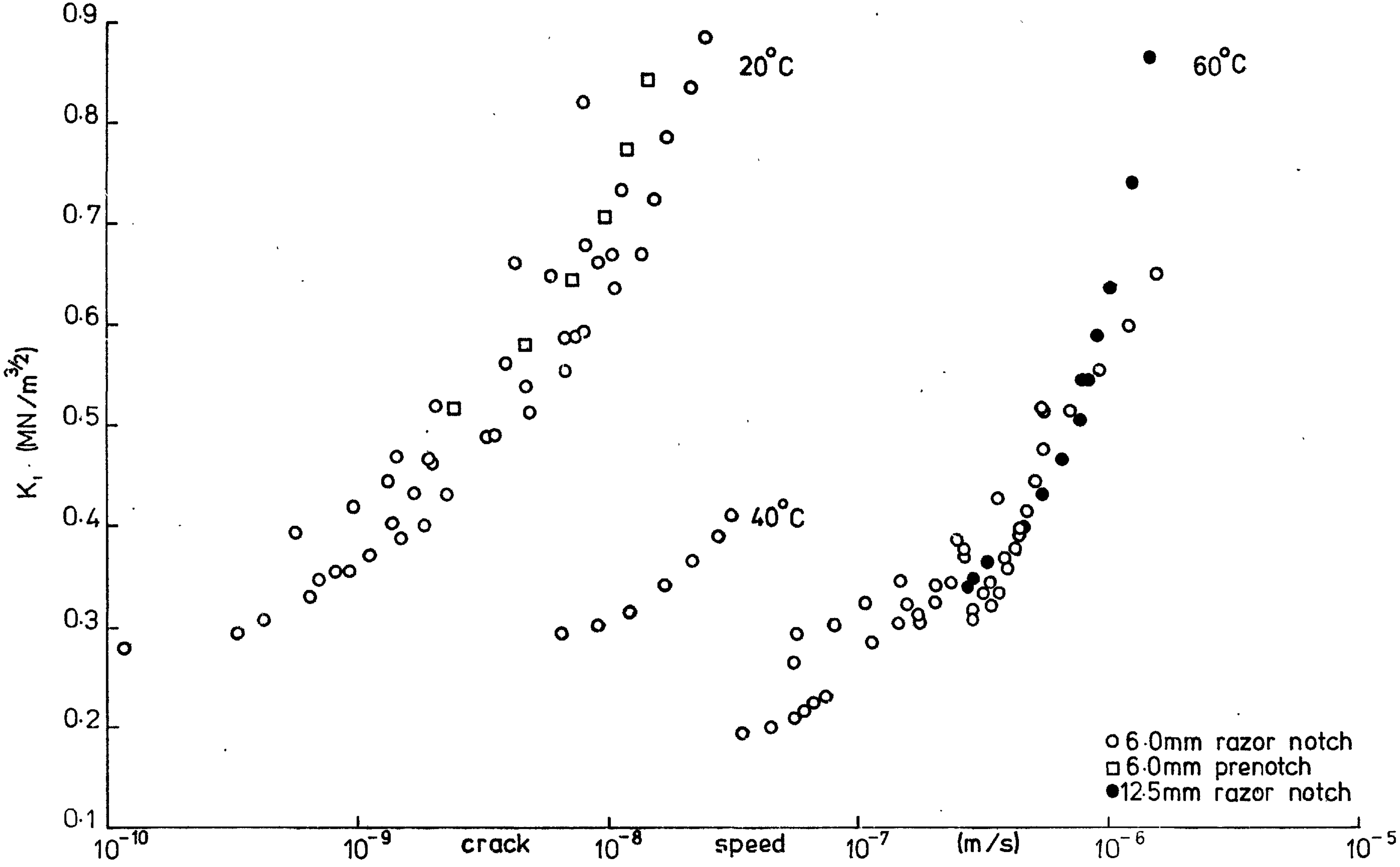
EFFECT OF TEST TEMPERATURE AND SPECIMEN GEOMETRY PE-F in ADINOL FIGURE 11



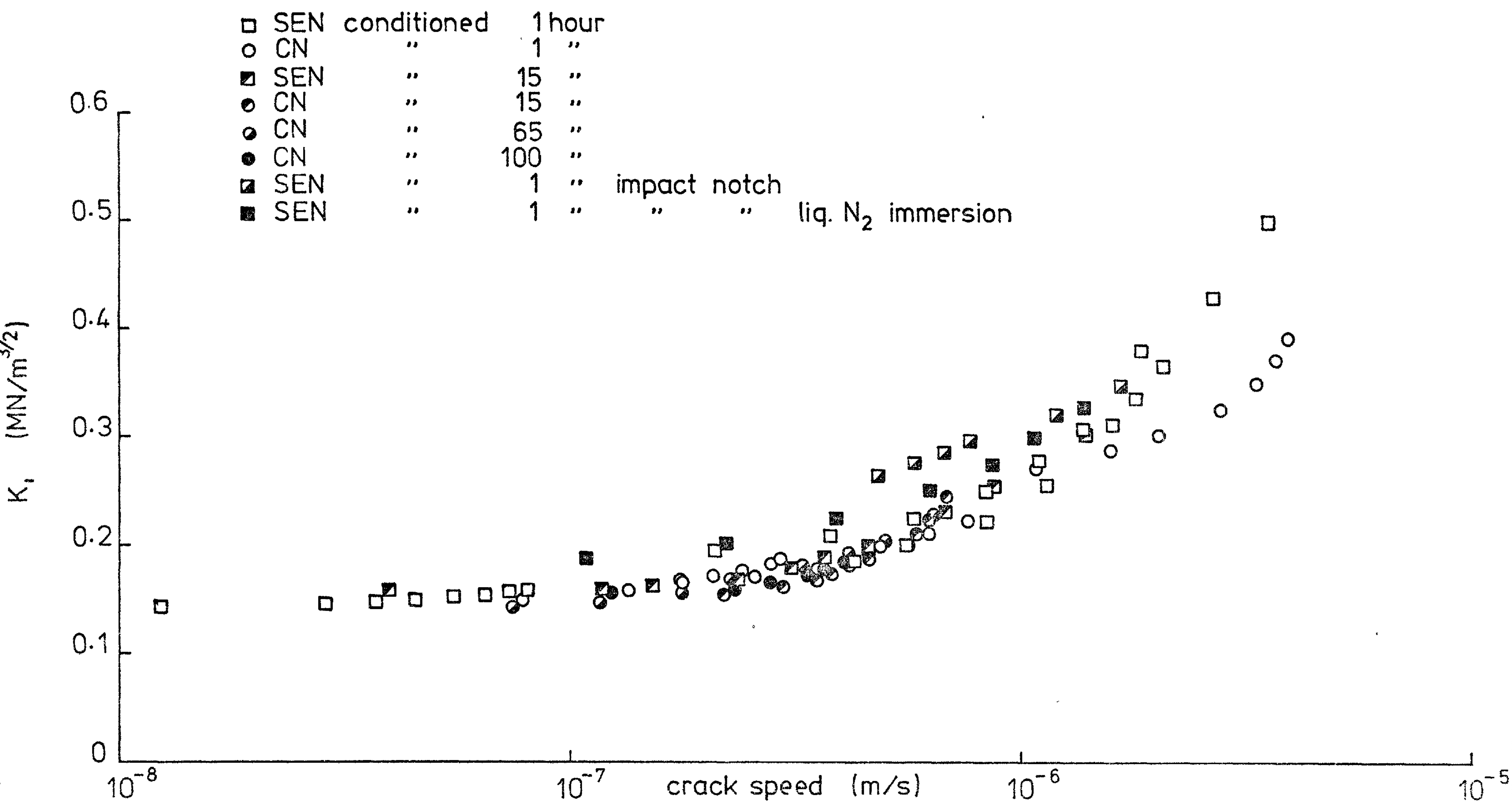
COMPARISON OF GEOMETRIES AND NOTCHES PE-C 60°C in ADINOL FIGURE 12



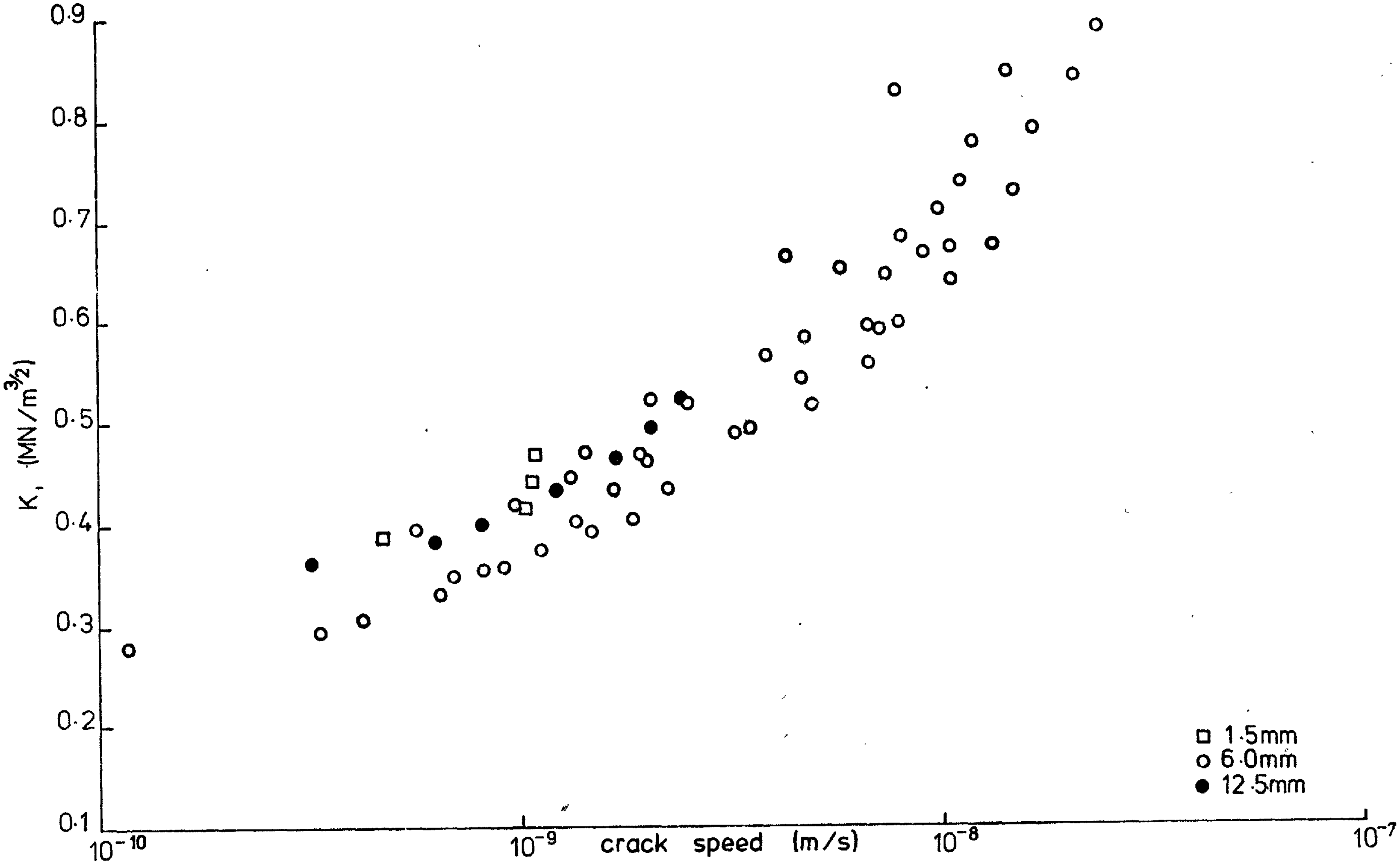
EFFECT OF SPECIMEN THICKNESS AND INITIAL NOTCH PE-E 20°C in TEEPOL FIGURE 13



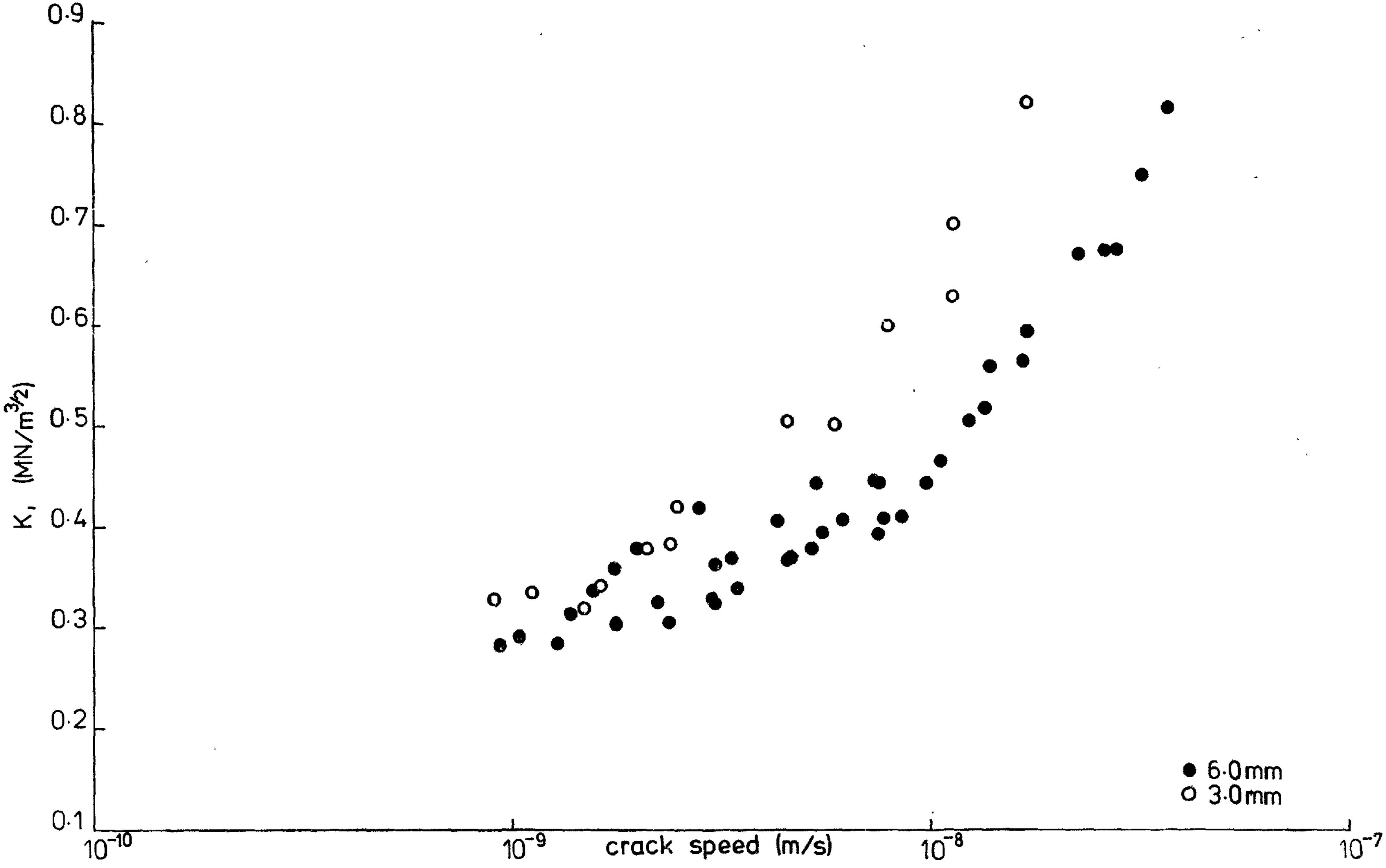
EFFECT OF TEST TEMPERATURE AND SPECIMEN THICKNESS PE-E in ADINOL FIGURE 14



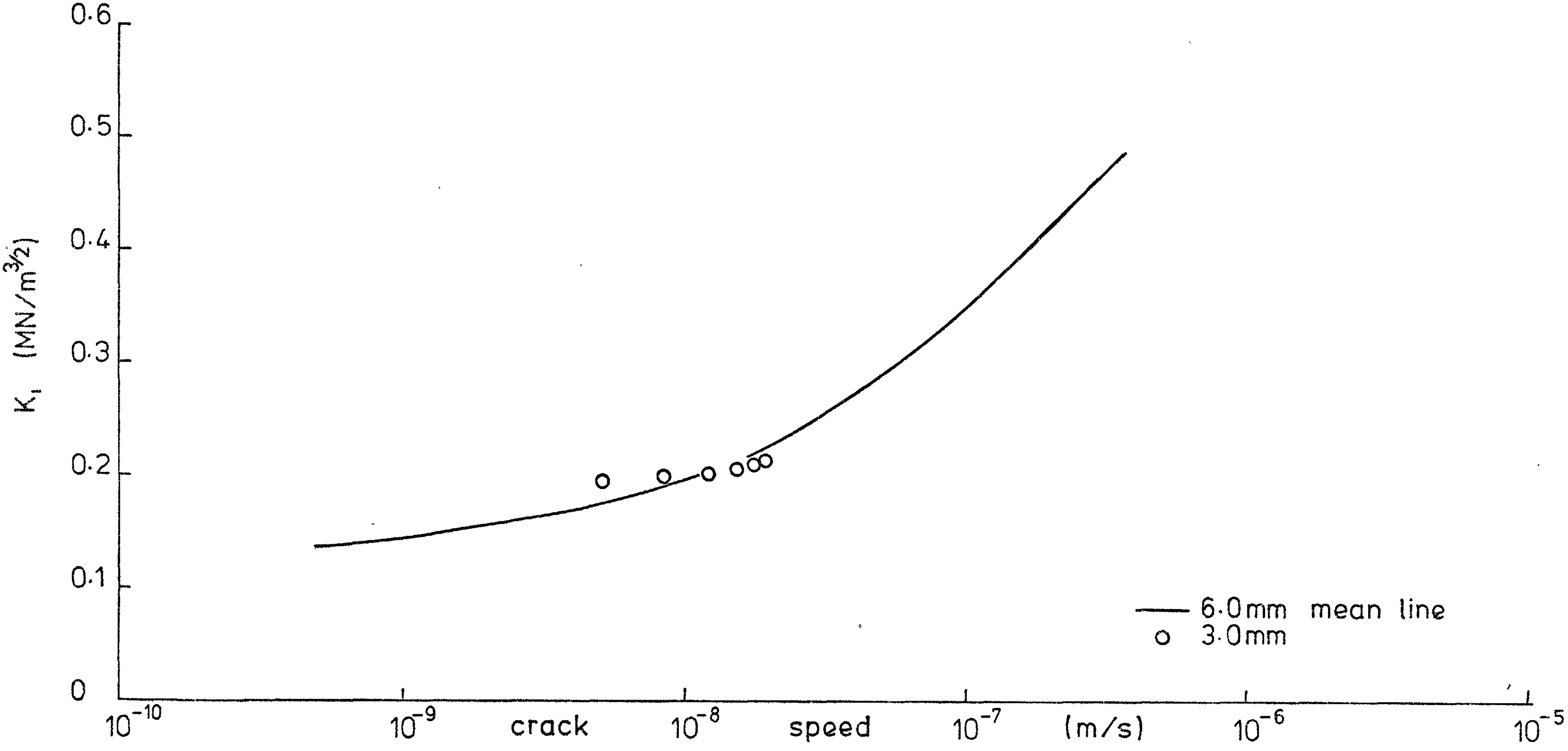
EFFECT OF CONDITIONING TIME AT TEST TEMPERATURE PE–F 60°C in ADINOL FIG. 15



EFFECT OF SPECIMEN THICKNESS PE-E 20°C in ADINOL FIGURE 16



EFFECT OF SPECIMEN THICKNESS PE-A 20°C in ADINOL FIGURE 17



EFFECT OF SPECIMEN THICKNESS PE-C 60°C in ADINOL FIGURE 18

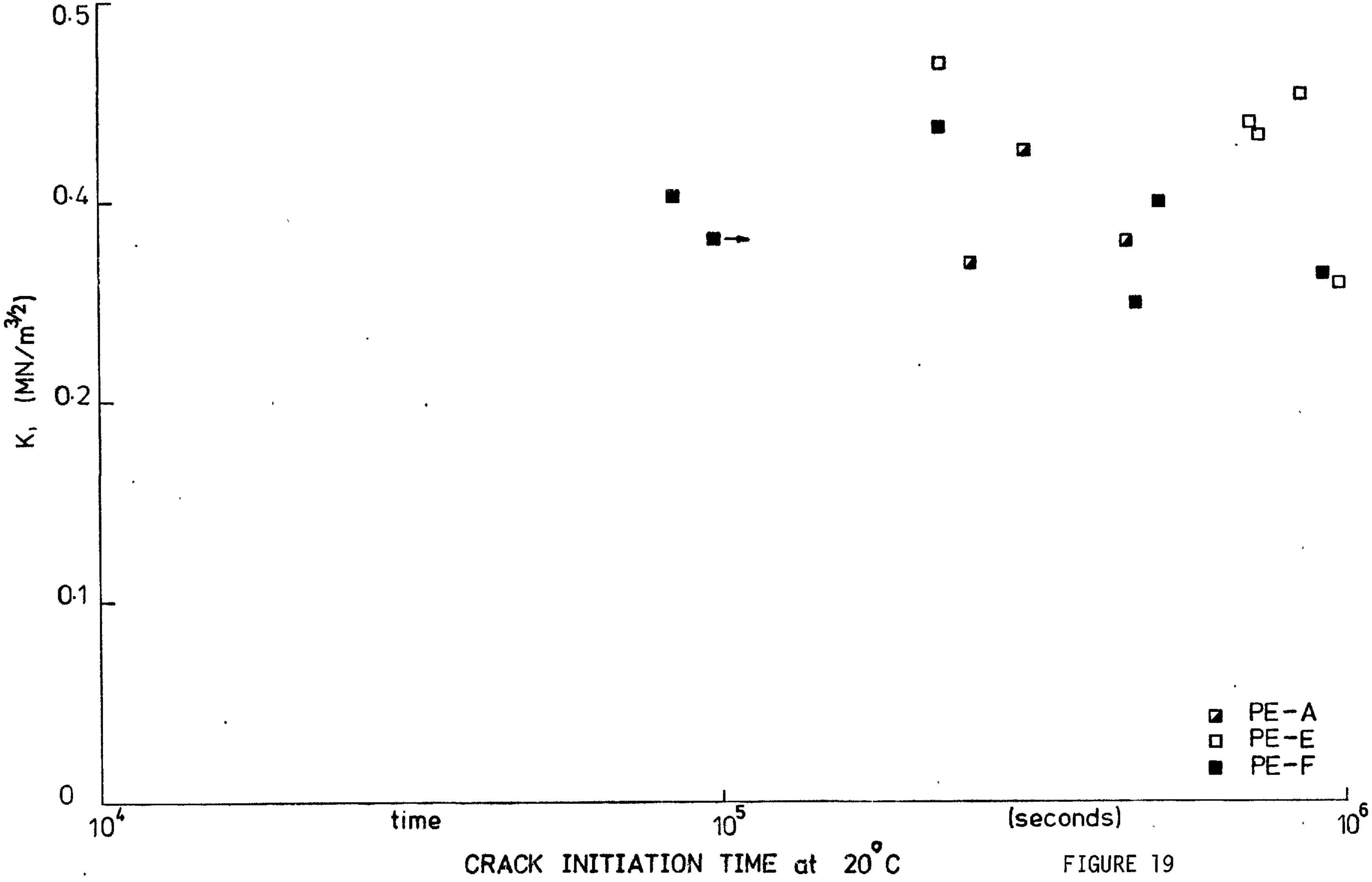
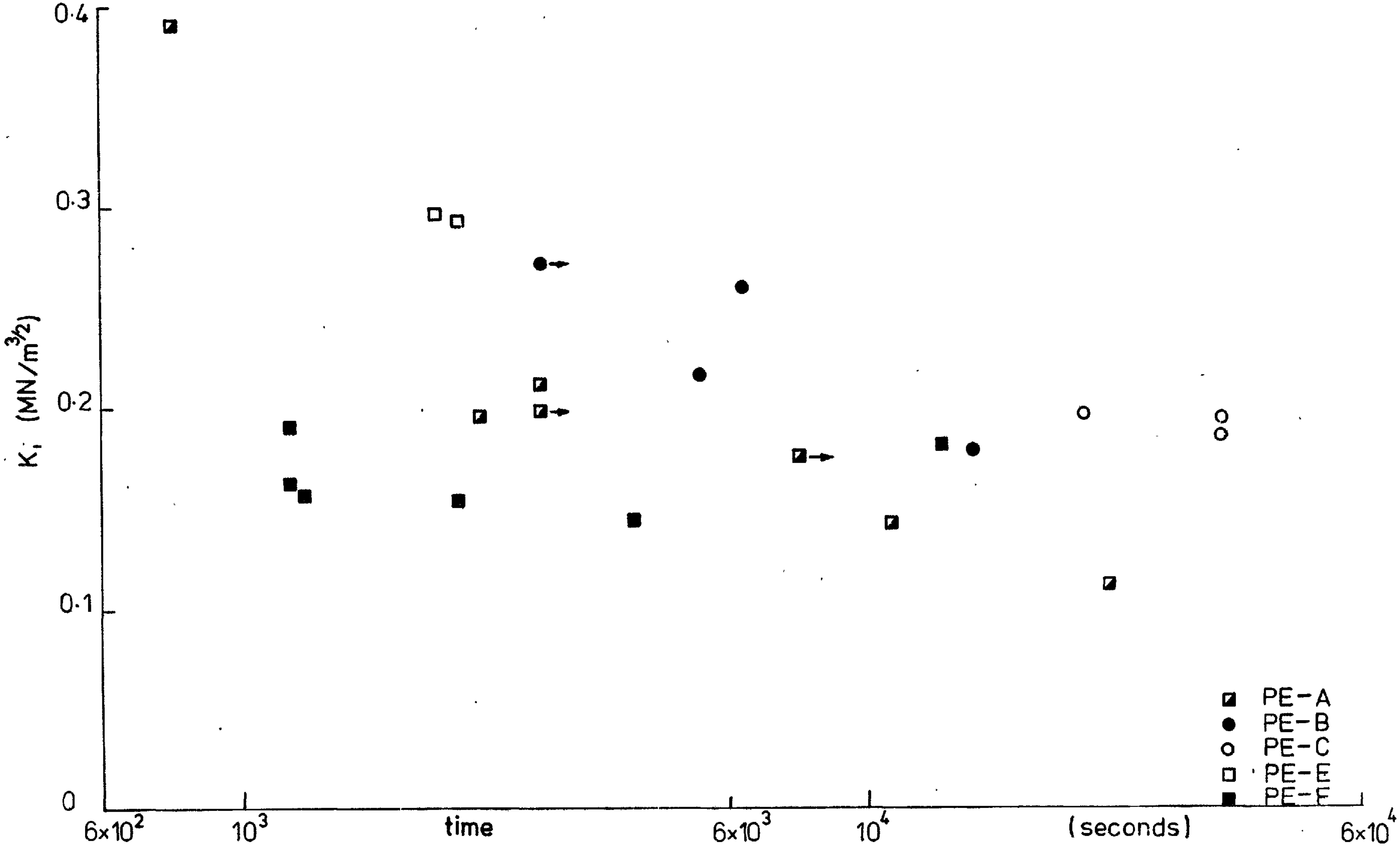
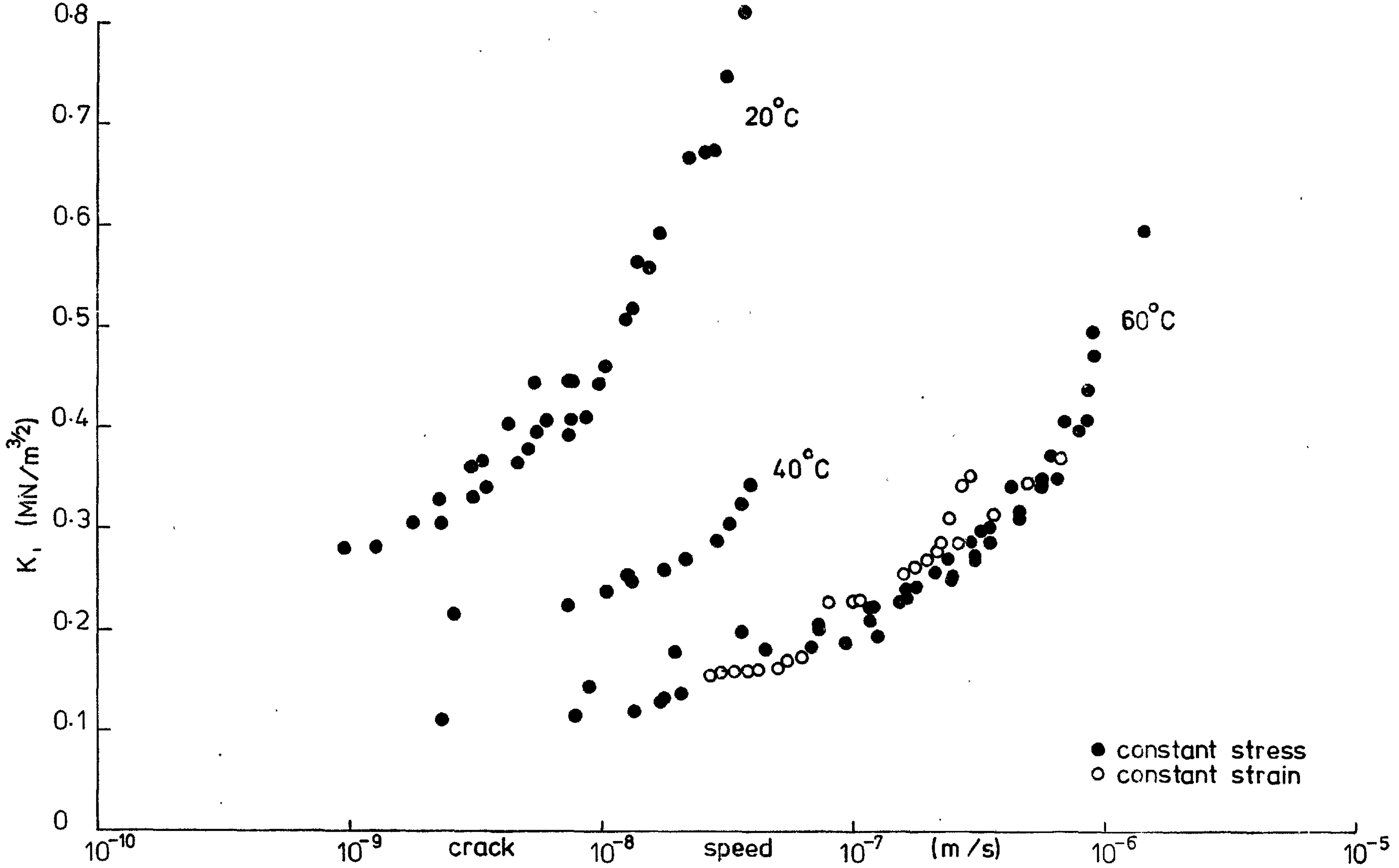

K, (MN/m$^{3/2}$)
0·5
0·4
0·2
0·1
0
10^4
time
10^5
(seconds)
10^6
CRACK INITIATION TIME at 20°C
◪ PE–A
□ PE–E
■ PE–F

FIGURE 19

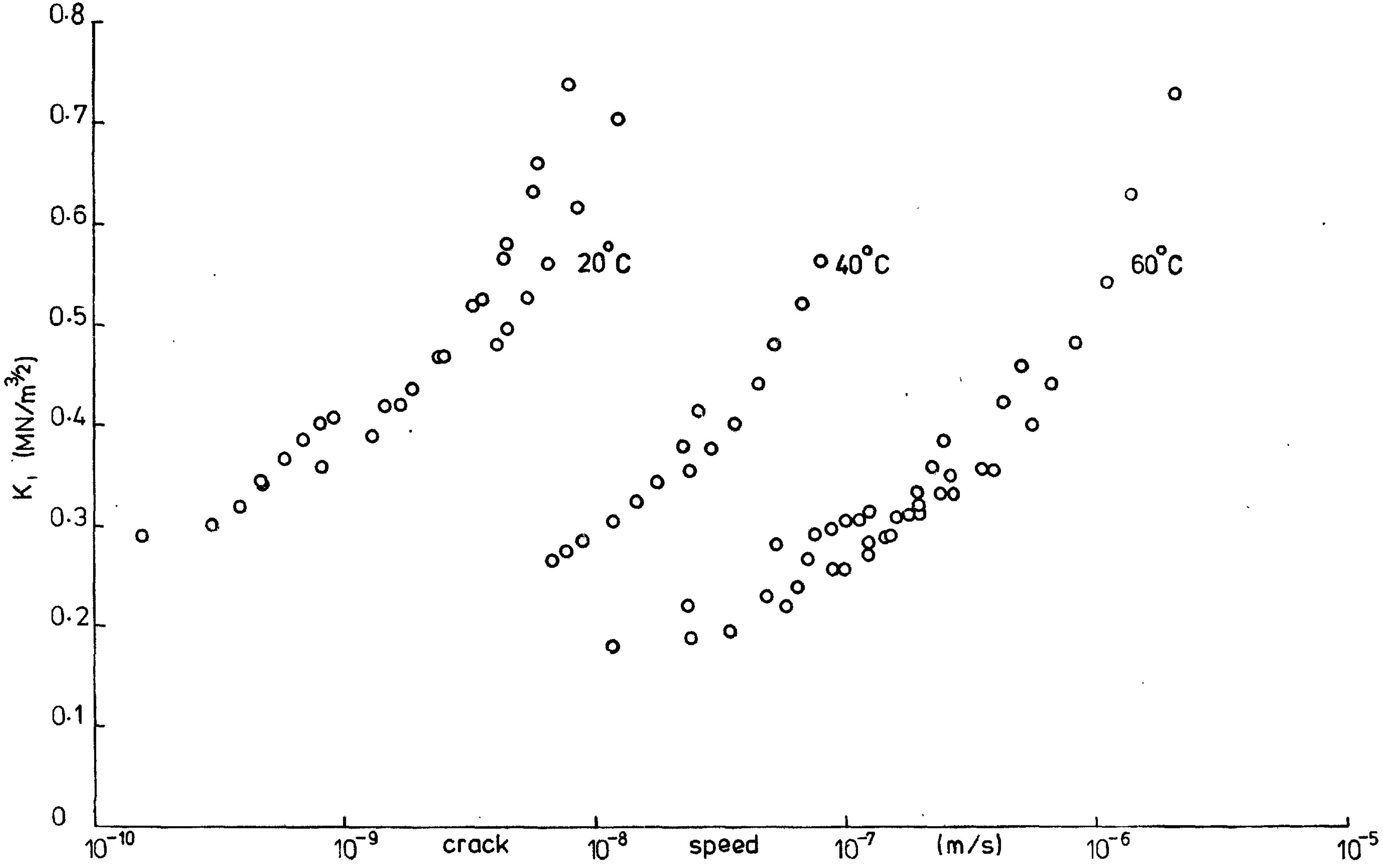


CRACK INITIATION TIMES at 60°C

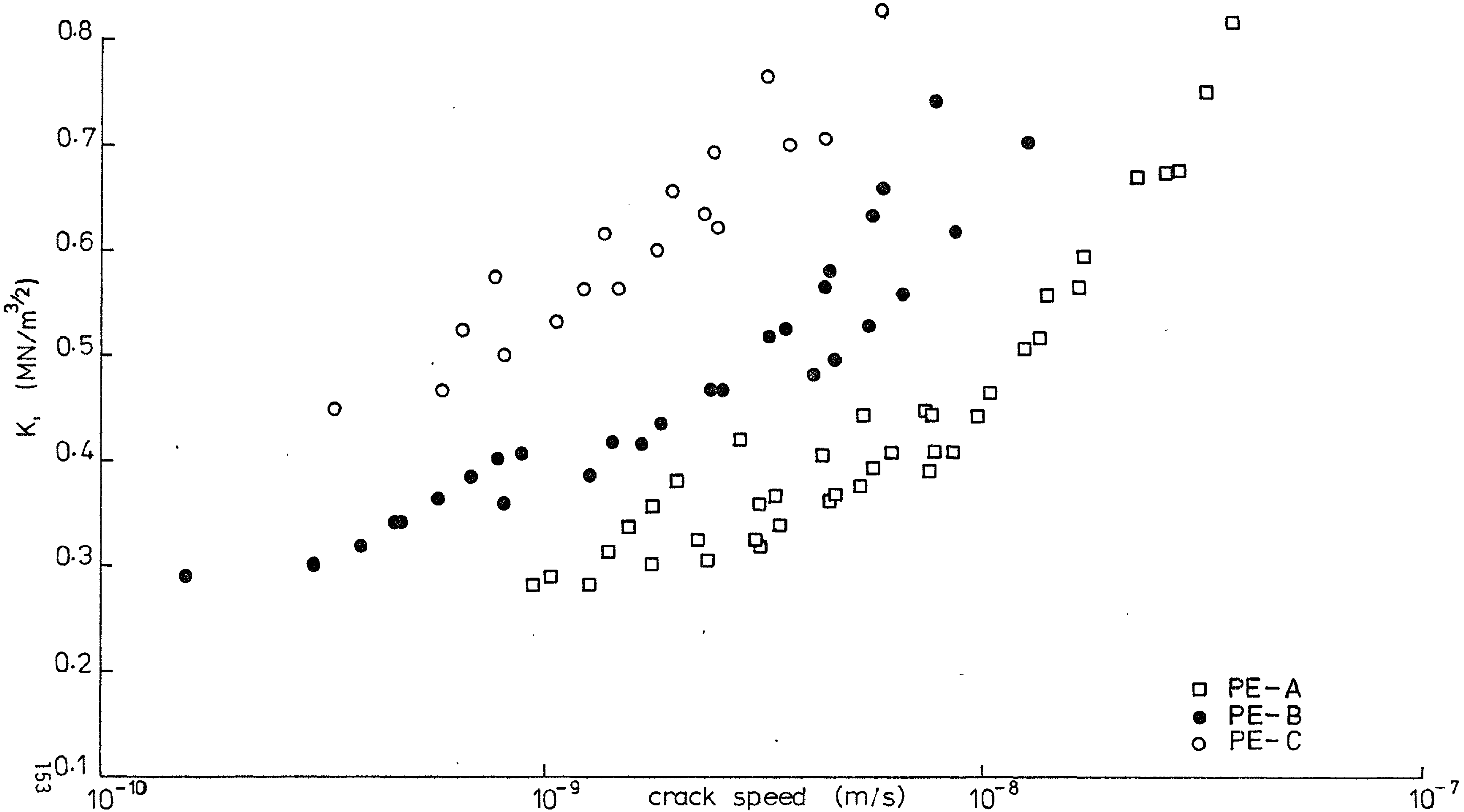
FIGURE 20



CONSTANT STRESS VERSUS CONSTANT STRAIN AND TEMPERATURE EFFECT PE-A in ADINOL FIGURE 21

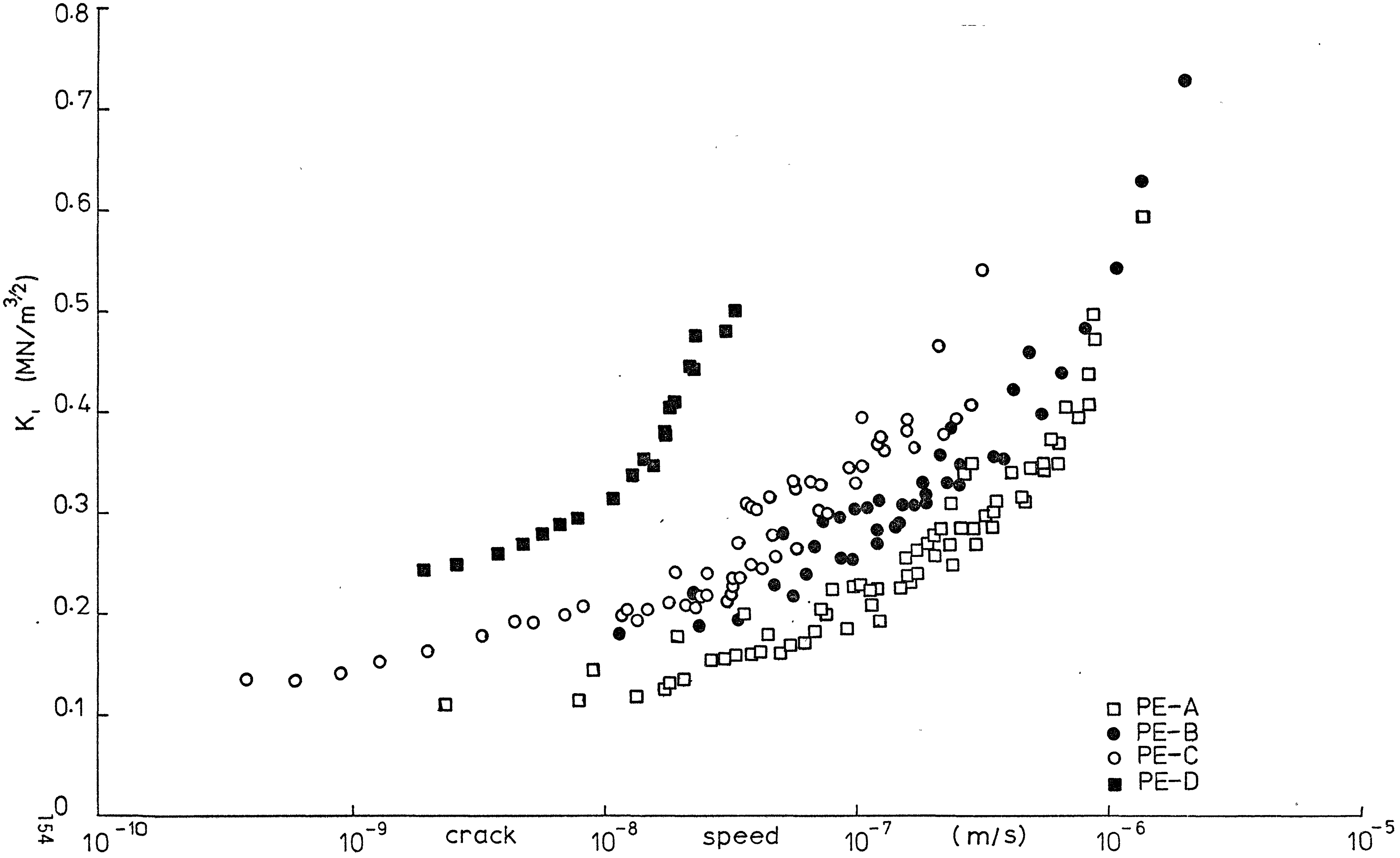


EFFECT OF TEST TEMPERATURE PE-B in ADINOL FIGURE 22

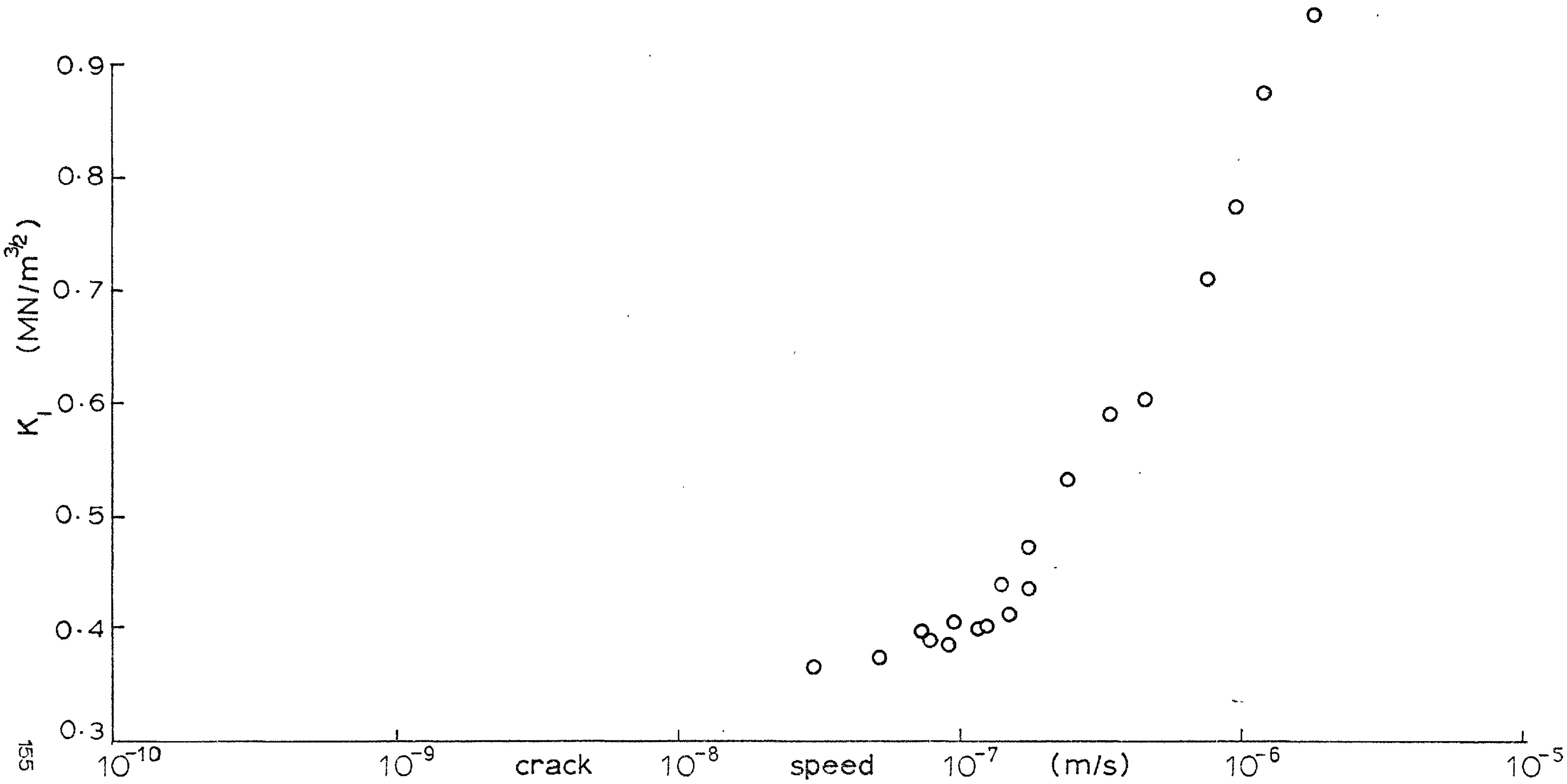


COMPARISON OF MATERIALS in ADINOL 20°C

FIGURE 23

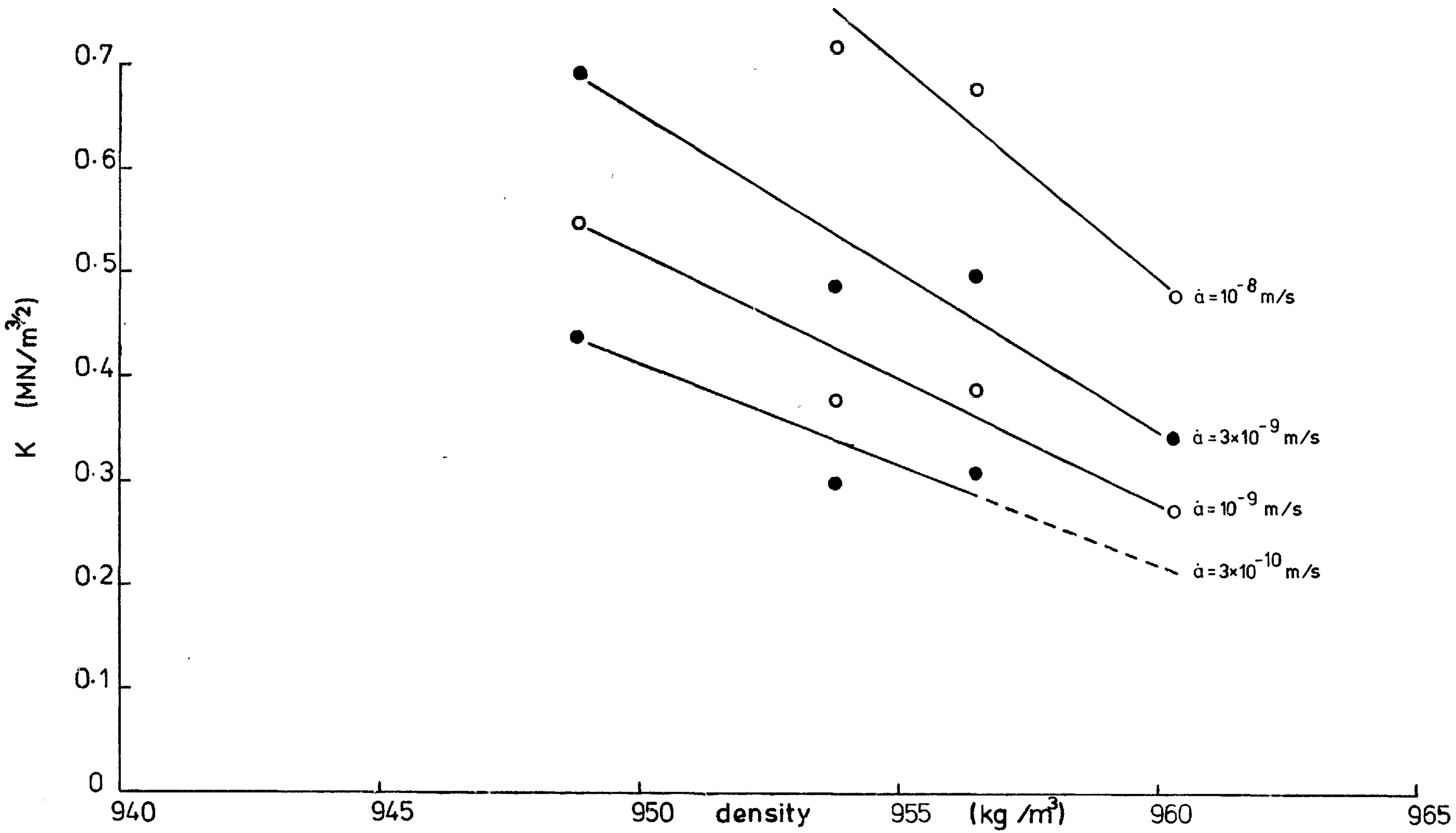


COMPARISON OF MATERIALS in ADINOL 60°C FIGURE 24

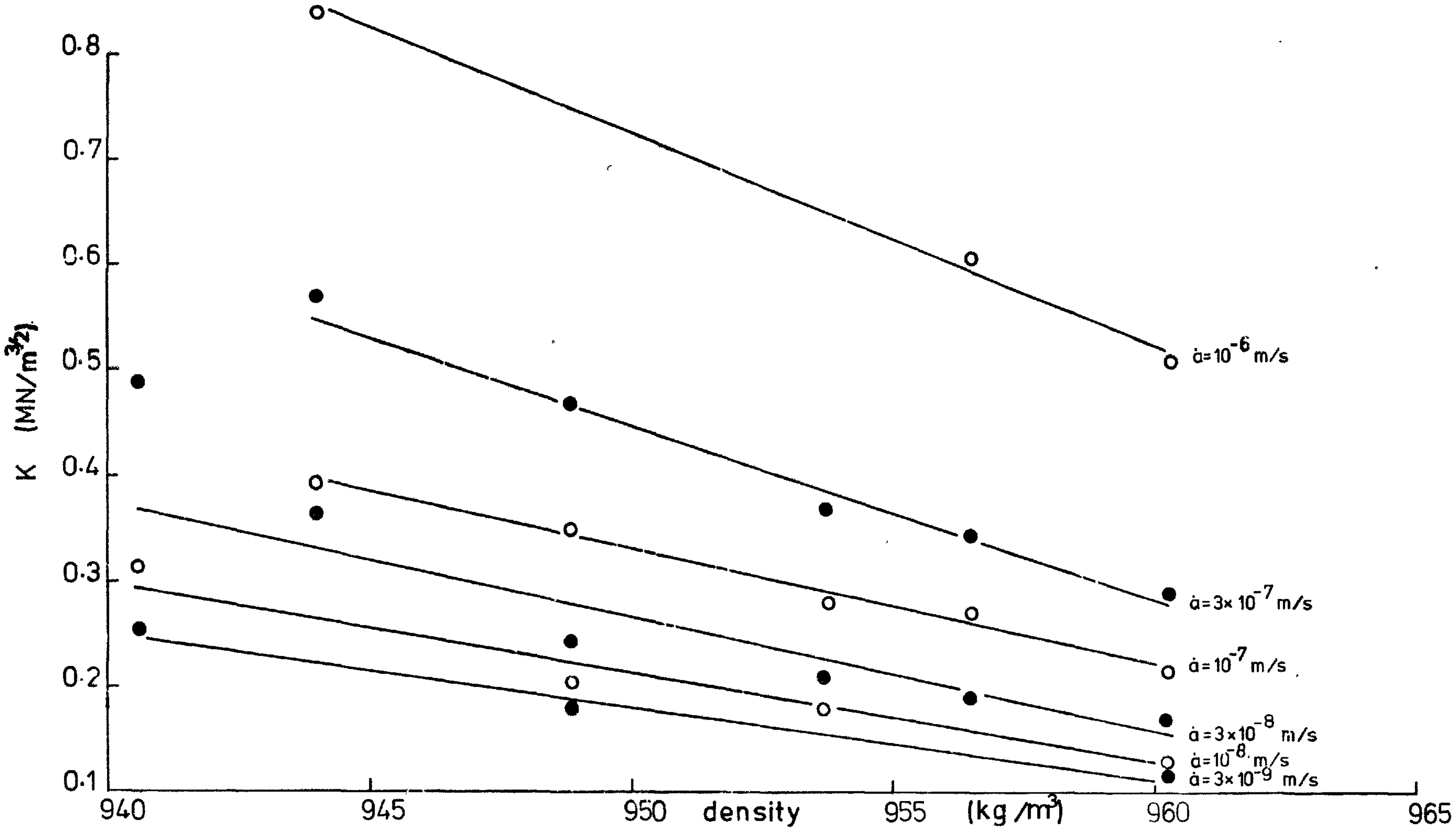


CRACKING OF PE-H 60°C in ADINOL

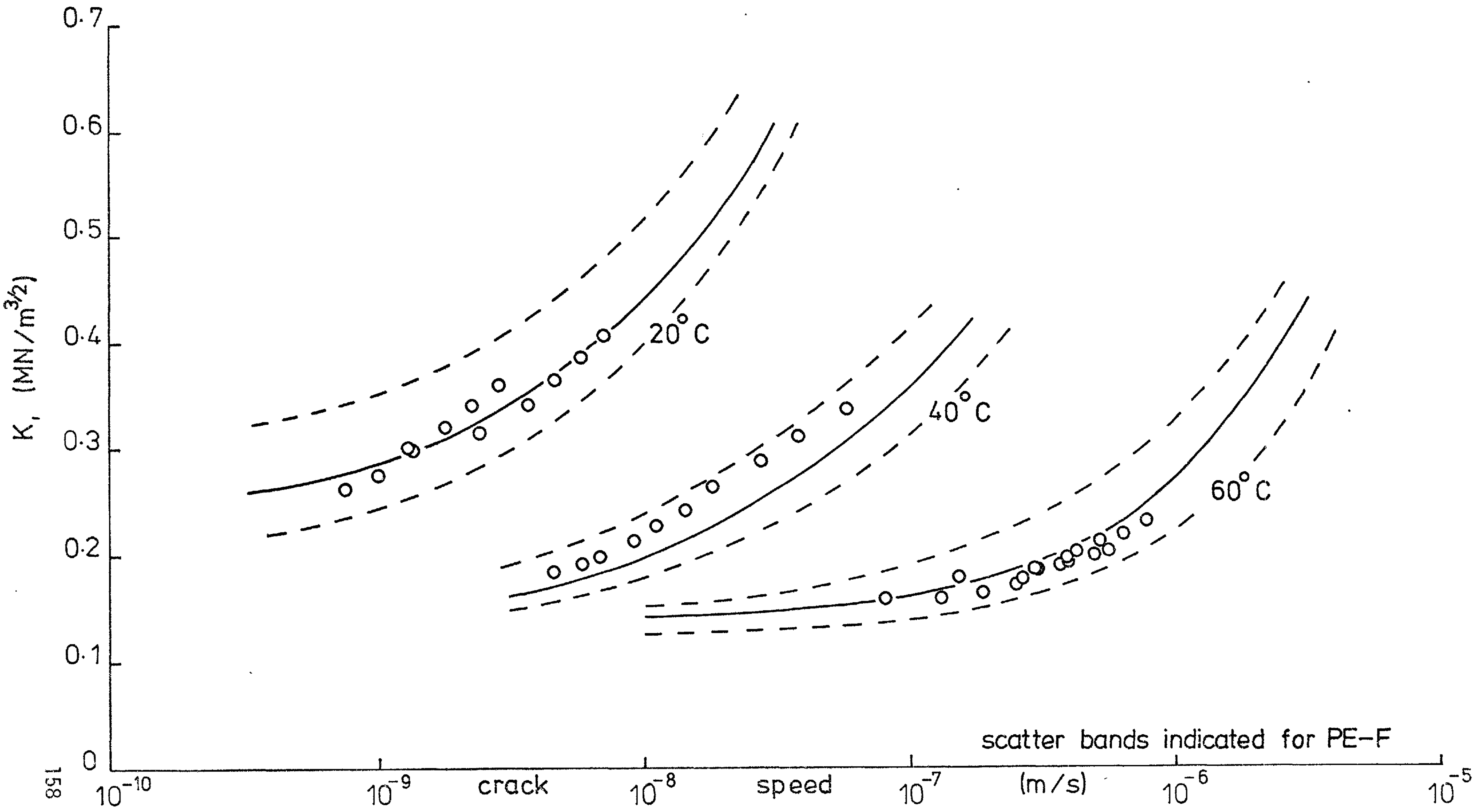
FIGURE 25



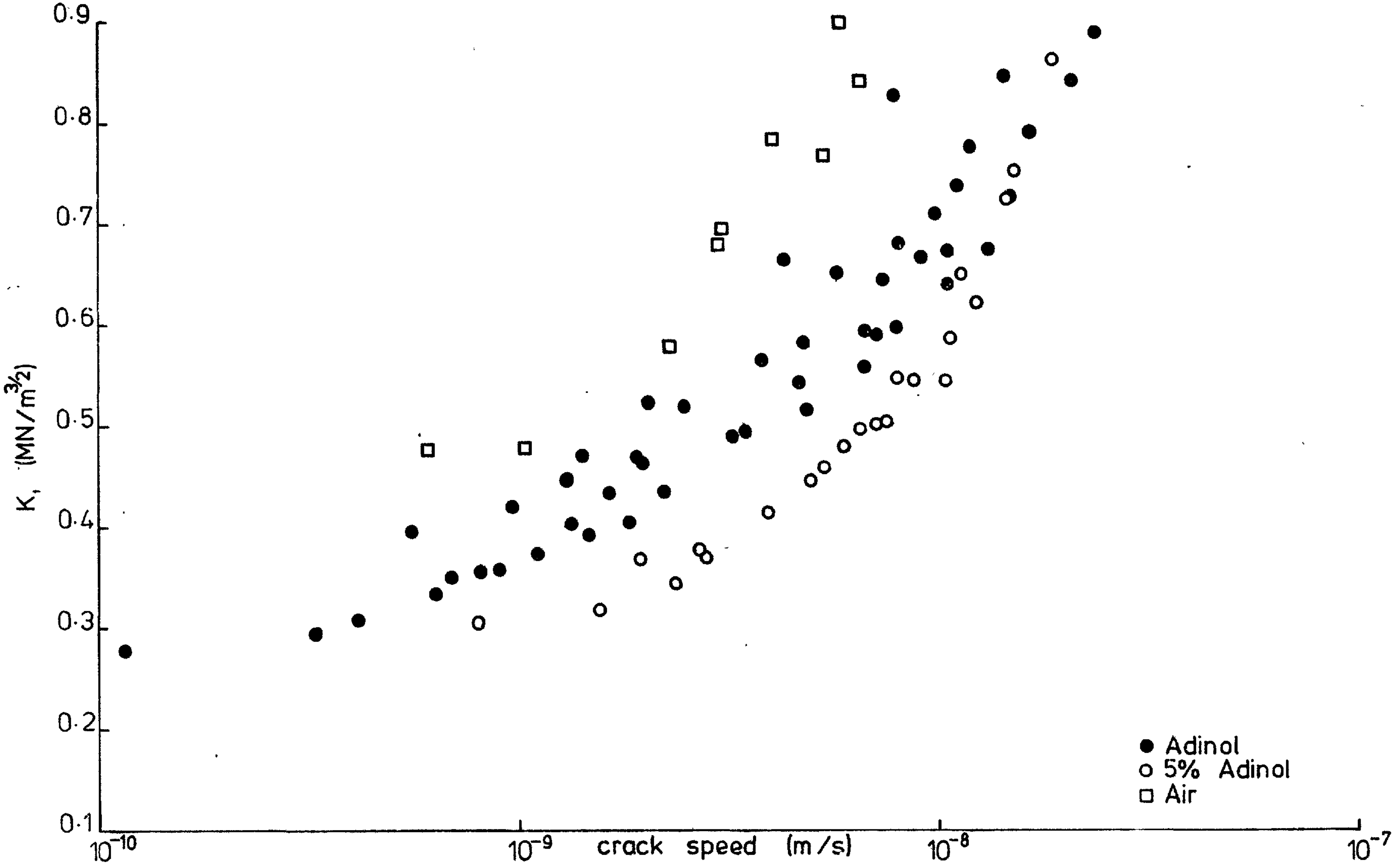
COMPARISON OF CRACKING OF COPOLYMERS IN ADINOL AT 20°C FIGURE 26



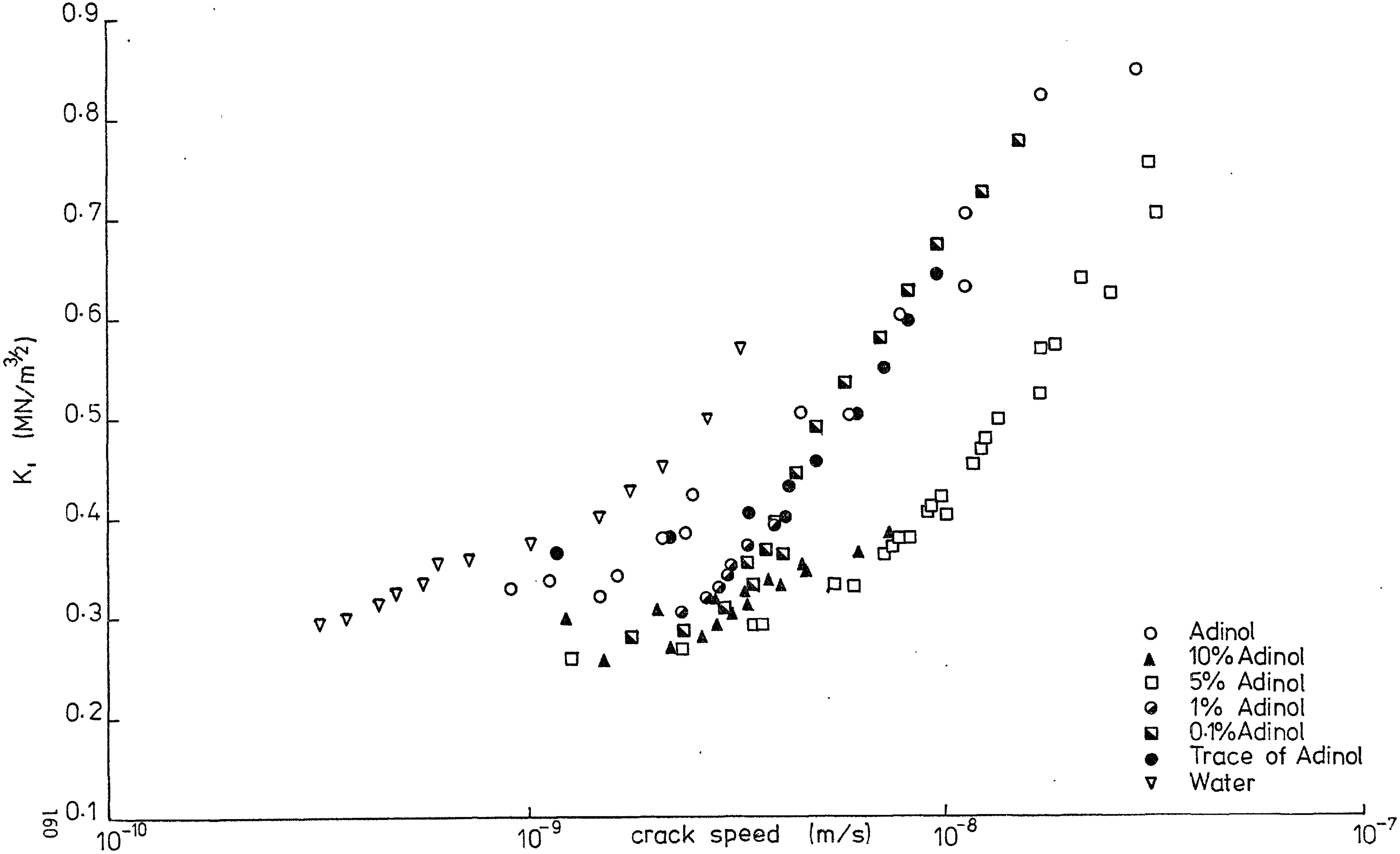
COMPARISON OF CRACKING OF COPOLYMERS IN ADINOL AT 60°C FIGURE 27



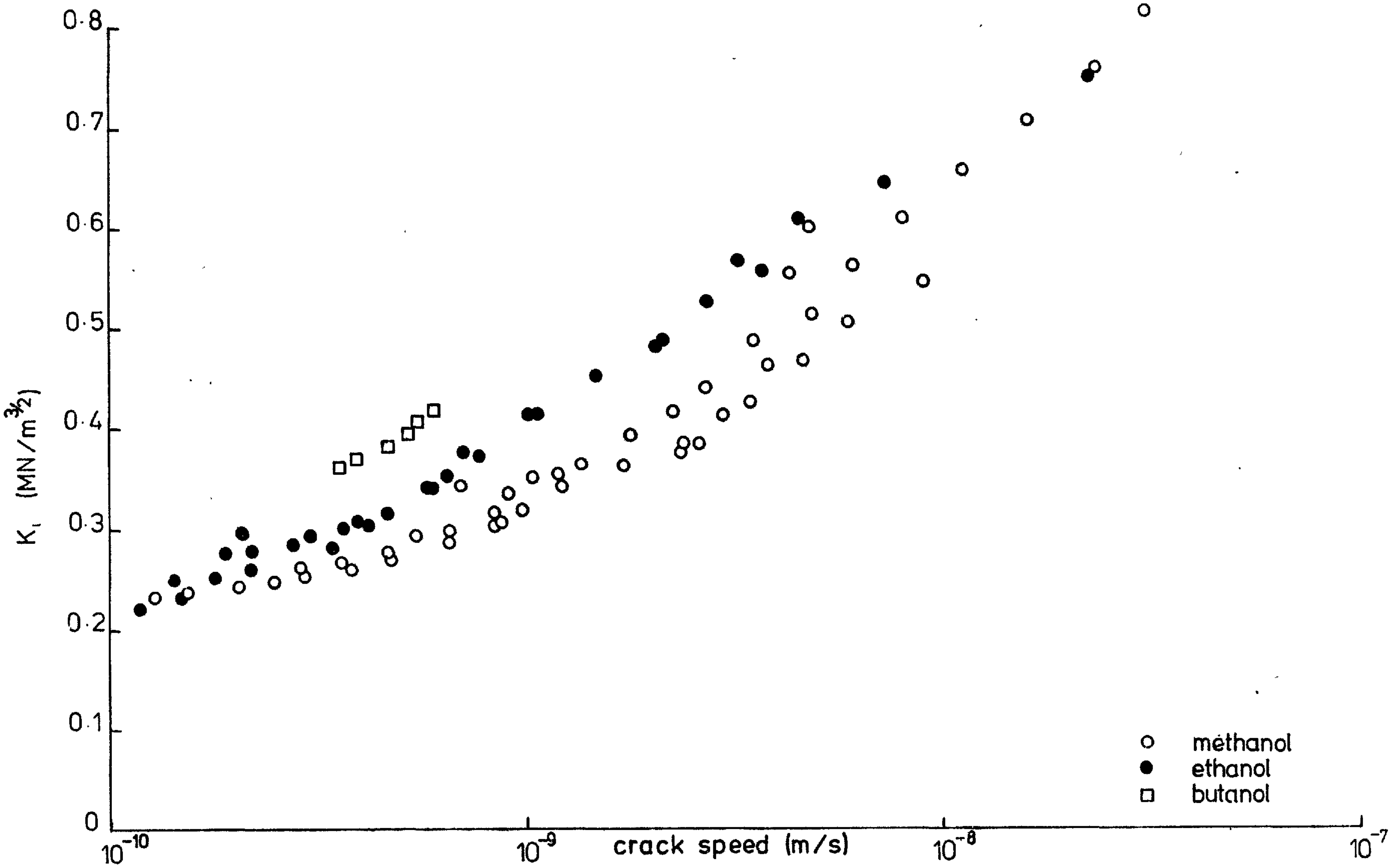
COMPARISON OF PE-G WITH PE-F in ADINOL FIGURE 28



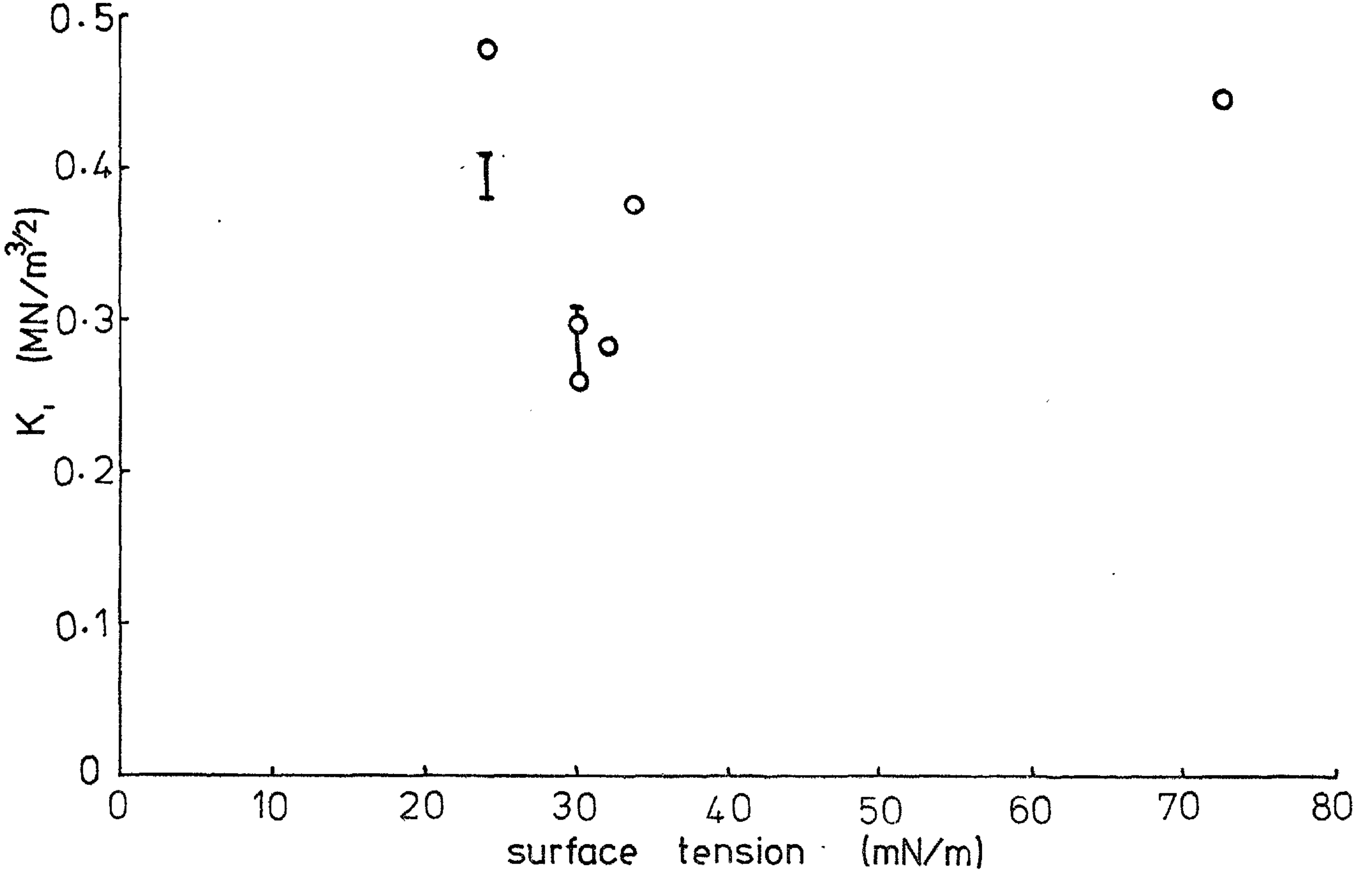
COMPARISON OF CRACK GROWTH IN DIFFERENT ENVIRONMENTS PE-E 20°C FIGURE 29



CRACKING IN DILUTIONS OF ADINOL PE–A 20° C FIGURE 30

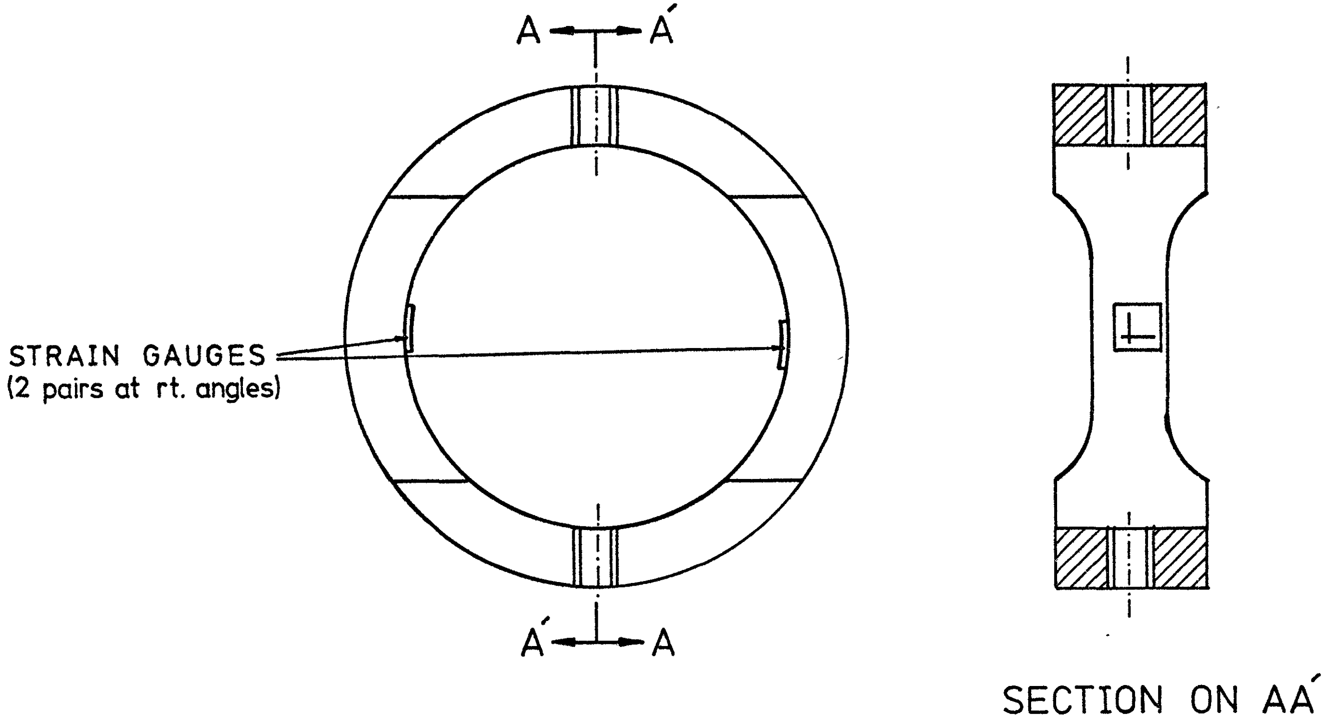


COMPARISON OF ALCOHOL ENVIRONMENTS PE-A 20°C FIGURE 31

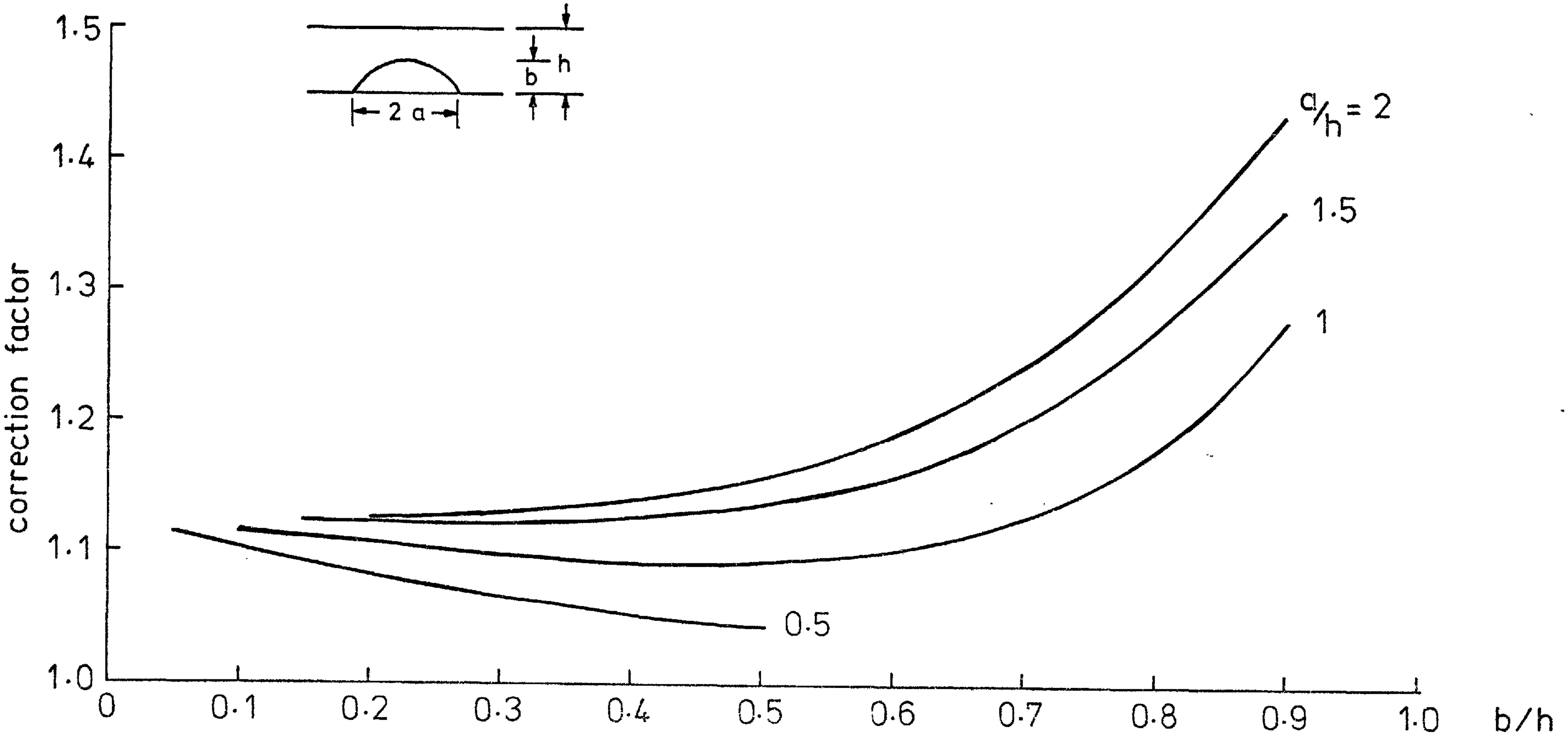


ENVIRONMENT SURFACE TENSION EFFECT PE–A 20°C 2×10^{-9} m/s FIGURE 32

FIGURE 33 CONSTANT STRAIN TEST APPARATUS

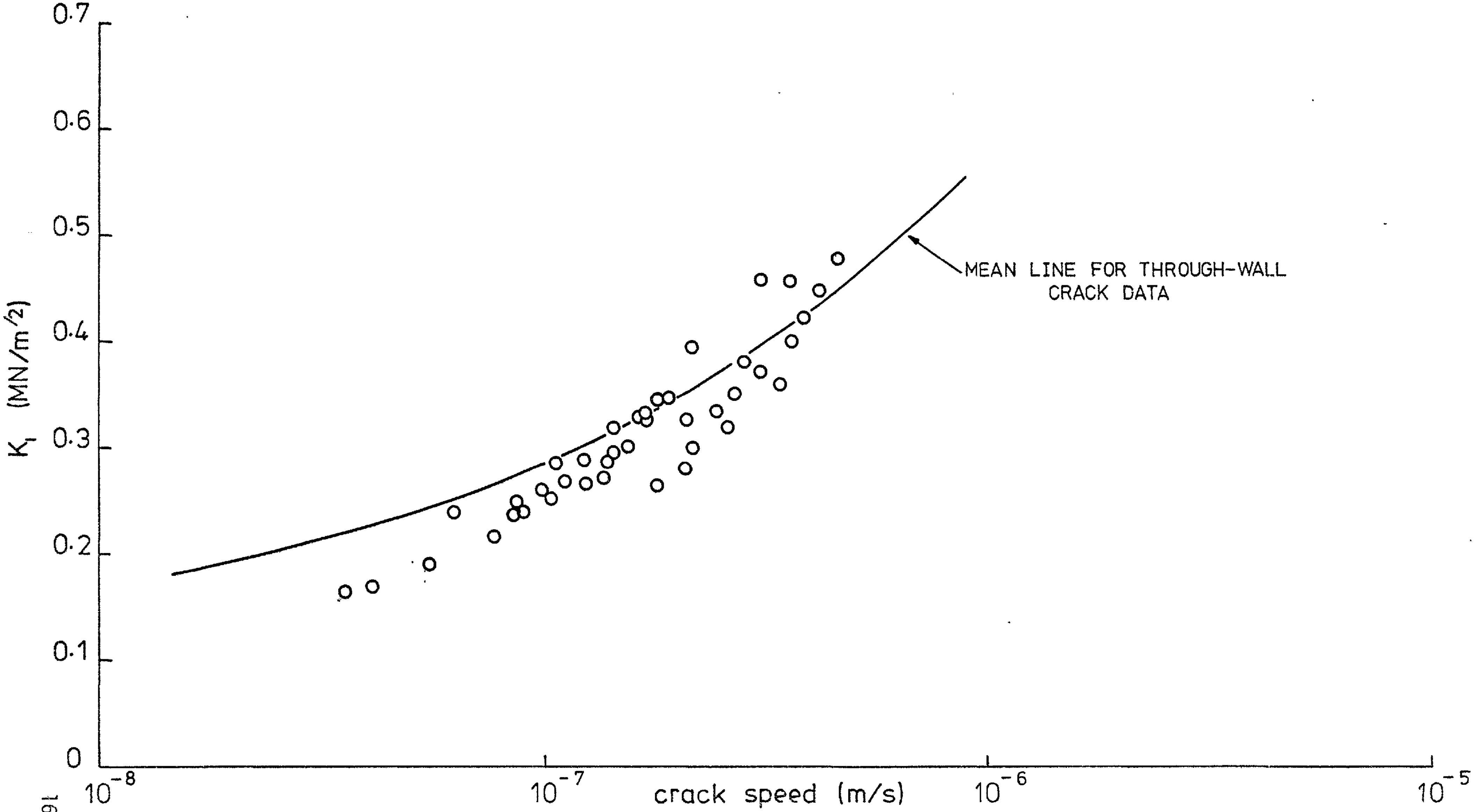


ALUMINIUM RING FOR LOAD DETERMINATION IN CONSTANT STRAIN TESTS FIGURE 34

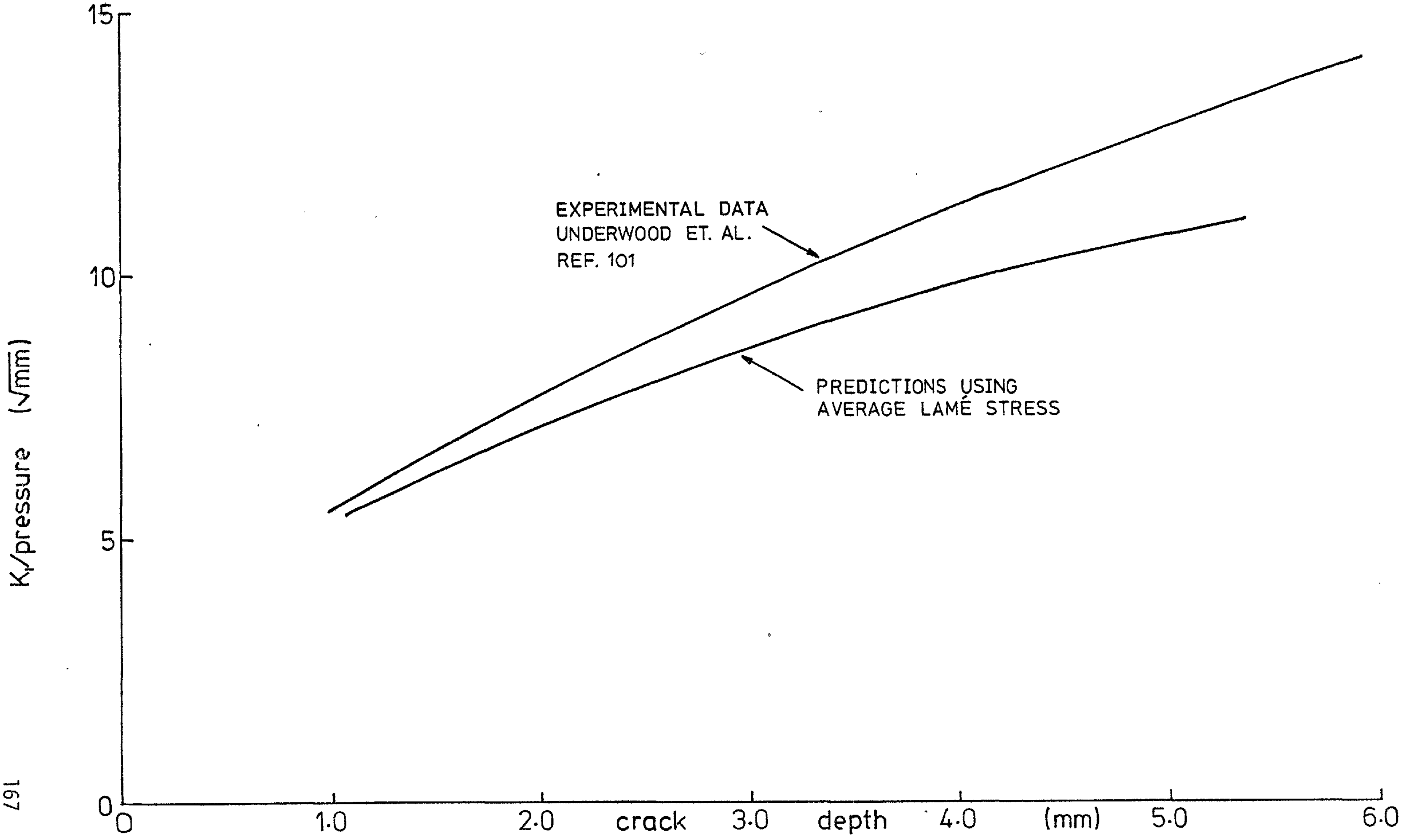


SHAH AND KOBAYASHI CORRECTION FACTOR

FIGURE 35



SURFACE NOTCHED PLATE RESULTS PE-B in Adinol at 20°C FIGURE 36



LONGITUDINAL CRACK IN INTERNAL PIPE WALL FIGURE 37

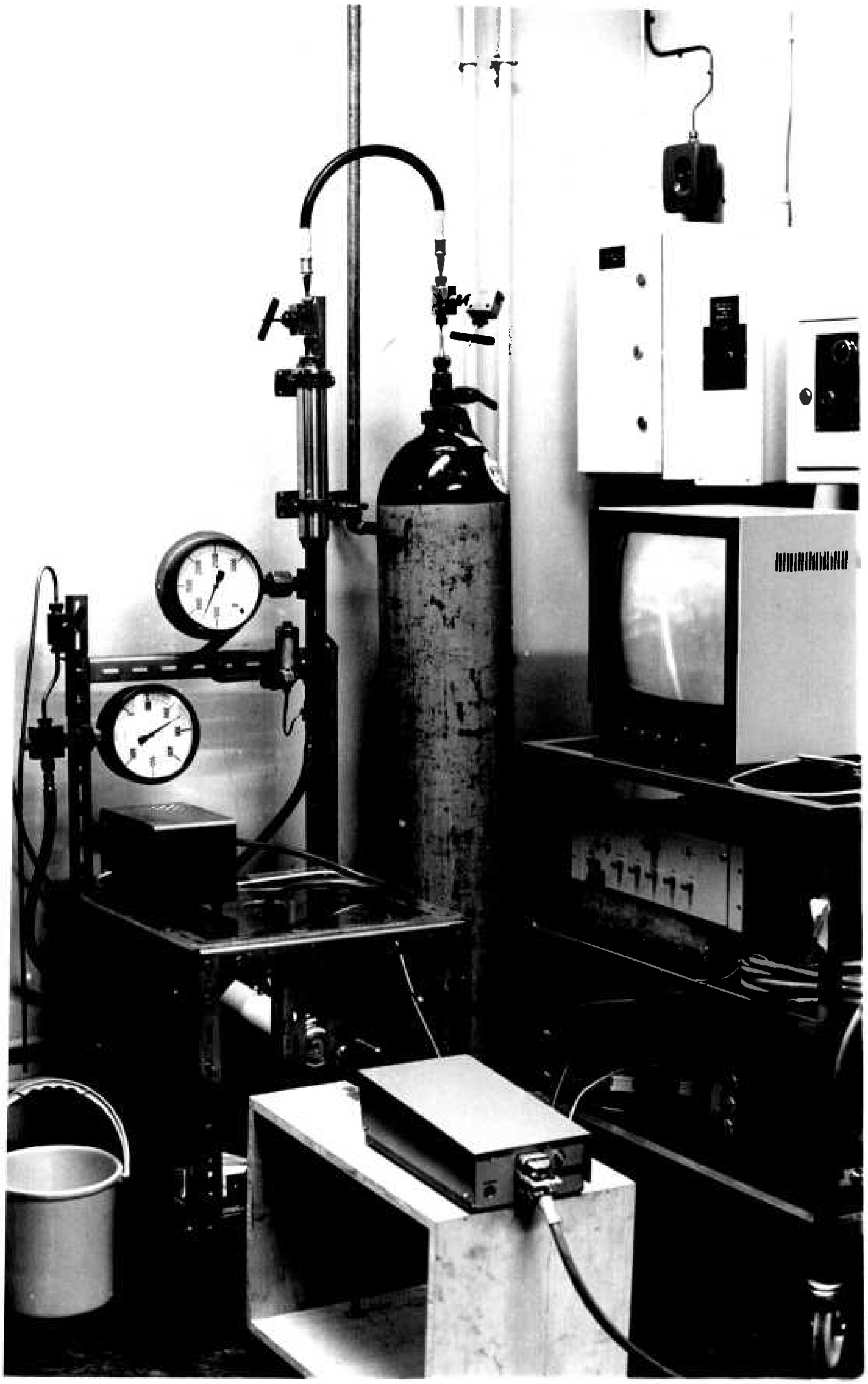
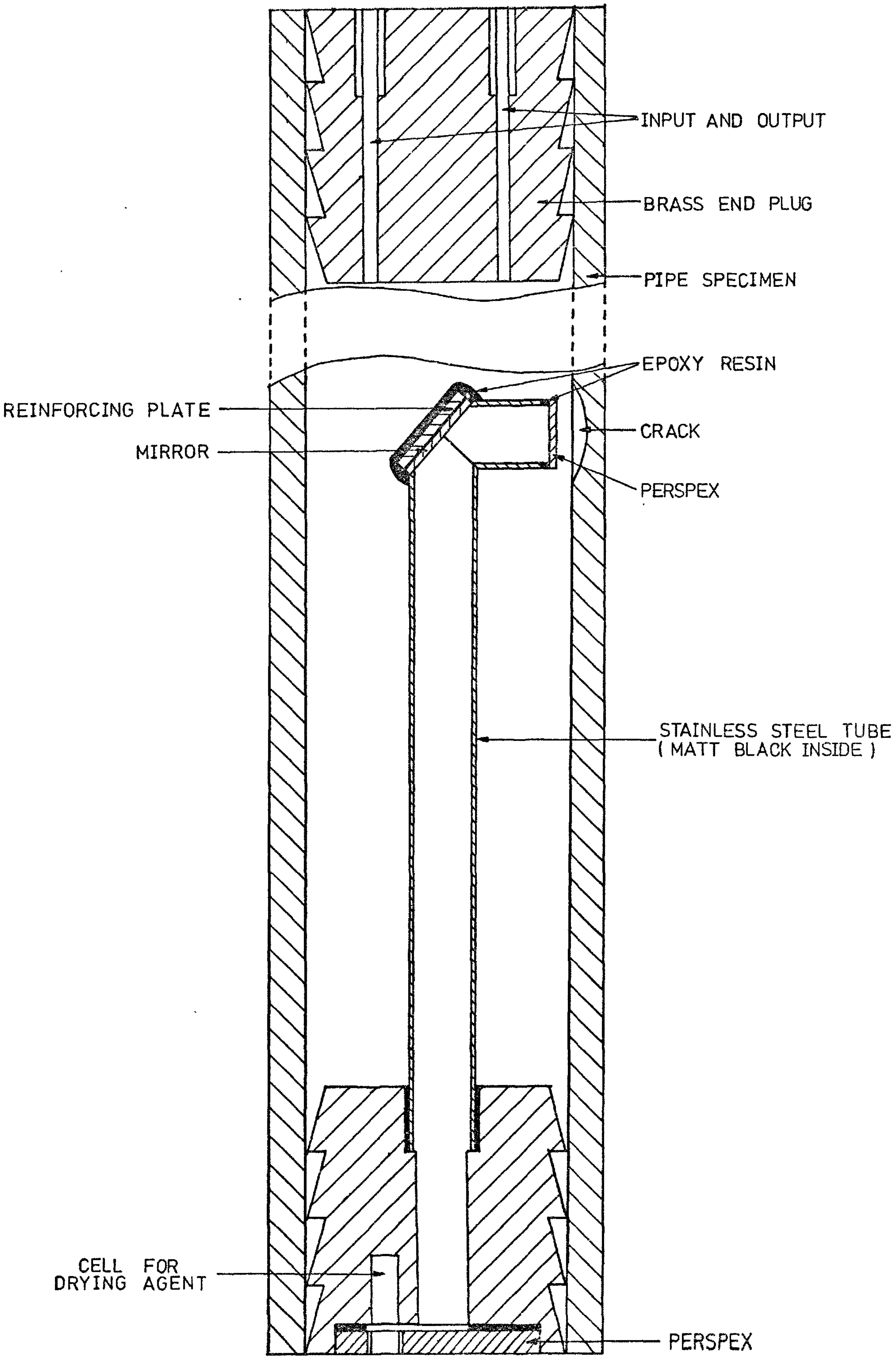


FIGURE 38 PIPE TEST RIG



PIPE TEST APPARATUS

FIGURE 39

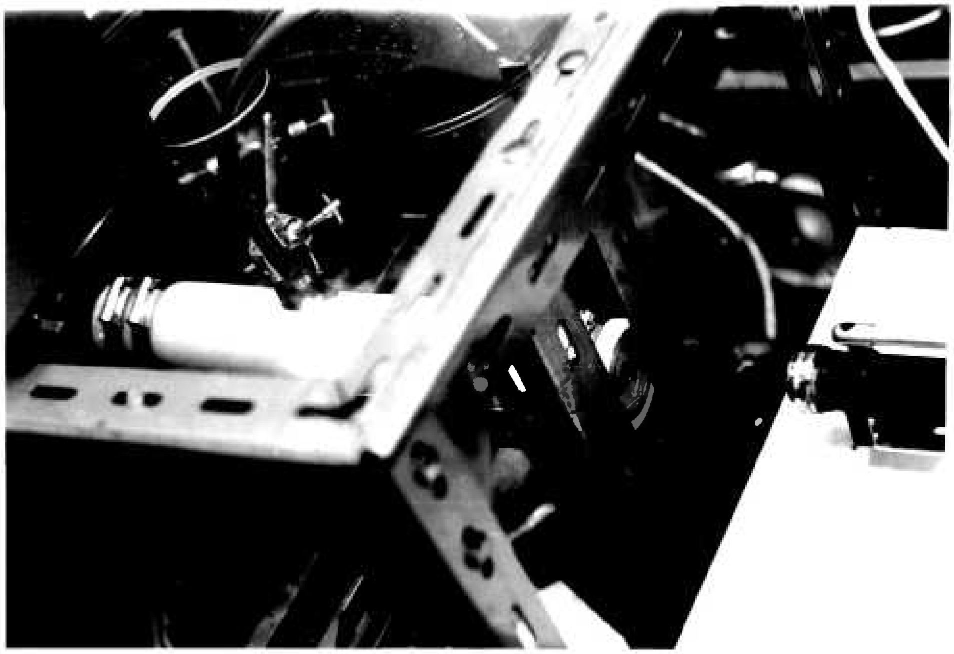


FIGURE 40 PIPE TEST SPECIMEN ON RIG

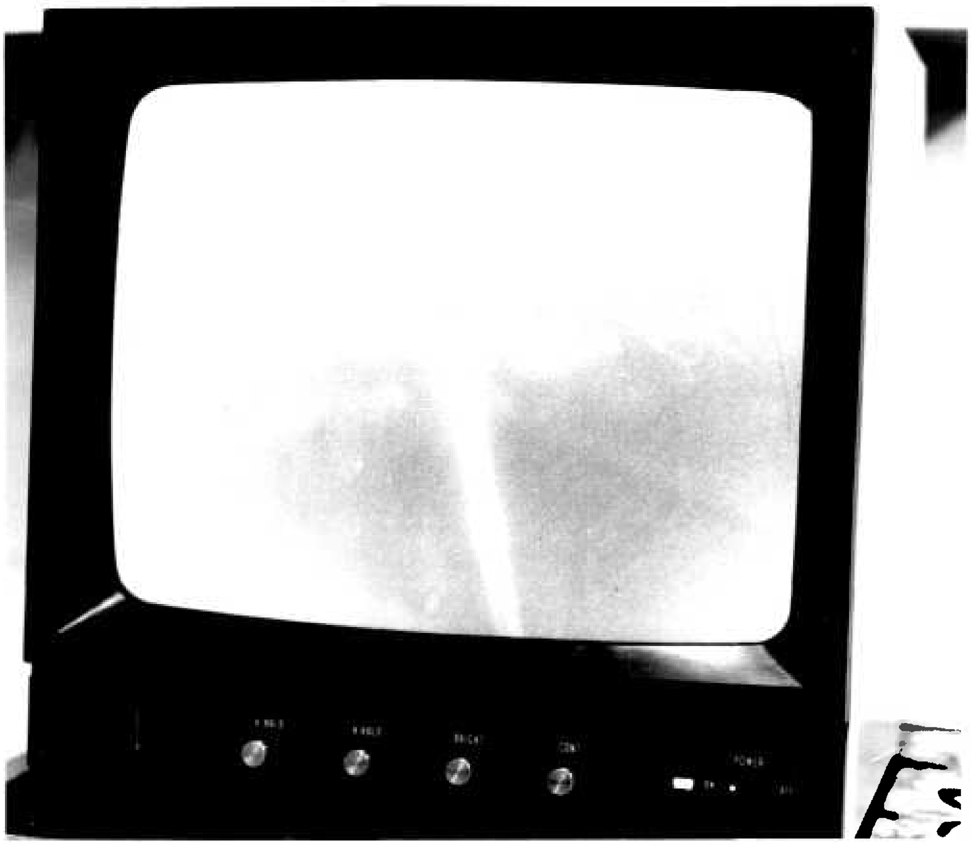
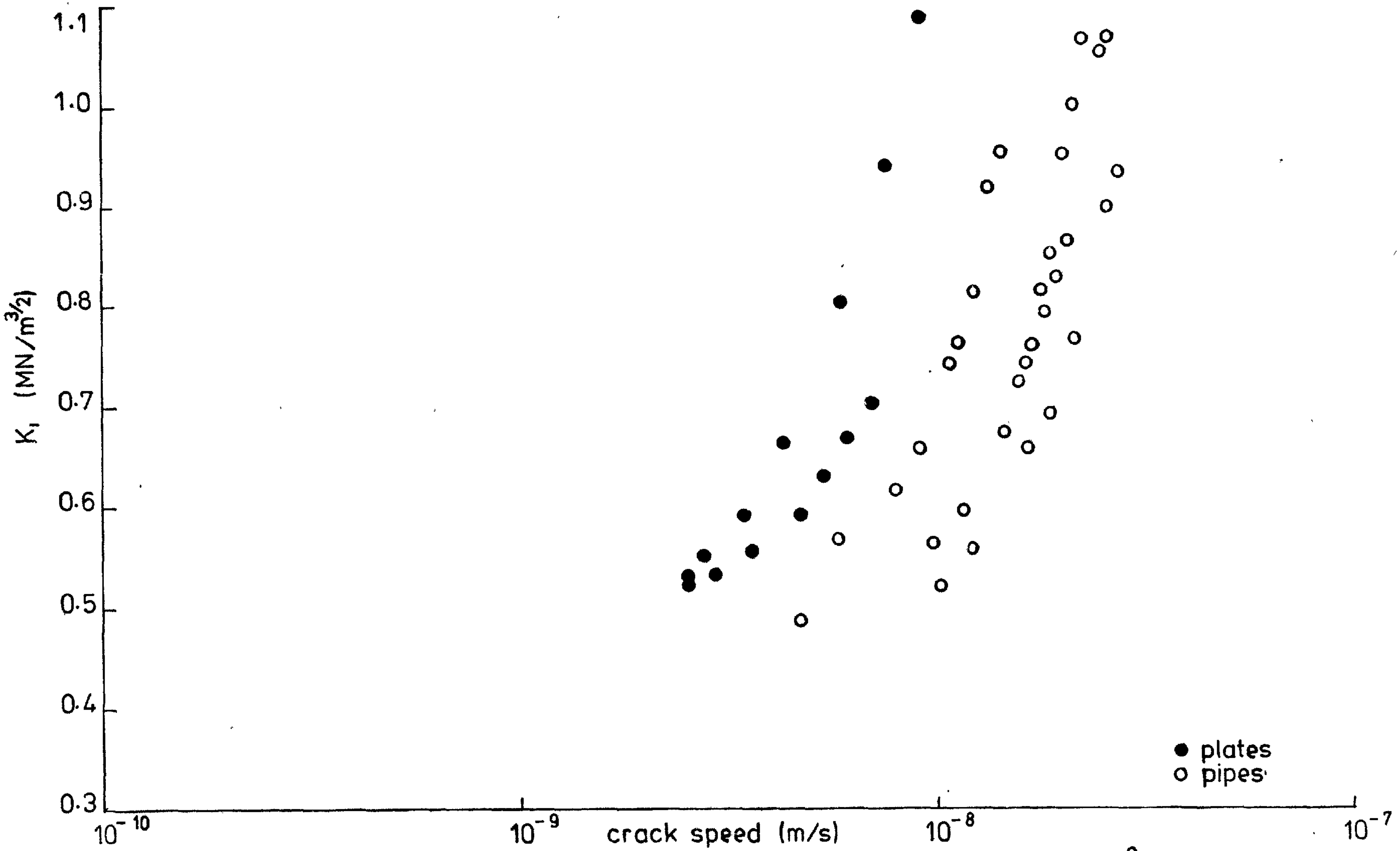
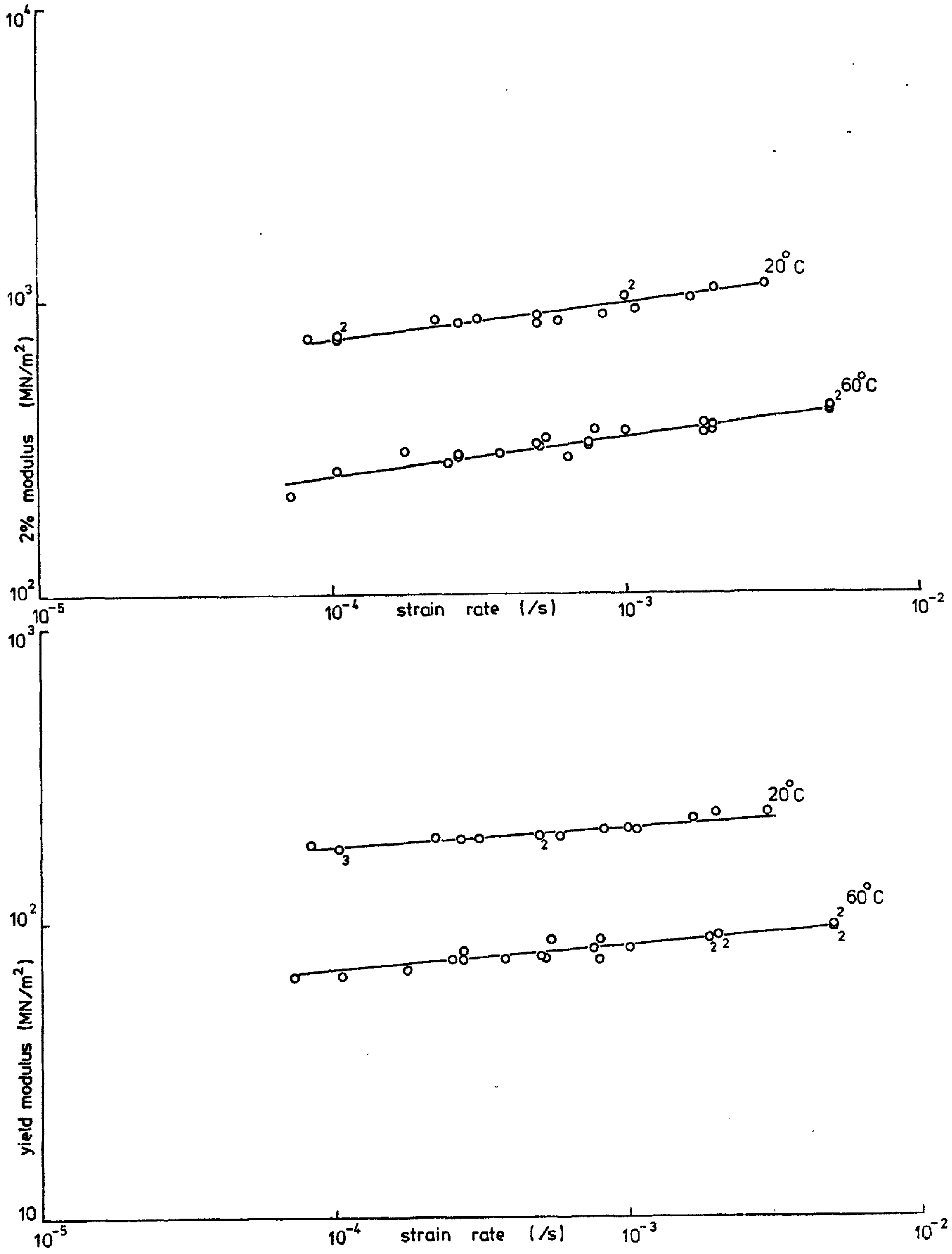


FIGURE 41 T.V. MONITOR SHOWING TYPICAL CRACK

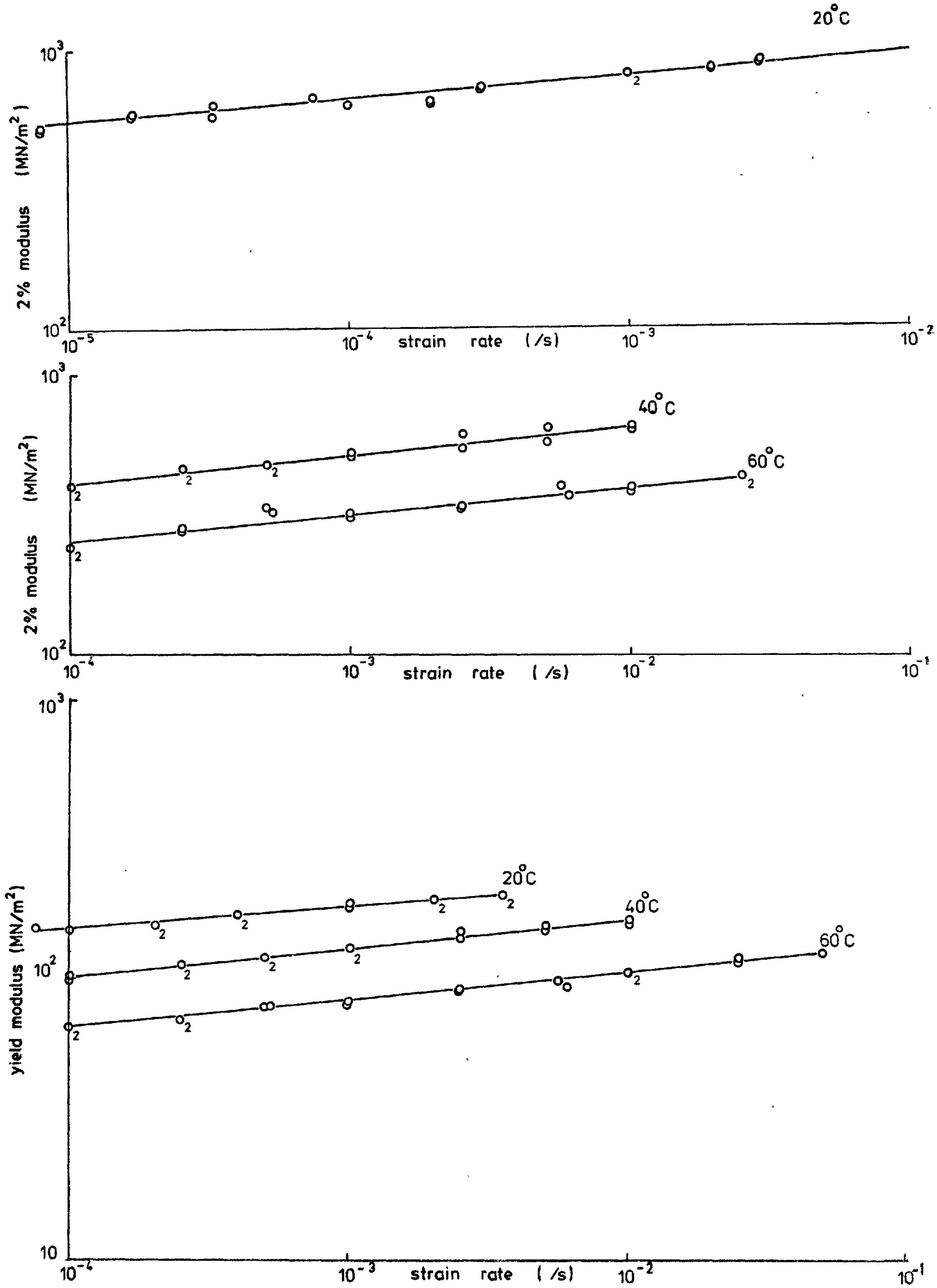


CRACK GROWTH THROUGH PIPE WALL in Water at 20°C FIGURE 42

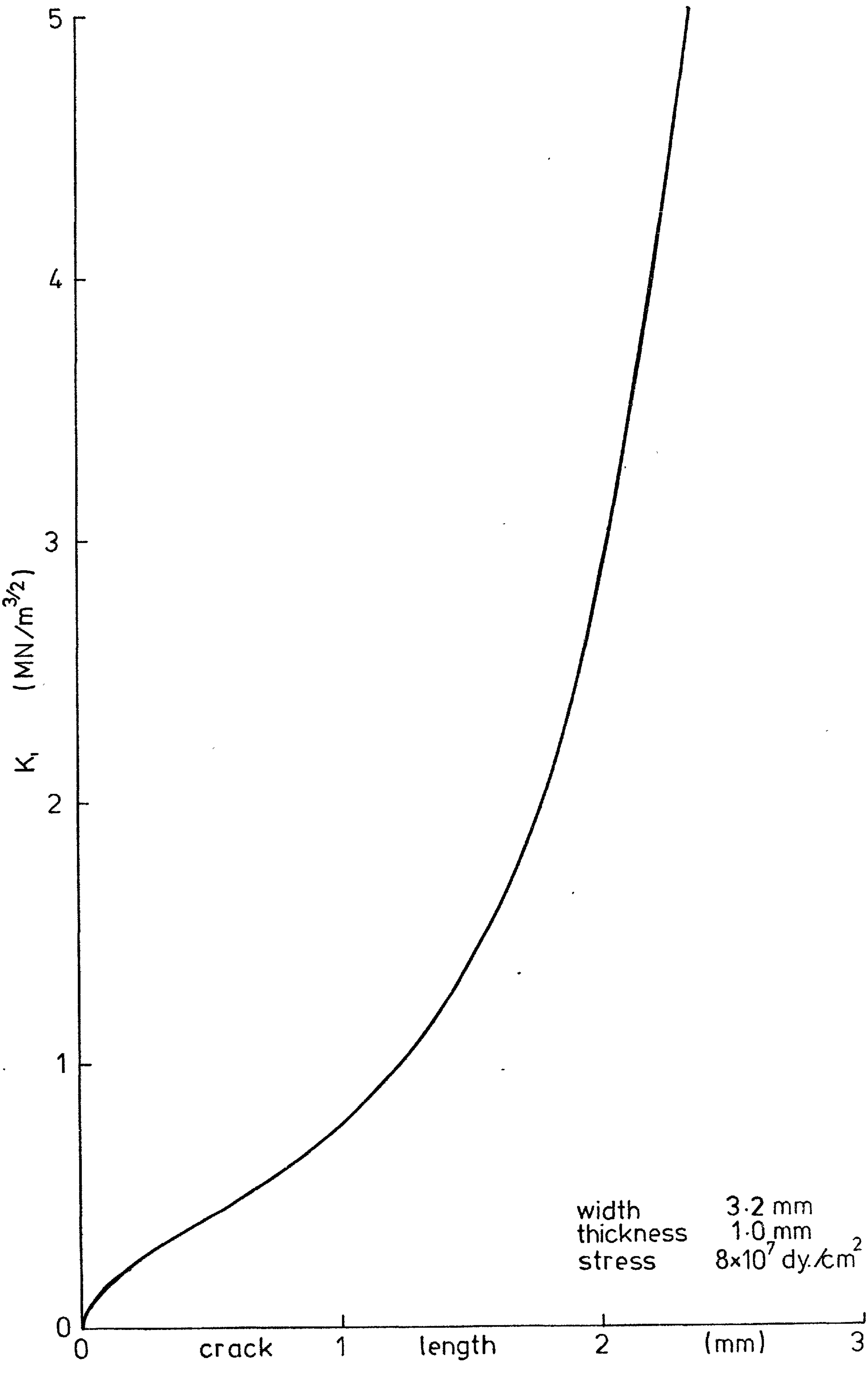
FIGURE 43 INSTRON TESTING MACHINE AND STRAIN MEASURING APPARATUS FOR MODULUS DETERMINATIONS.



MODULUS DATA PE-A FIGURE 44

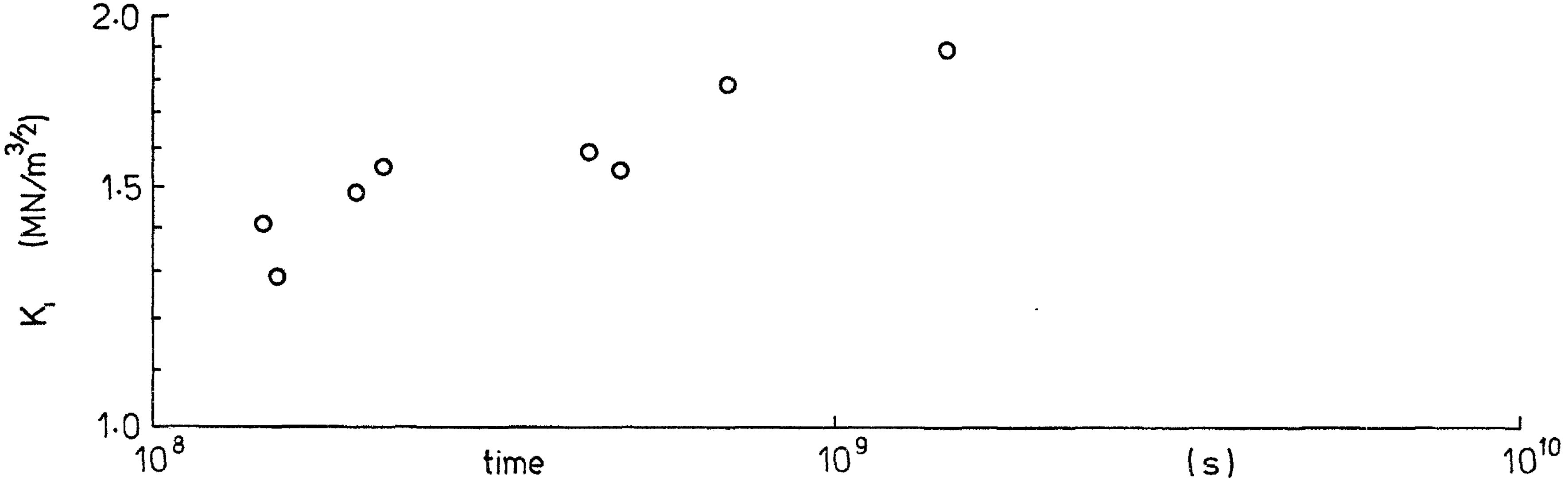


MODULUS DATA PE-B FIGURE 45



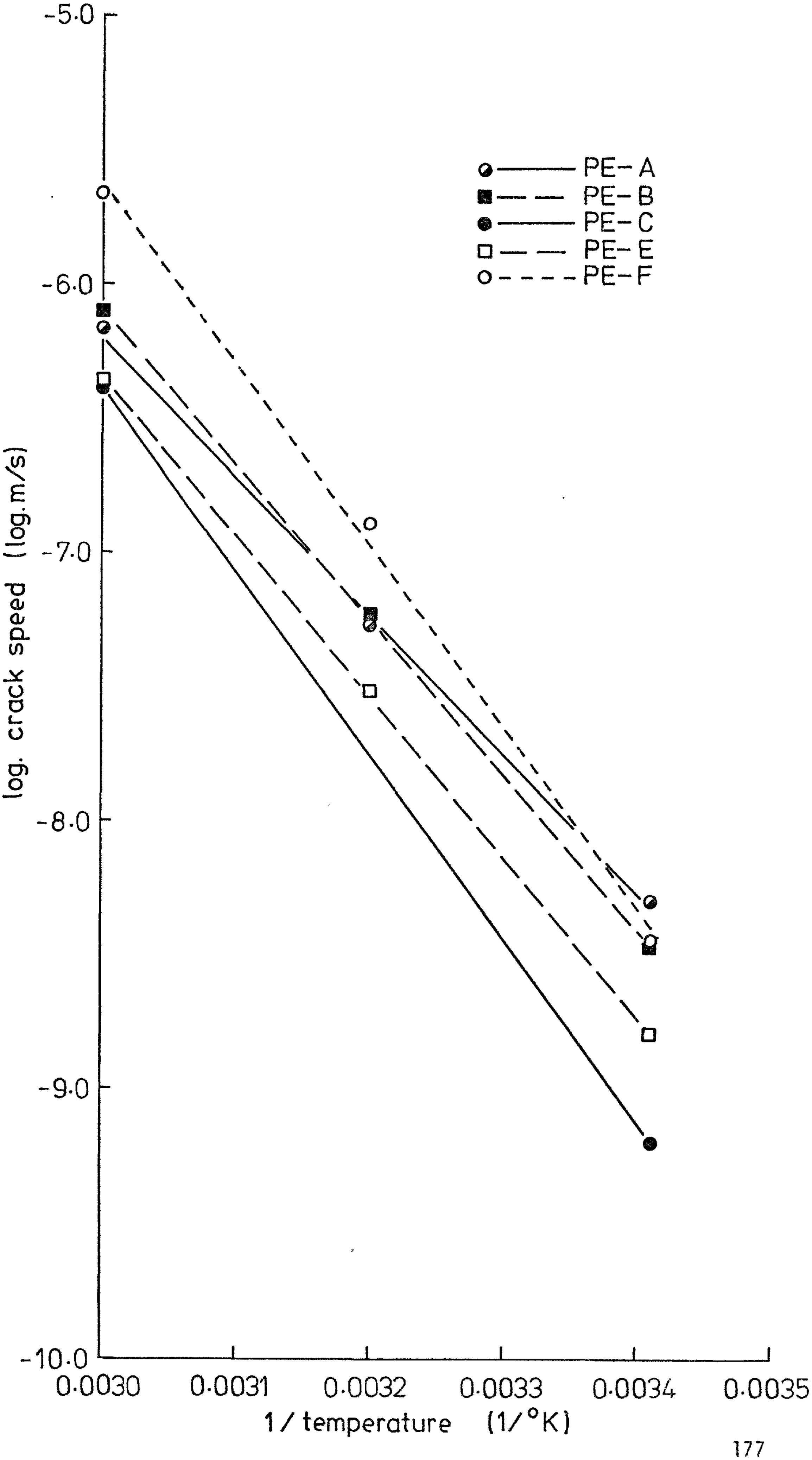
ASTM D 2552 (LANDER) SPECIMEN ASSUMING SEN GEOMETRY

FIGURE 46



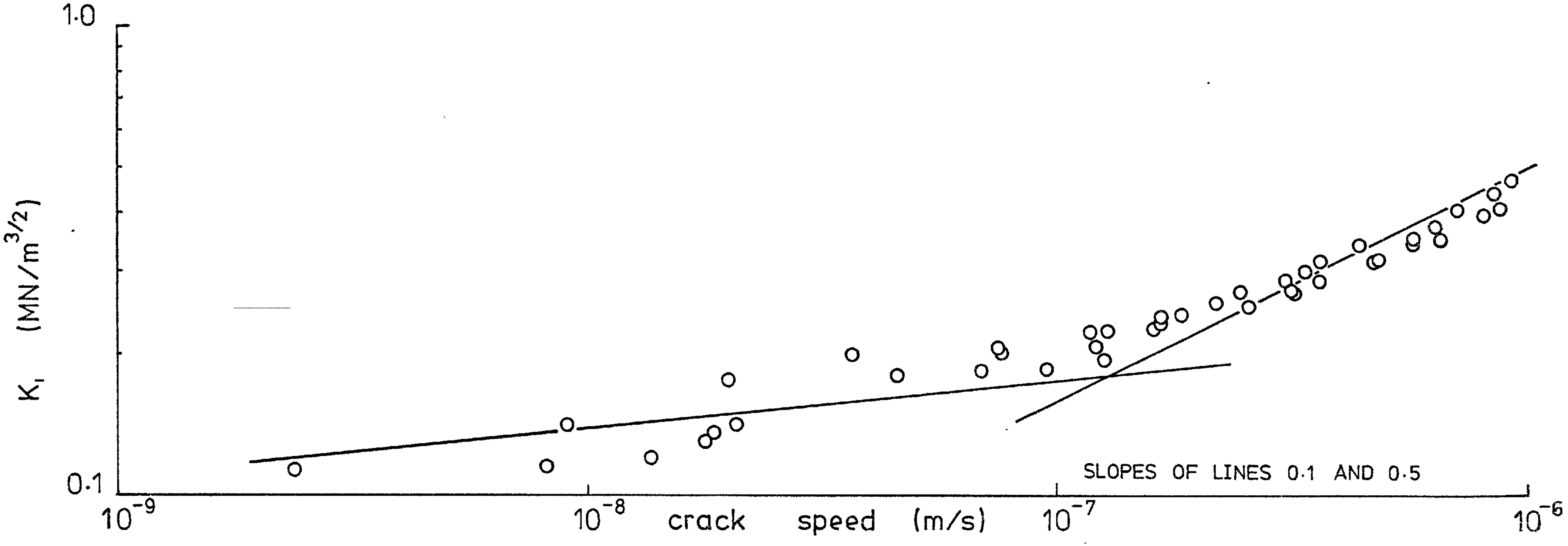
OCCURRENCE OF VISIBLE YIELDING AT THE EDGES OF SPECIMENS PE-E 20°C in TEEPOL

FIGURE 47



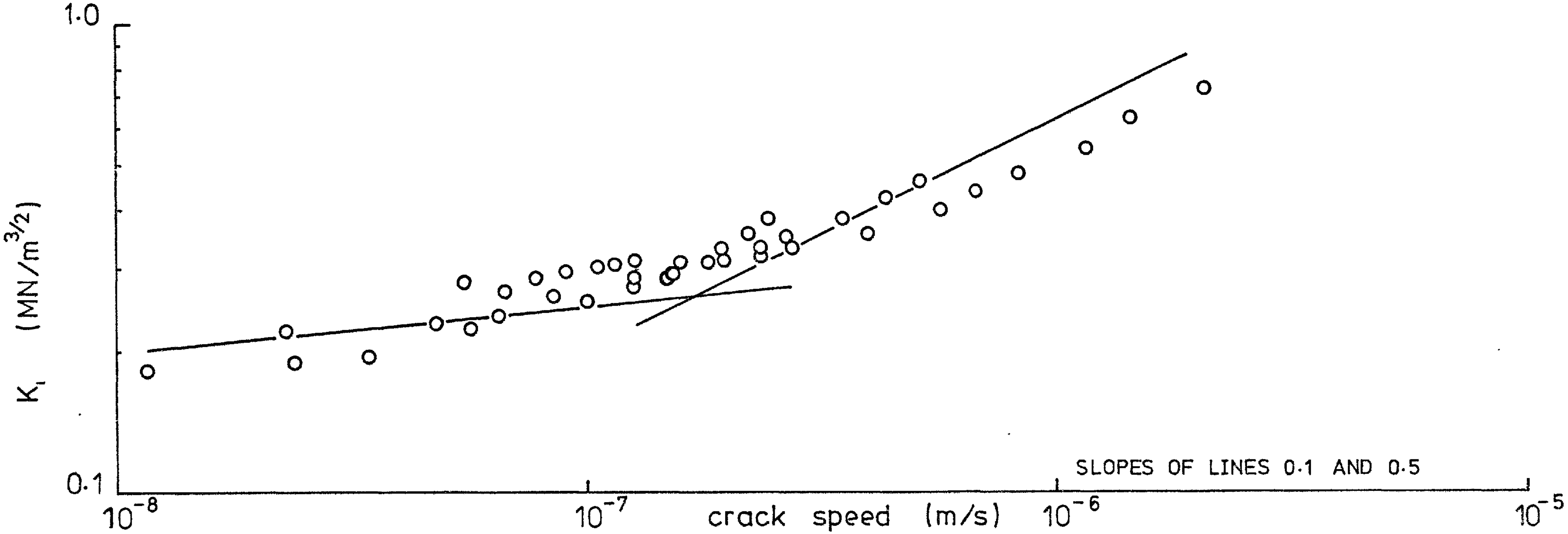
TEMPERATURE EFFECT (ARRHENIUS TYPE PLOT)

FIGURE 48

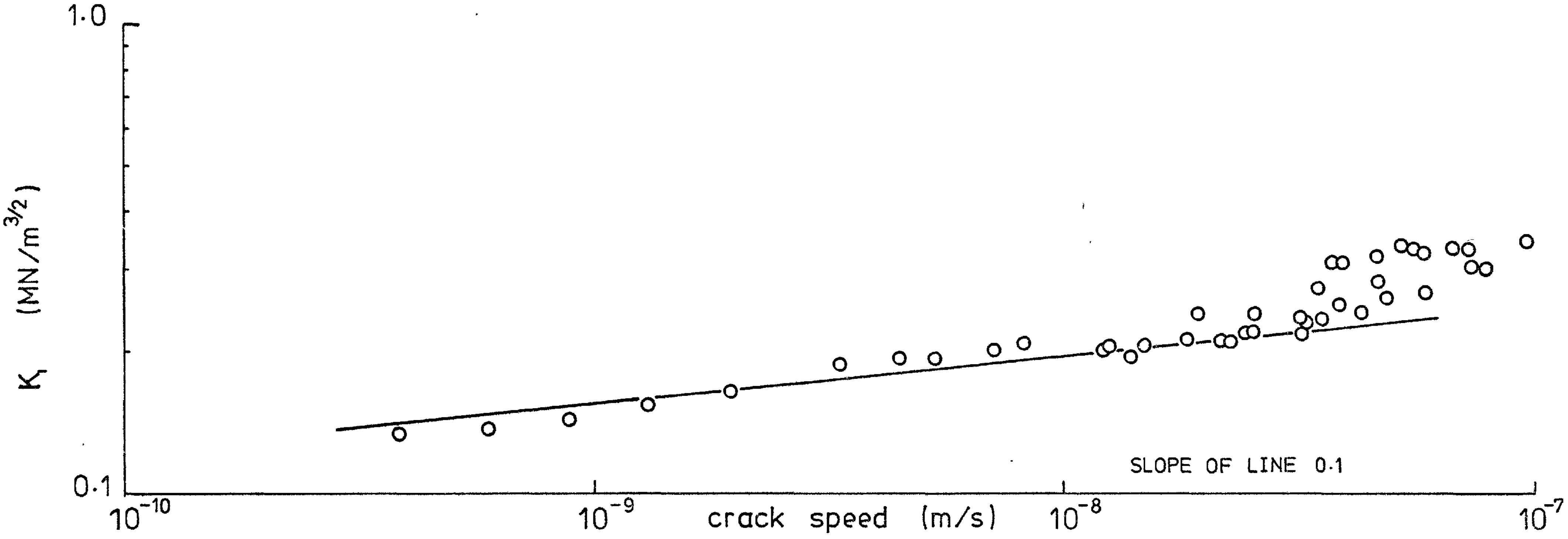


SLOPES OF LINES 0.1 AND 0.5

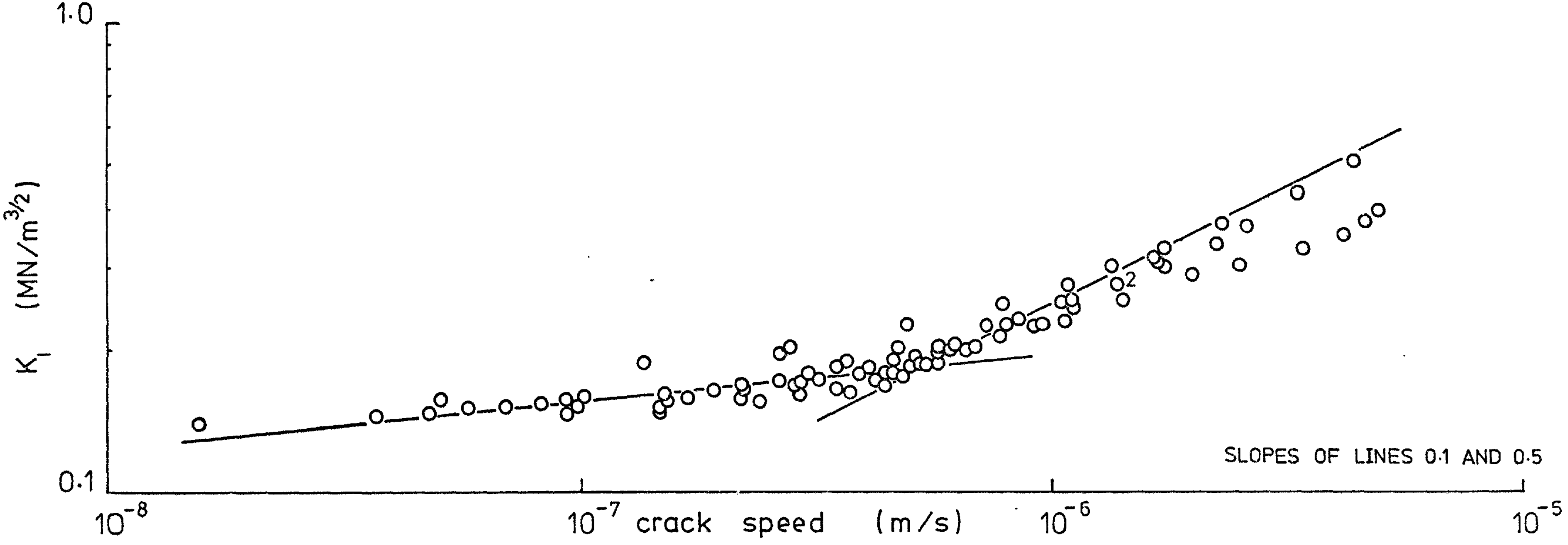
PE-A 60°C in ADINOL FIGURE 49



PE - B 60°C in ADINOL FIGURE 50



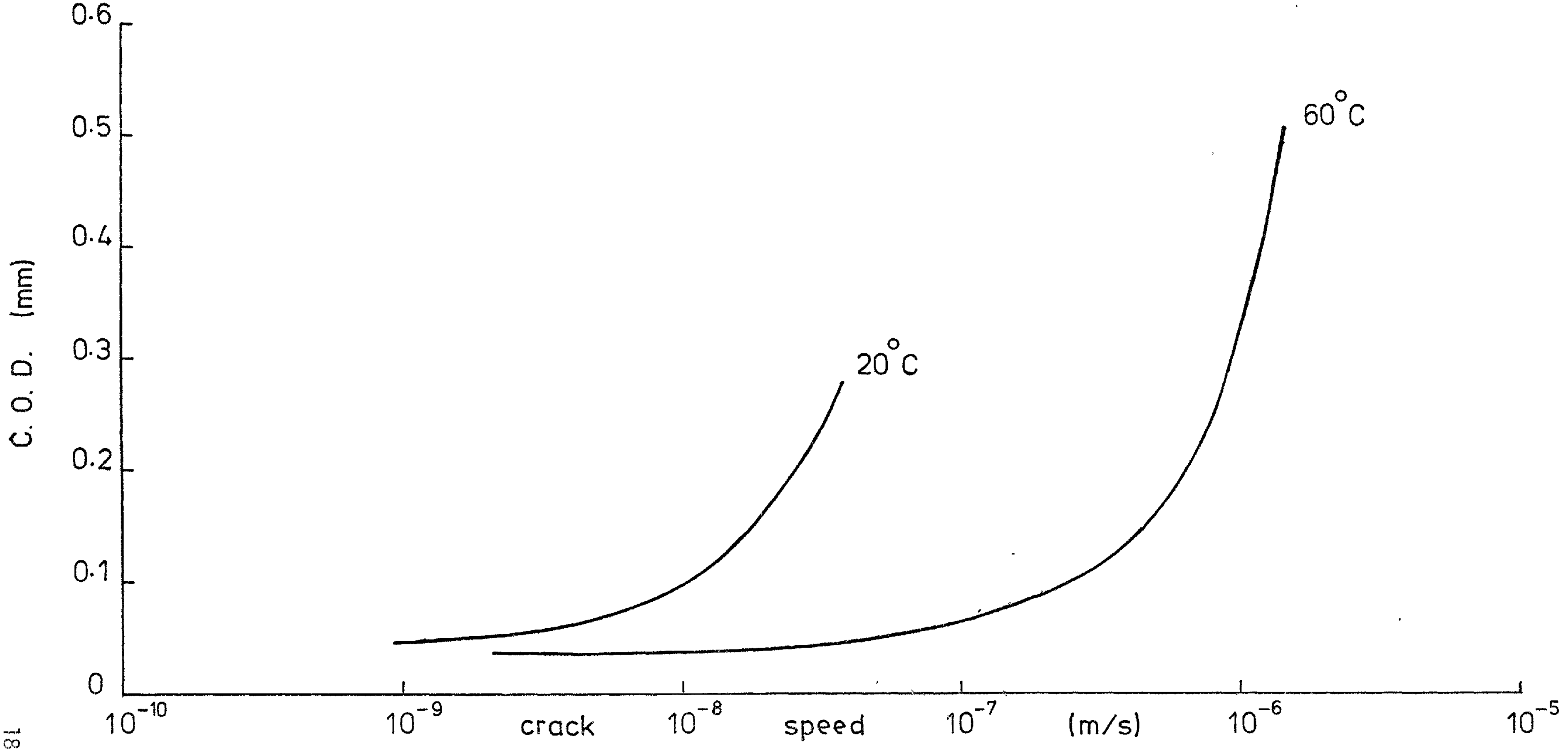
PE-C 60°C in ADINOL FIGURE 51



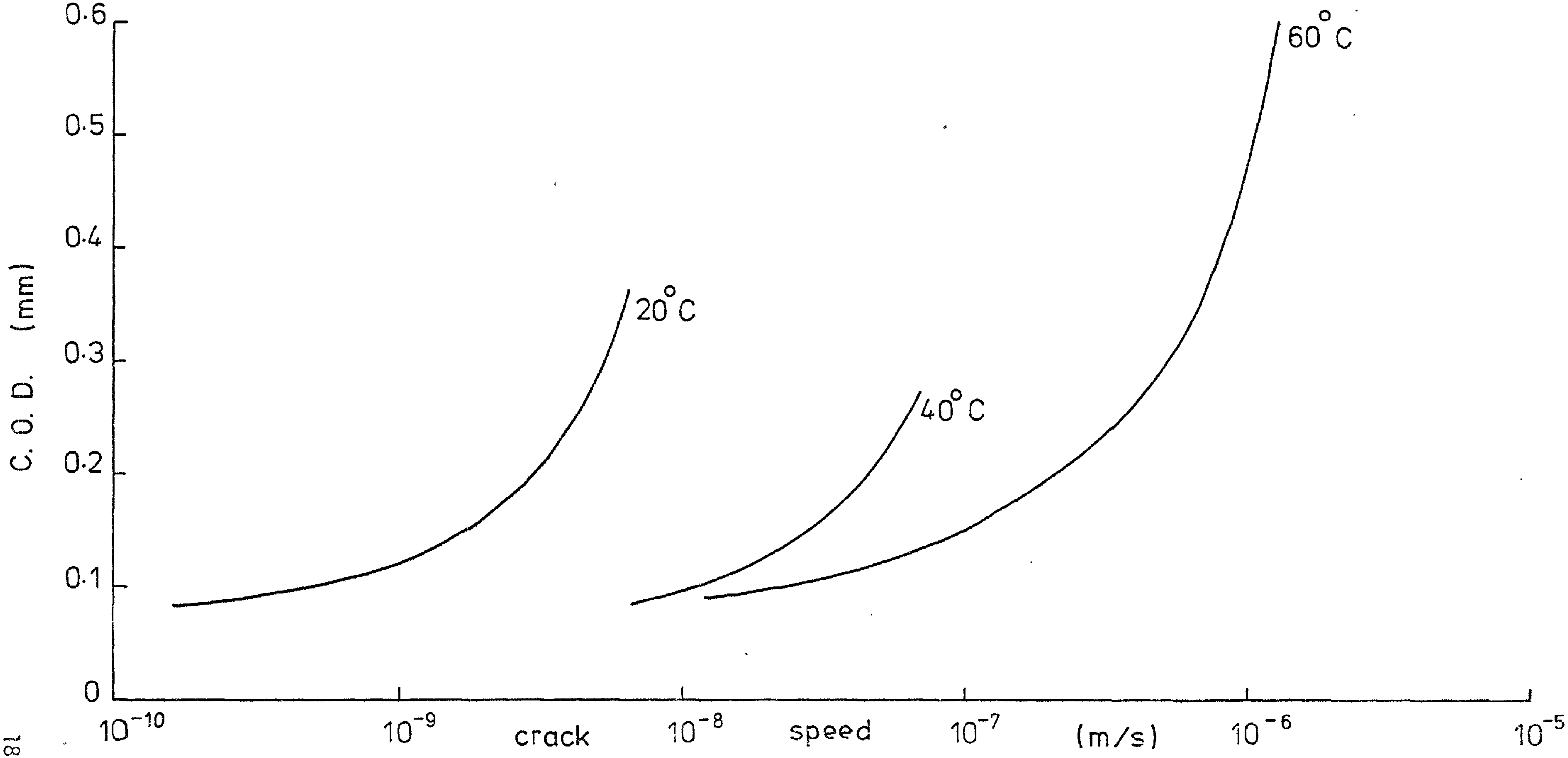
SLOPES OF LINES 0.1 AND 0.5

PE-F 60°C in ADINOL

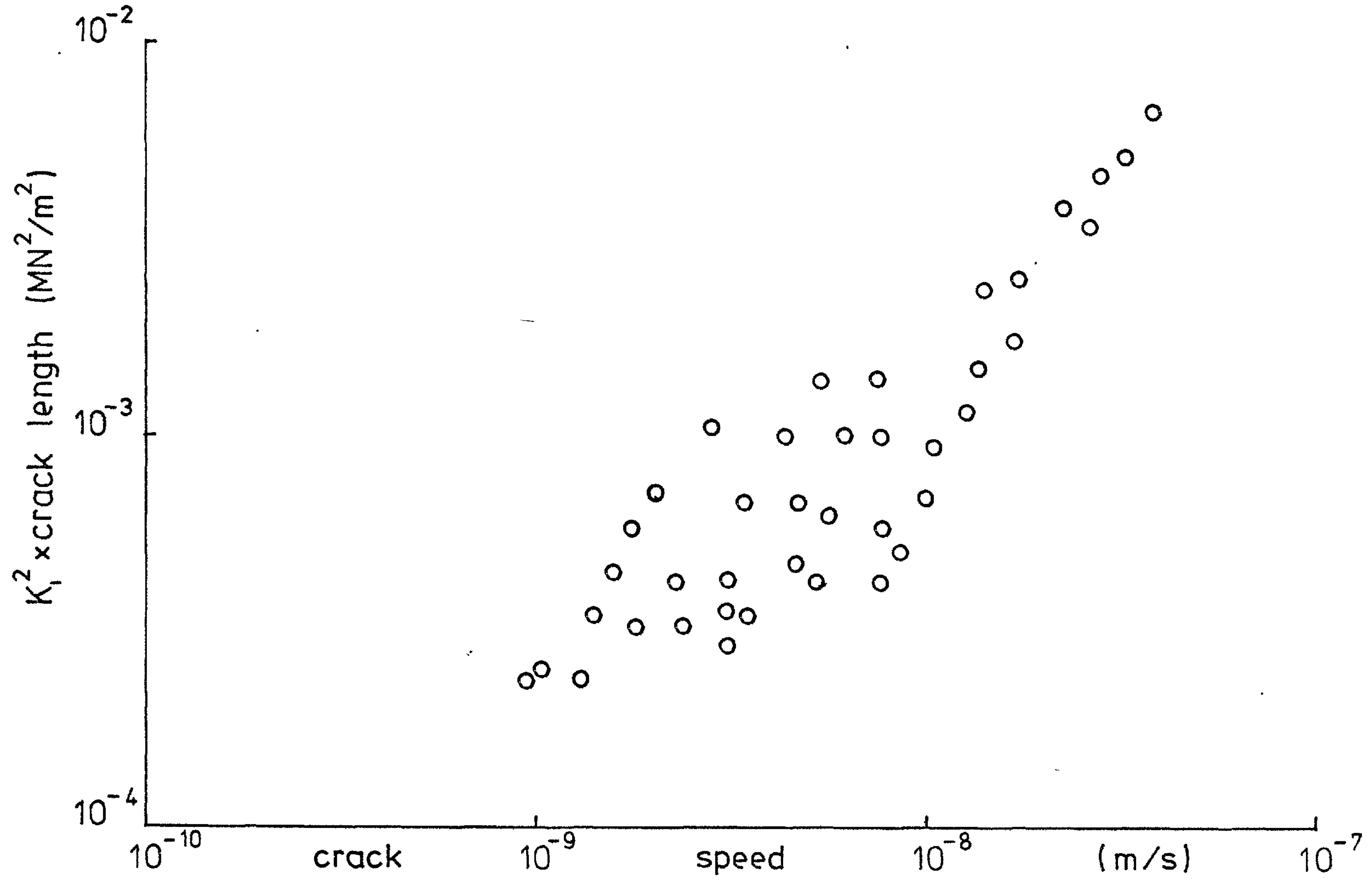
FIGURE 52



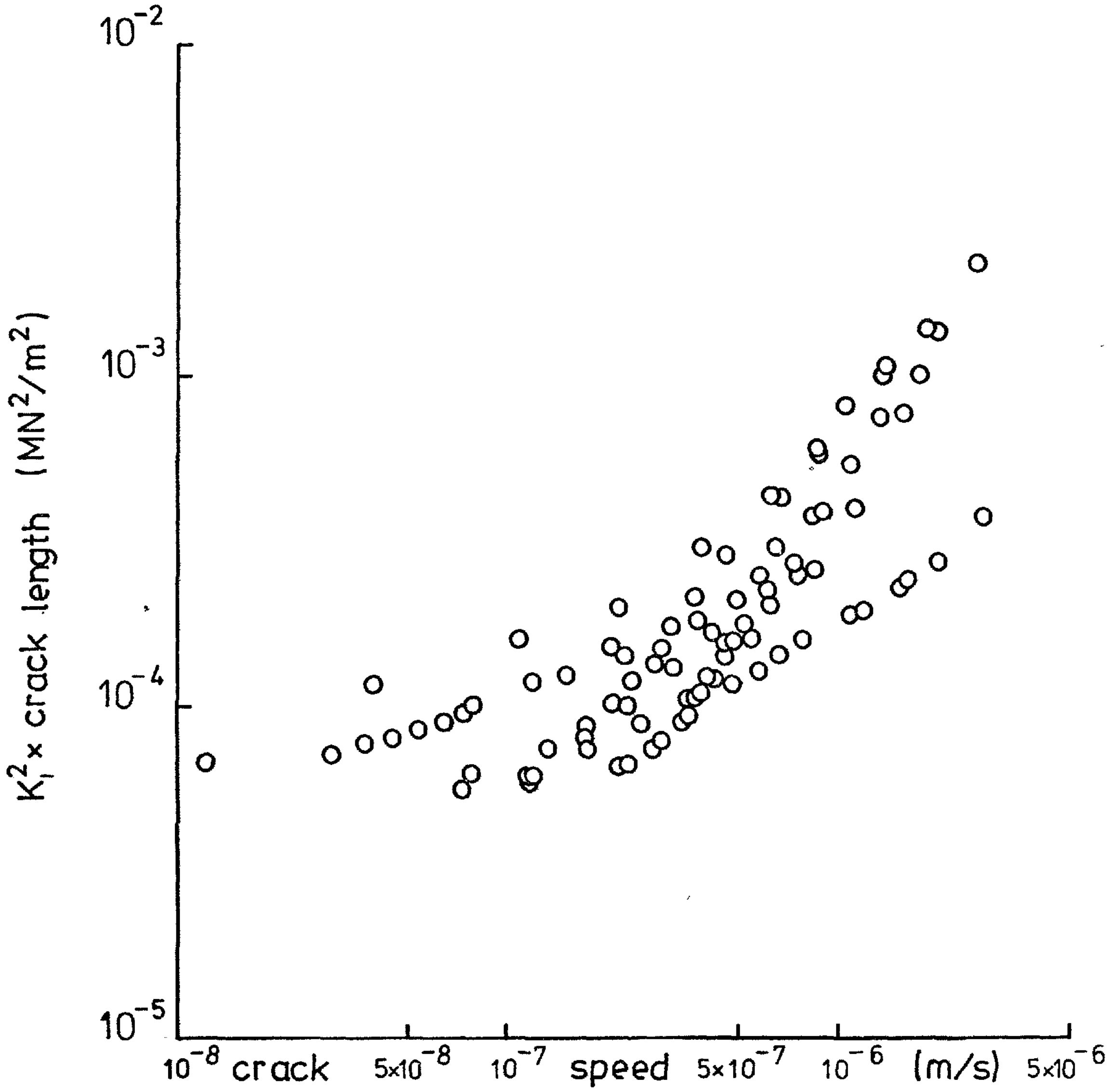
PE-A in ADINOL FIGURE 53



PE - B in ADINOL FIGURE 54

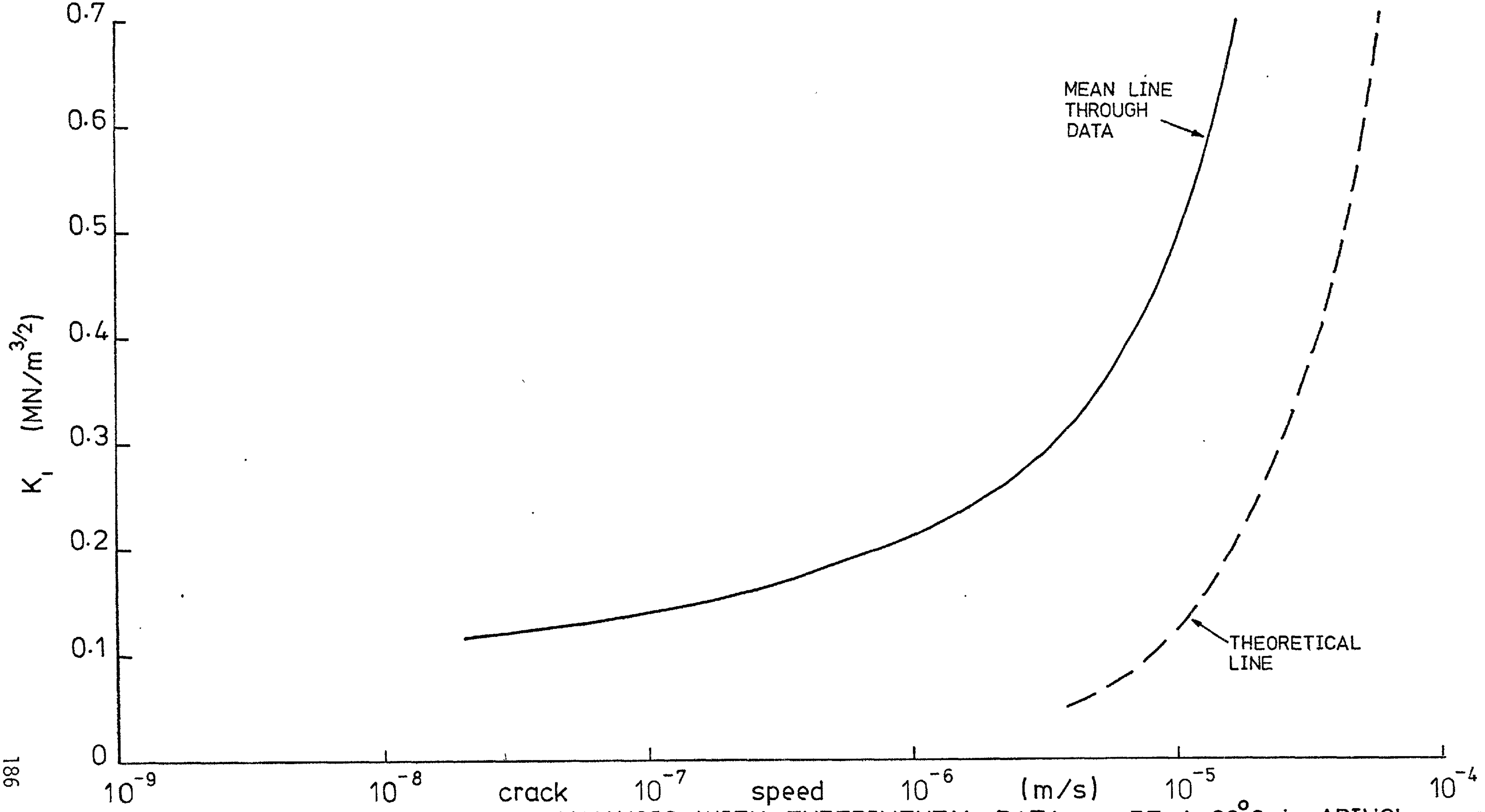


CHEREPANOV ANALYSIS PE-A 20°C in ADINOL FIGURE 55

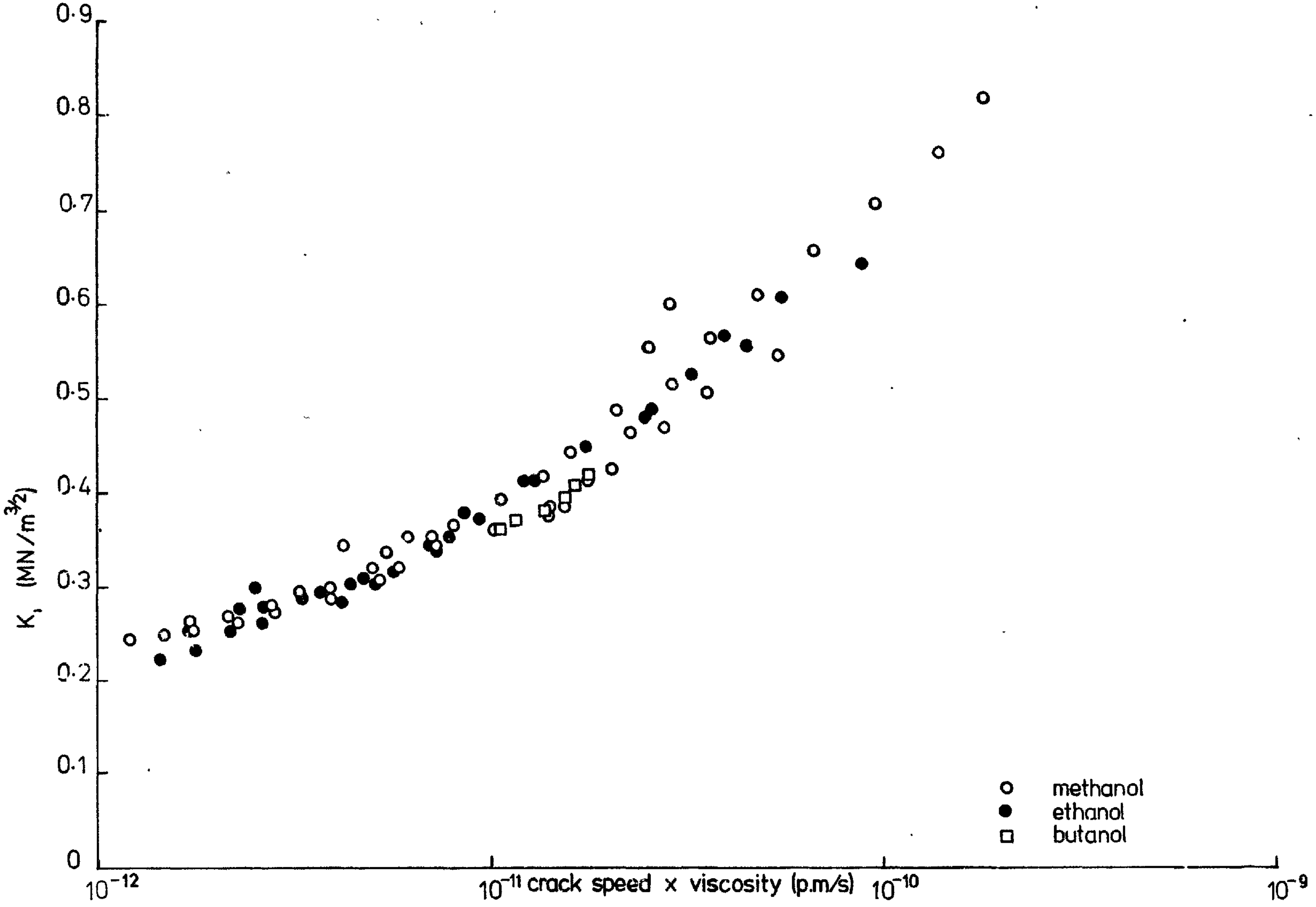


CHEREPANOV ANALYSIS PE-F 60°C in ADINOL

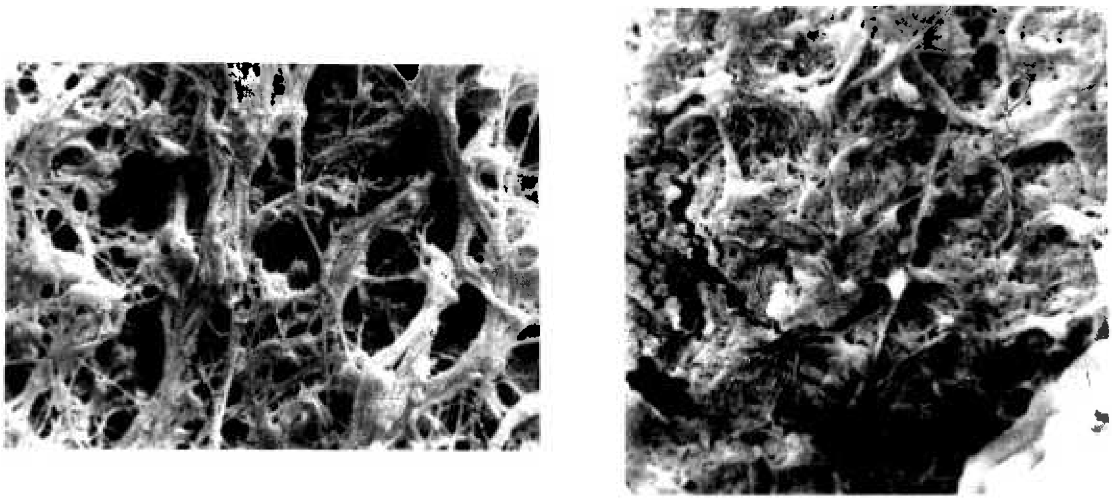
FIGURE 56



COMPARISON OF M.L.WILLIAMS ANALYSIS WITH EXPERIMENTAL DATA PE-A 60°C in ADINOL FIG.57

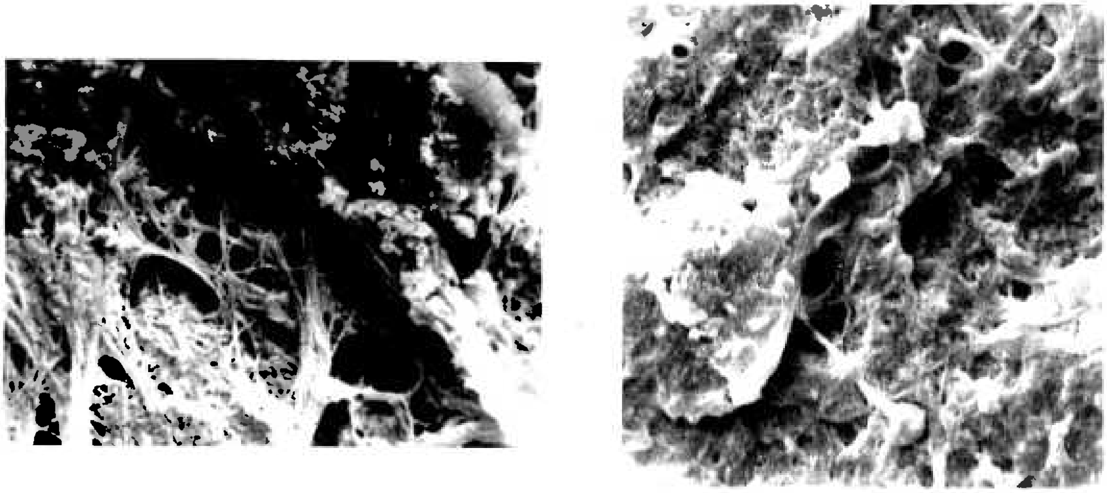


MASTER CURVE FOR CRACKING IN ALCOHOL ENVIRONMENTS PE-A 20°C FIGURE 58



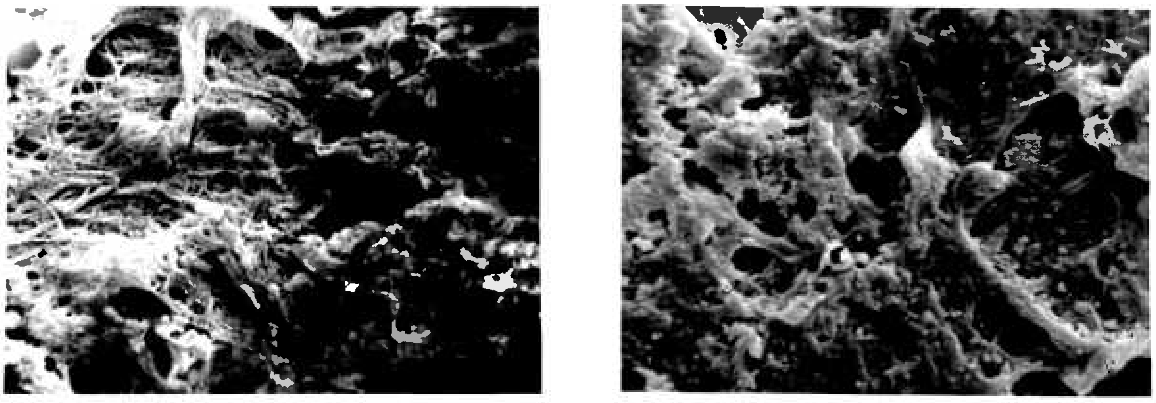
1. 1.2 x 10^{-9} m/s Specimen A

2. 2.0 x 10^{-9} m/s Specimen B



3. 3.2 x 10^{-9} m/s Specimen A

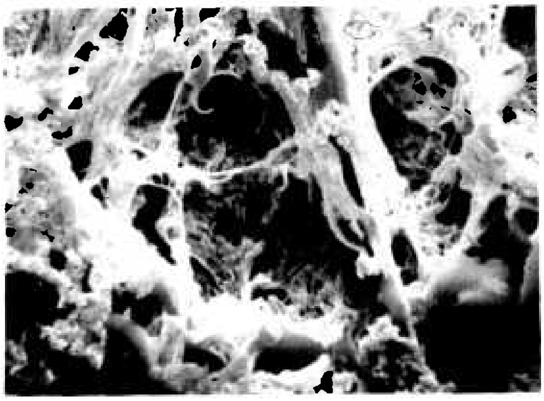
4. 4.1 x 10^{-9} m/s Specimen B



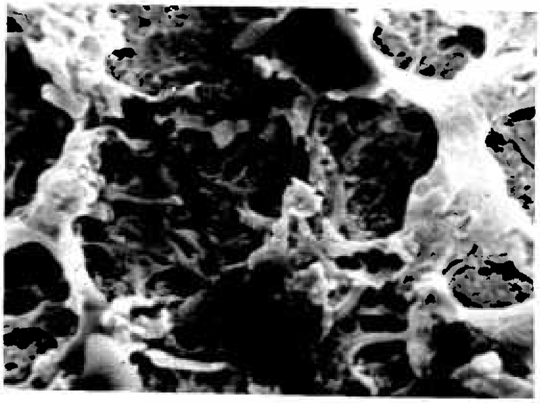
5. 6.2 x 10^{-9} m/s Specimen A

6. 8.4 x 10^{-9} m/s Specimen B

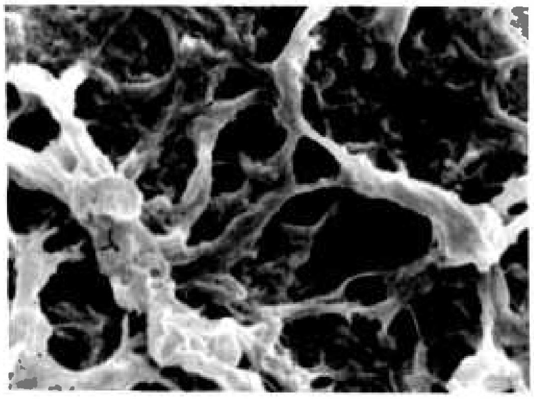
FIGURE 59 MICROGRAPHS OF PE-A FRACTURE SURFACES ADINOL 20°C
(Magnification 2100 x)



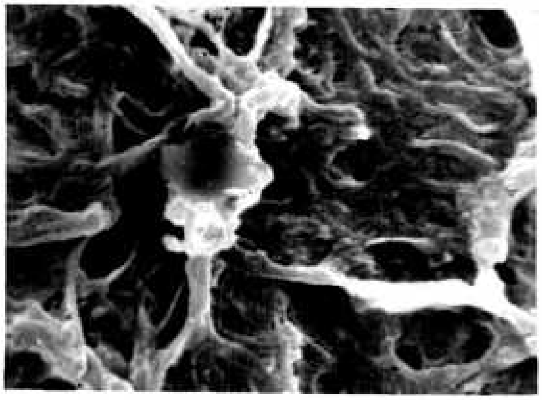
7. 9.0 x 10^{-9} m/s Specimen A



8. 1.35 x 10^{-8} m/s Specimen B

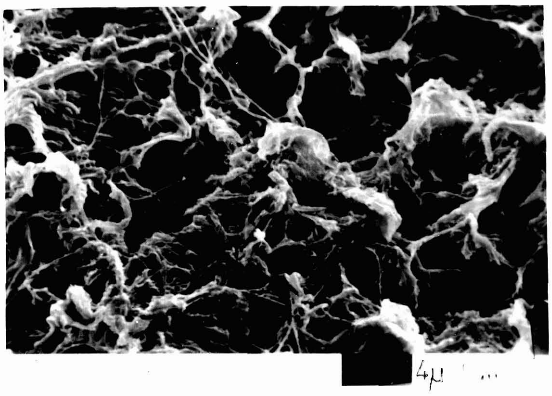


9. 2.4 x 10^{-8} m/s Specimen B

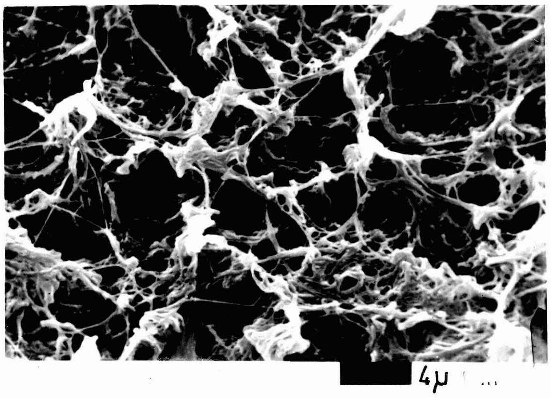


10. 4.0 x 10^{-8} m/s Specimen B

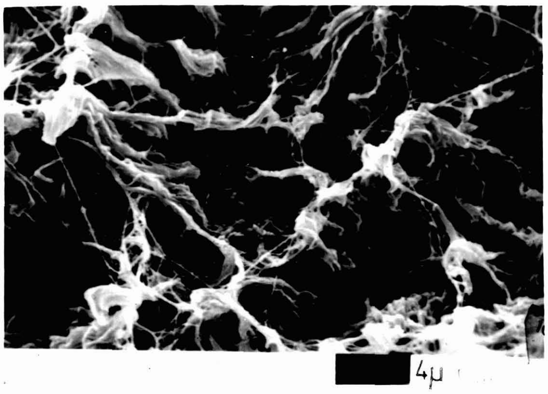
FIGURE 59 CONTINUED



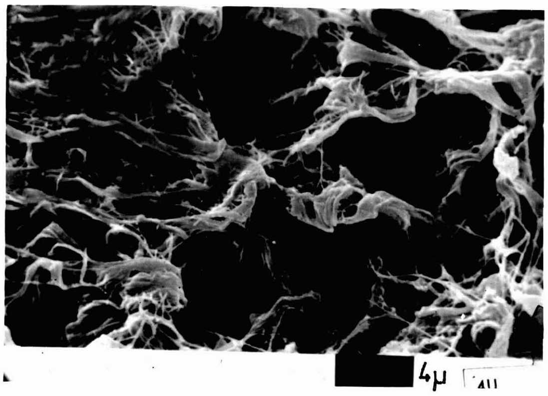
1. 5.0×10^{-10} m/s



2. 1.7×10^{-9} m/s

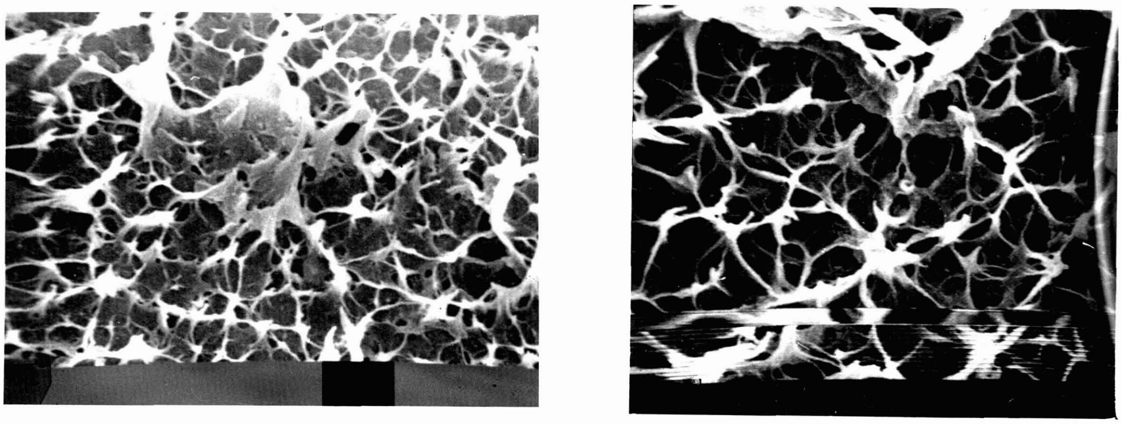


3. 4.0×10^{-9} m/s



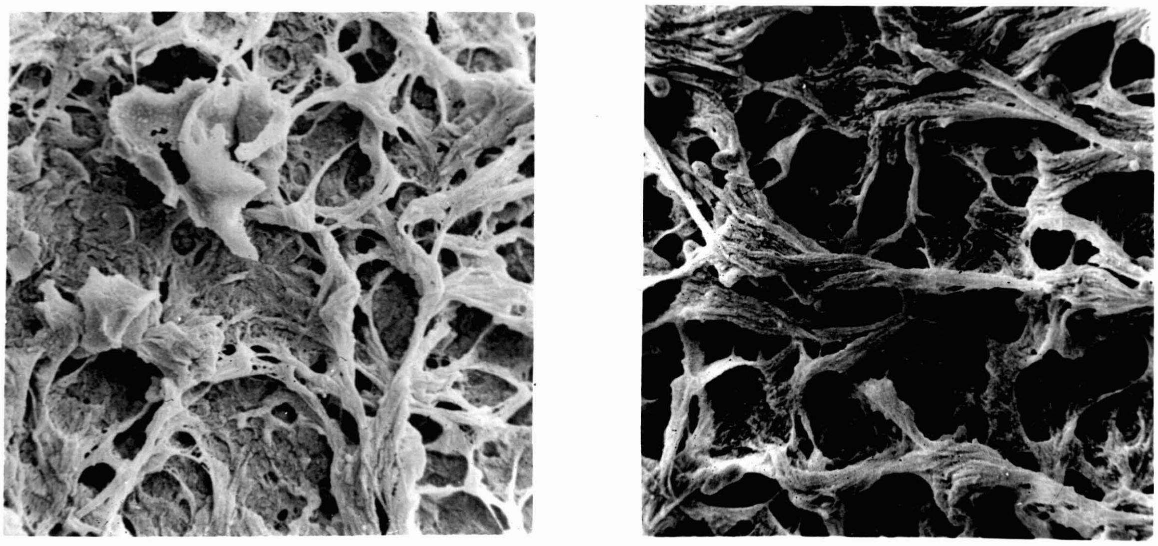
4. 7.0×10^{-9} m/s

FIGURE 60 MICROGRAPHS OF PE-A FRACTURE SURFACES METHANOL 20°C



1. 7.6 x 10^{-10} m/s Adinol

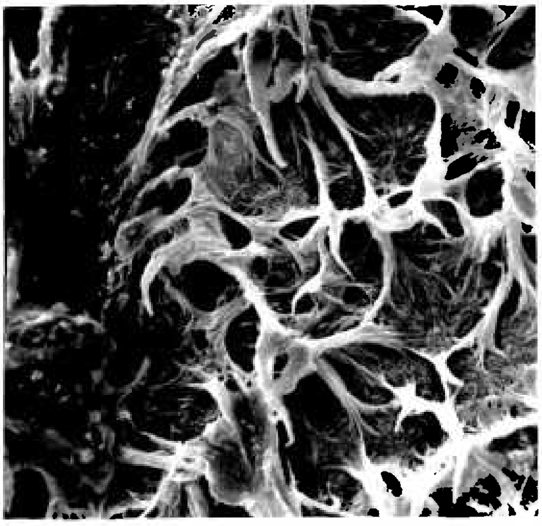
2. 4.0 x 10^{-9} m/s Adinol



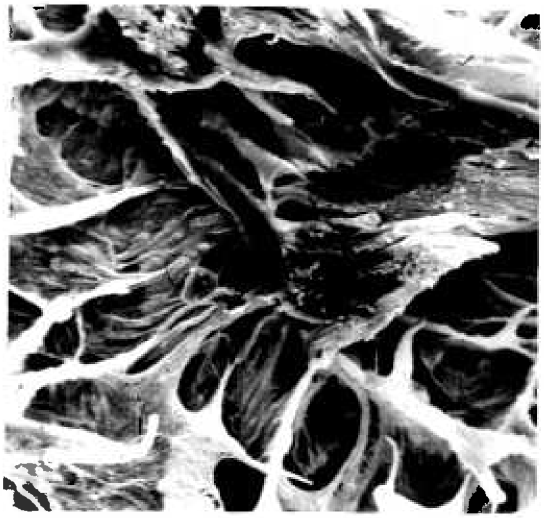
3. 8.8 x 10^{-10} m/s 5% Adinol
(1500 x)

4. 4.2 x 10^{-9} m/s 5% Adinol
(1500 x)

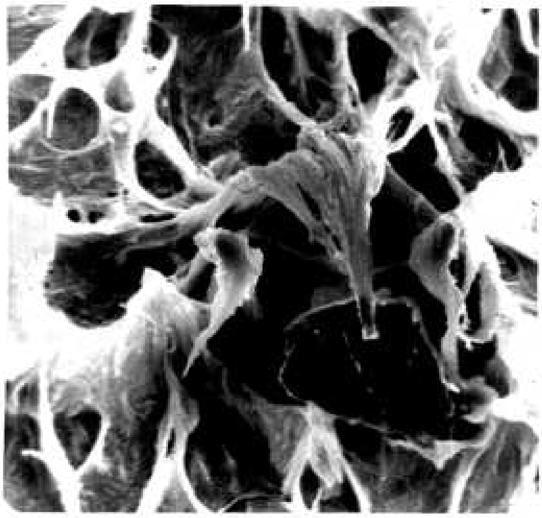
FIGURE 61 MICROGRAPHS OF PE-F FRACTURE SURFACES 20°C



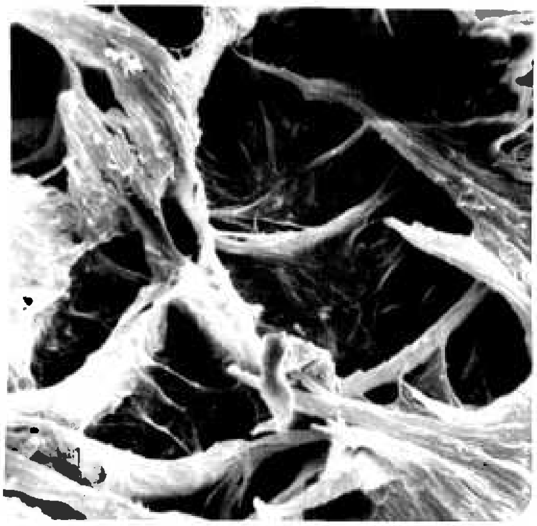
1. 1.6 x 10^{-8} m/s



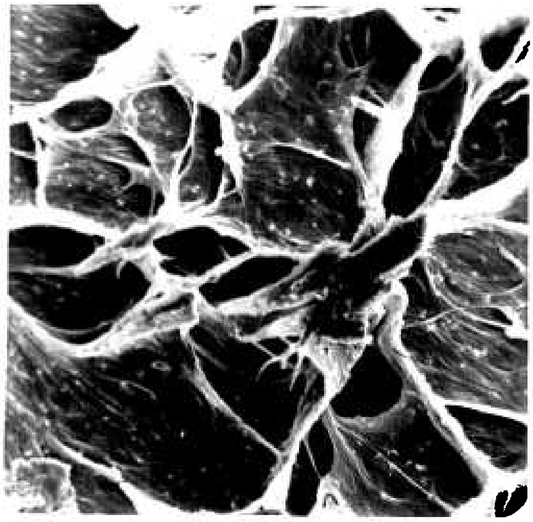
2. 6.0 x 10^{-8} m/s



3. 1.2 x 10^{-7} m/s

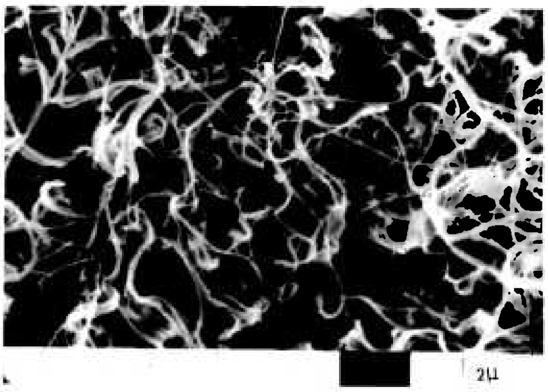


4. 1.8 x 10^{-7} m/s

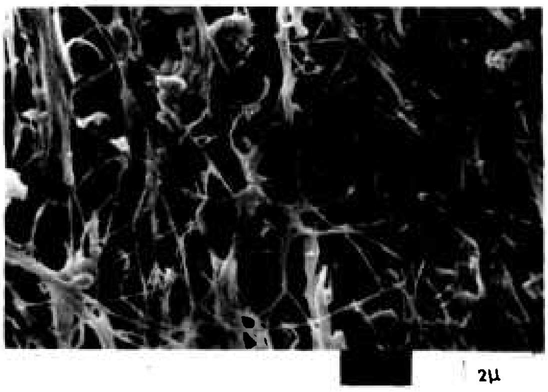


5. 2.0 x 10^{-7} m/s

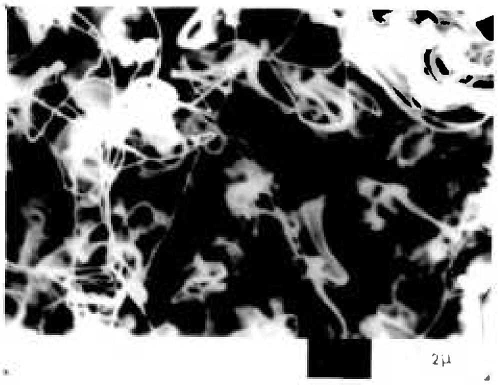
FIGURE 62 MICROGRAPHS OF PE-C FRACTURE SURFACES ADINOL 60°C
(Magnification 2100 x)



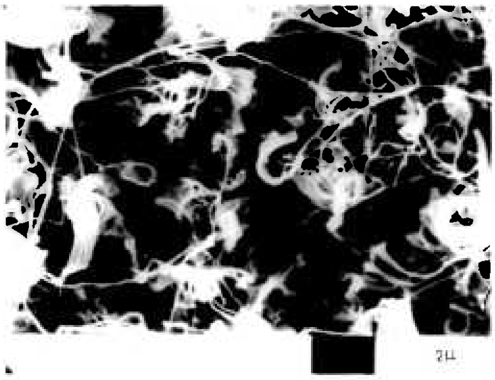
1. 2.0 x 10^{-9} m/s Specimen C



2. 1.0 x 10^{-8} m/s Specimen C



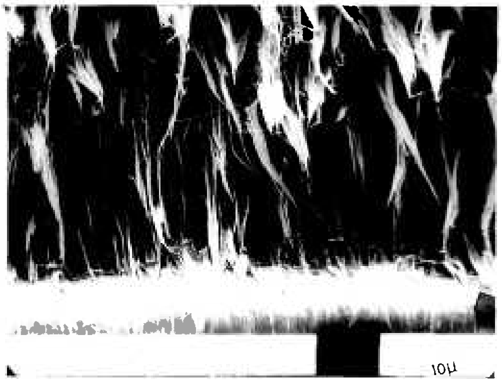
3. 1.9 x 10^{-8} m/s Specimen D



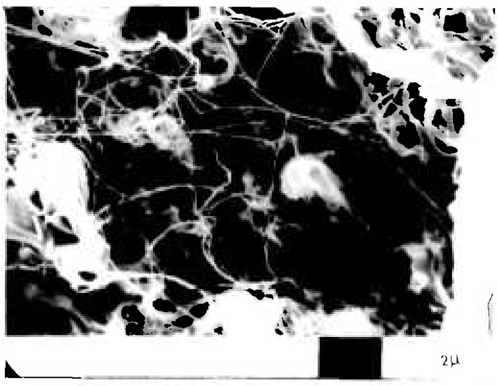
4. 1.1 x 10^{-7} m/s Specimen D

5. 2.0 x 10^{-7} m/s Specimen D

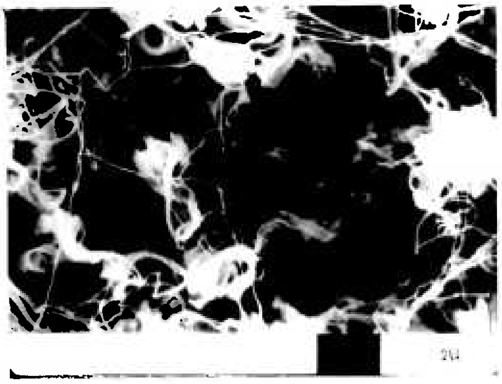
FIGURE 63 MICROGRAPHS OF PE-C FRACTURE SURFACES AIR 60°C



1. AT EDGE OF SPECIMEN



2. 0.25 mm FROM EDGE
(Centre of Micrograph)



3. 1.00 mm FROM EDGE
(Centre of Micrograph)

FIGURE 64 MICROGRAPHS OF PE-C FRACTURE SURFACE TRAVERSE ACROSS SPECIMEN AIR 60°C

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APPENDIX 1

CURVE FITTING

The geometrical method of finding crack speeds was considered quite adequate for the data produced by the tests in this work but it was thought that a simple curve fitting procedure would give the analysis a firmer mathematical background. It would also have made the calculations easier, given access to a computer, and may have reduced scatter.

The first type of curve fit attempted was a least squares fit to a polynomial. The program used was based on a polynomial curve fitting program (CURFIT written by Davraj Sharma, available from ICCC library) which could employ any combination of powers of x from -5 to +5. It was found that some of the crack length-time curves were fitted accurately and examples of two of the resulting K_1-crack speed curves for one set of data are compared with the measured values in figure A1. Other data were very badly fitted causing obvious errors in the differential (crack speed) values. Because of this the analysis was changed to see if an exponential would give better results. The equation used was

$$y = e^{f(x)}$$

but this gave similar results to the polynomials.

It became obvious that the data which were not being fitted were those which gave log K_1-log crack speed curves with two slopes and

Table A1 shows for one typical test of this type, why these data could not be fitted.

TABLE A1 TIME-CRACK LENGTH DATA

Time (x)	Crack Length (y)	$\Delta y/\Delta x$
0	5.53	
		0.004
30	5.65	
		0.003
45	5.69	
		0.010
100	6.22	
		0.008
122	6.39	
		0.013
152	6.78	
		0.016
188	7.37	
		0.018
213	7.82	
		0.011
291	9.65	
		0.029
349	11.33	
		0.045
409	14.00	
		0.043
444	15.93	
		0.067
455	16.67	
		0.093
502	21.03	
		0.124
523	23.63	

The important feature of this data is the rapid increase in $\Delta y/\Delta x$ beyond $x \simeq 275$. It means that a simple function cannot be used with sufficient accuracy because the data represents two simple functions.

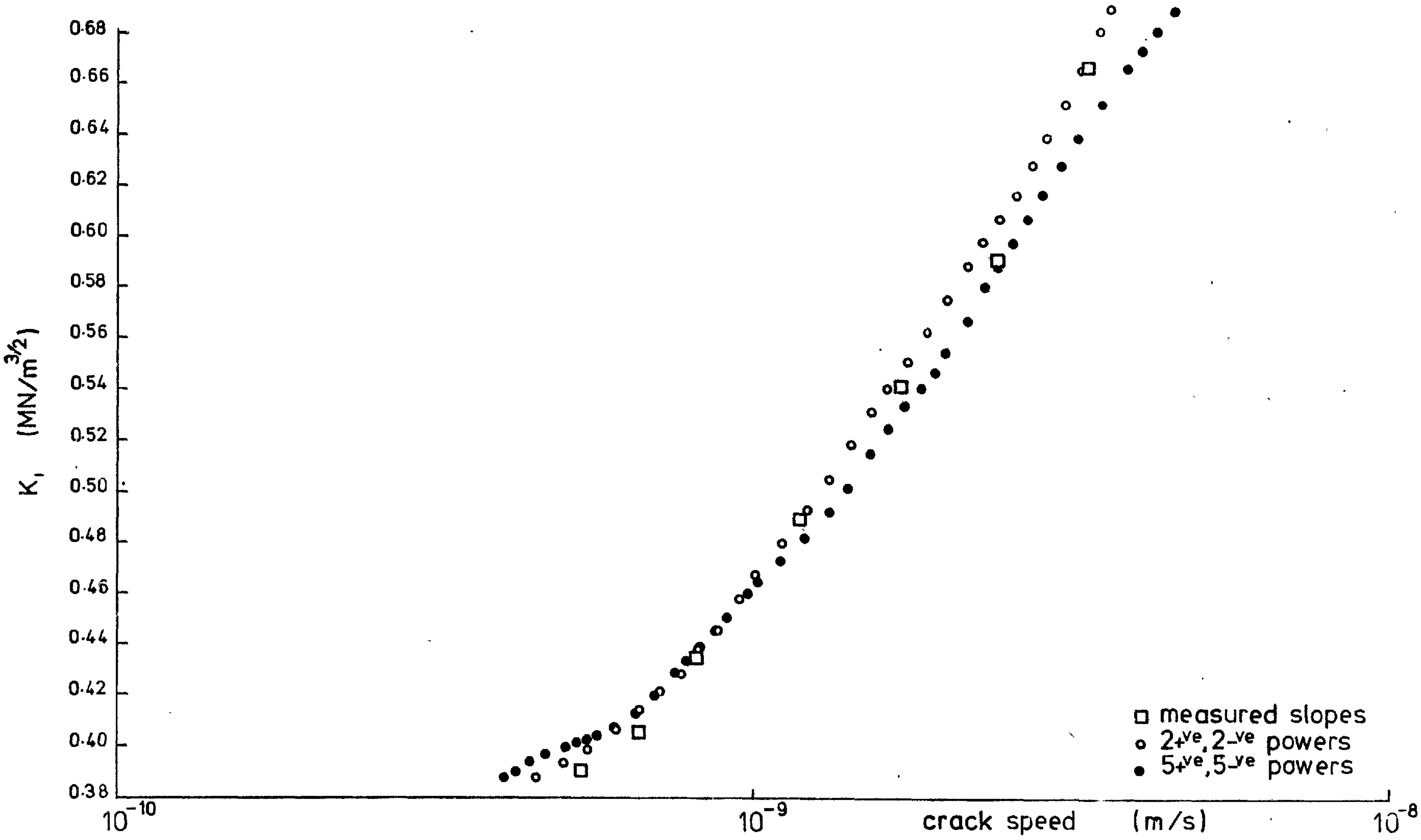
An alternative curve fitting procedure, which can accommodate step changes in d^2y/dx^2, is to employ spline functions. This method has the added advantage that approximations to the differentials are used in the prediction of interdata points so the crack speed is readily available without further computation. The first program used was SPLIN3 by T. Havie (from the ULCC Cern library). This routine computes a third order spline approximation by fitting points in the intervals between data by the equation

$$f(x) = y_i + (x - x_i)f'(x_i) + \tfrac{1}{2}(x - x_i)^2 f''(x_i) + \frac{1}{6}(x - x_i)^3 f'''(x_i)$$

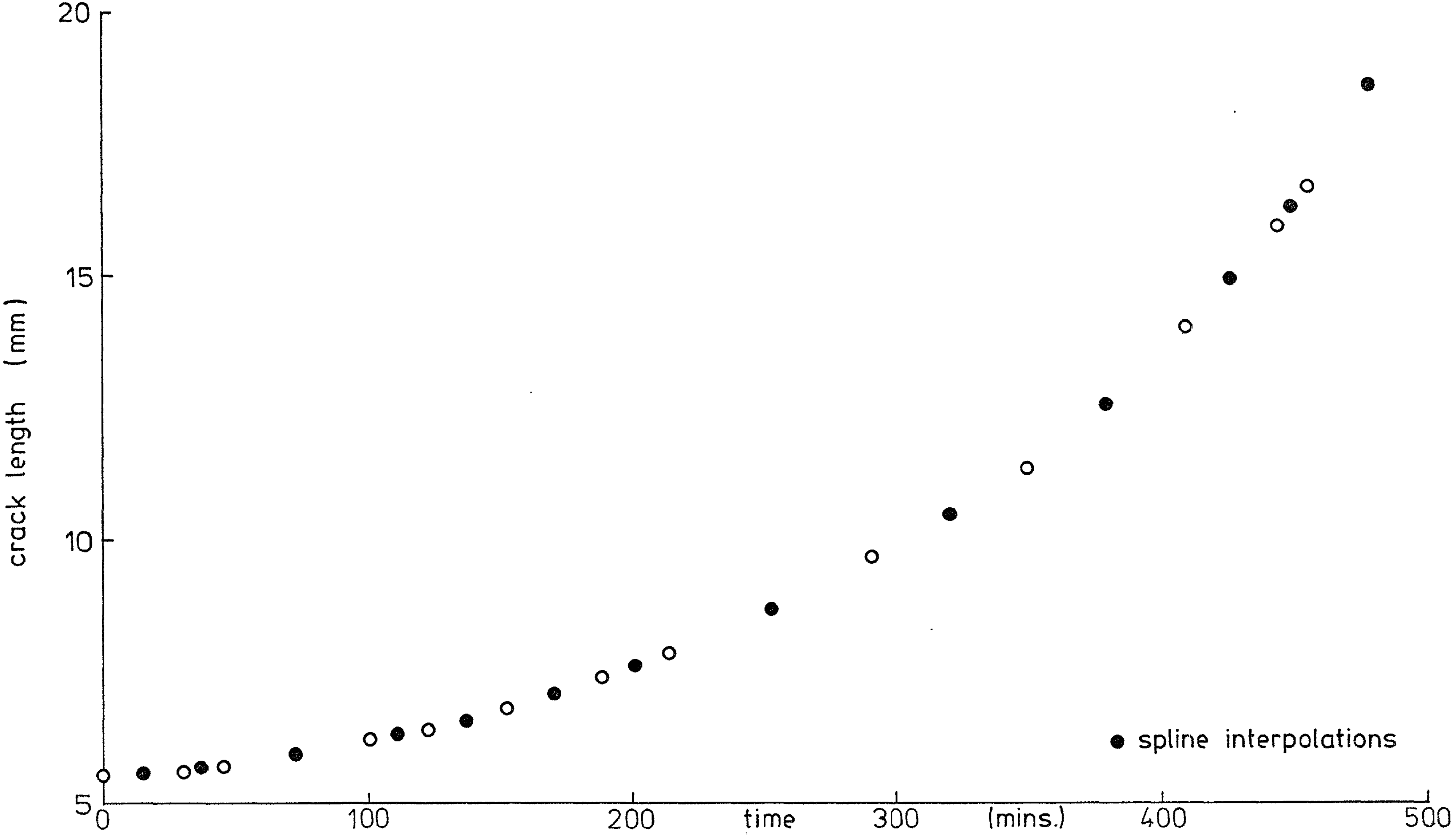
where x_i and y_i represent a data point. This operation is performed by assuming an initial $f''(x_0)$ and using a predictor-corrector method to determine all the second derivatives, then the first derivatives and $f(x)$. The third derivative is a piecewise constant function of $f''(x)$.

This method did not predict points on the crack length-time curve well when there was a large gap in the available data. The approximations to the derivatives were not sufficiently good to enable predictions away from the preceding data point and the output points strayed from the required curve.

The errors in the derivatives were obviously unacceptable so a further spline fitting routine was employed. This program by T.F. Jones (available from ICCC library) was based on one by Greville (38). It overcame the problem of the previous program by having the facility to iterate a specified number of times. Each iteration made the functions and derivatives fit the experimental points more accurately and an optimum had to be chosen between not fitting the data and fitting it so well that the experimental scatter caused the derivatives to reflect differences between individual points, rather than the trend of the curve. The output for the set of data in Table A1 is shown in figure A2. It can be seen that this method fits the data well in spite of the step change in d^2y/dx^2. Unfortunately even this method did not work for data which had a large scatter. It was found that even when the number of iterations was changed from one through to ten the worst data could not be fitted to give consistently increasing derivatives.



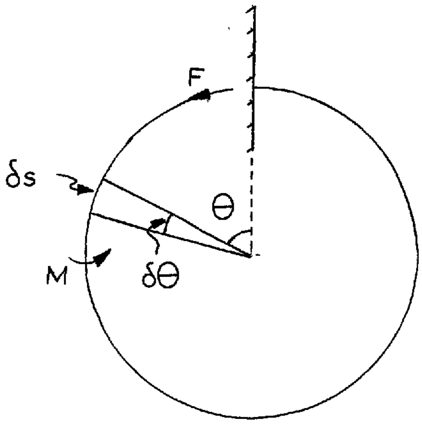
DATA FROM "GOOD" POLYNOMIAL CURVE FITS FIGURE A1



SPLINE INTERPOLATIONS COMPARED WITH THE DATA IN TABLE A1 FIGURE A2

APPENDIX 2

RING ANALYSIS



$$M = -F(R - R\cos\theta)$$

$$\delta s = R\,\delta\theta$$

Energy stored in ring

$$\int \frac{M^2}{EI}\,ds$$

$$= \frac{F^2R^3}{2EI}\int_0^{2\pi}(1-\cos\theta)^2\,d\theta$$

$$= \frac{F^2R^3}{2EI}(3\pi)$$

This is equal to the energy used displacing the force F

Putting force F = Px

$$\text{Then Energy} = \int_0^a P\,x\,dx$$

$$= Pa^2 / 2$$

$$= Fa / 2$$

These energies must be equal

$$\text{Therefore} \quad \frac{3\pi F R^3}{E I} = a$$

$$\text{Therefore} \quad \underline{\underline{F = a E I / 3\pi R^3}} \qquad \text{A1}$$

Consider a section of PE pipe of length equal to the width of a typical surface crack, having a very thin slit completely through the wall. The stress required to open the slit by 1 mm is given below. This calculated stress represents a worst case approximation to the part-through crack studied in this work because true displacements should take the form of a semi-ellipse with maximum opening 1 mm. The values substituted in equation A1 are :-

$a = 10^{-3}$ m $\qquad$ $E = 500$ MN/m^2 $\qquad$ $I = \frac{bd^3}{12}$ m^4

$R = 0.025$ m $\qquad$ $b = 0.015$ m $\qquad$ $d = 0.005$ m

Giving

$$\text{Stress} = \frac{F}{bd} = \underline{6.2 \times 10^{-3}\ \text{MN/m}^2}$$

This stress is so small compared with the other stresses induced in the pipe wall that it can be ignored.

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Environmental Stress Cracking in Polyolefins

Fracture mechanics has already proved a sensitive measure of polyethylene resistance to ESC. Its application to other polyolefins is just a matter of time

During the late 1950's and early 1960's there was an intense amount of interest in the problem of environmental stress cracking (ESC) of polyolefins, in particular, polyethylene, largely because polyethylene was being widely used as an insulation and coating for undersea telephone cable and for underground pipework. But in spite of the time and effort expended on the problem, there is no convincing argument to explain ESC. The main stumbling block has been the absence of a test method which is able to give satisfactory data from which to predict service performance. Numerous tests have been proposed and then found wanting, mainly because data on similar materials cannot be reproduced in different laboratories and also because there is still a dispute as to the most critical parameter by which to measure resistance to ESC.

Lander (1) used unnotched tensile strips subjected to constant loads to measure a limiting stress (σ_c) below which failure would not occur within a finite time, at any given temperature. In a somewhat different test, McFedries et al (2) used specimens shaped in the form of a Maltese cross to measure critical stresses under biaxial tensile loading conditions. Although the experimental data in each case appears to be good, critics point out the test's limitations, since the results are not totally reproducible between one material and another and since there are variations in σ_c *when* loading conditions or specimen dimensions are changed. Doll and Plajer (3) proposed, instead, the use of a critical strain (ϵ_c) criterion (obtained from constant strain tests), since reproducibility is enhanced.

Whatever the criterion, whether critical stress or strain, there are bound to be discrepancies in data, since the results of both tests are highly dependent on the surface condition of test samples and on the mode of specimen preparation.

The bent strip or Bell Telephone test has tried to overcome the reproducibility problem by using a razor-notched specimen. The slit is made down the longitudinal axis of a 12 by 36 by 3 mm thick specimen which is then immersed in a test tube of Igepal (concentrated detergent) at a temperature of 50°C. Specimens are usually tested in batches of 10, and the time at which 50% of them have failed is taken as the stress cracking time. Failure is in evidence by the development of cracks perpendicular to the slit and near the peak of the bend. Although the bent strip test is the current ASTM standard test (4) for evaluating ESC resistance in polyethylenes, test results are by no means universally accepted. Indeed ASTM itself admits that the test is "not capable of giving precise, universally reproducible values" (5).

Not only is data difficult to reproduce in any of the above tests, but at least in one major area the tests give completely different results. In constant loading tests, increasing the density of polyethylene increases the life of the specimen in any given environment (1 and 2). However, in constant strain tests and the bent strip test, increasing the density results in shorter life and lower critical cracking strain. Howard (6) claims the latter two tests give the most accurate result because they best represent service conditions, particularly in cable sheathing applications. McFedries et al (2) fundamentally disagree. They point out that much of the scatter on times to failure in the bent strip test is due to variations in modulus and related stress rather than to time variations in failure behavior. When the most 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 effect in failure time. (They also cite a number of practical cases where high-density material is found to have superior stress crack resistance.) The conflict is still unresolved and the bent strip test remains an unsatisfactory standard. From a commercial point of view, the situation is particularly undesirable because it can lead to much waste.

The very inconsistency of all test results is a sure sign that no real understanding of the ESC phenomenon exists and that they are little more than educated guesses. Manufacturers are left with little alternative but to follow "standard" test procedures. The unfortunate fact remains that articles made from polyethylene still break because of environmental stress cracking. Manufacturers can produce grades of polyethylene with virtually total resistance to cracking, but only at a price; the cost of making and reprocessing these grades is often prohibitive to end users.

- In general, vinyl foams outperform SBR latices. They are stronger and reinforced by superior tuft-lock coatings.
- Monsanto's system was the best of the vinyl systems tested. It exhibited a balance of processability (as measured by its improved tuft-lock and physical strength) and low volatility (as measured by pollution effluent results and by improved dimensional stability).

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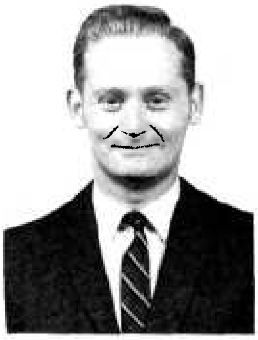
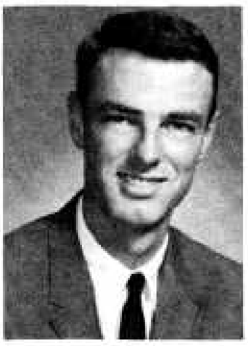
About the Authors


J. T. Renshaw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This situation was once widespread in all types of fracture testing, but the study of fracture mechanics as expounded by Irwin (7) has led to increased rationalization. There are now several examples of the successful application of these concepts in the polymer field to explain previous confusion (8 and 9). It has been felt for some time that it would be profitable to apply the ideas and concepts of fracture mechanics to the ESC problem in general and in particular to the cracking of polyolefins. In a previous paper, the authors (10) showed it was possible to perform reproducible tests by measuring the "fracture toughness" of polyethylene in liquid environments. A brief explanation of fracture mechanics will now be given, but the reader is referred to the detailed text (10) for a more complete story.

Fracture Mechanics

The subject of fracture mechanics has been built up around the ideas put forward by Griffith (11) in 1921 to explain the failure of brittle materials such as glass. He calculated the true theoretical strength of glass, and found that in practice it was well below his idealized value. As explanation, he postulated that any commercial material contains cracks and other inhomogeneities and that failure occurs because of crack propagation and resultant preferential bond breakage. Griffith reasoned that if one had a plate subjected to an applied stress, σ, then the introduction of a crack of length $2a$, would result in a decrease in the stored elastic energy, by an amount, W, where

$$W = \frac{\pi}{2} \cdot \frac{\sigma^2 a^2}{E} \quad (1)$$

and E is Young's Modulus. This energy is given up because of the introduction of the crack.

If the crack is now supposed to grow by a small amount δa then the energy released is

$$\frac{\partial W}{\partial a} \cdot \delta a \quad (2)$$

Griffith said that a brittle material requires a particular amount of energy/unit area, γ, to form new surfaces; this energy being of similar origin to the surface tensions. Introducing γ, the energy absorbed by the creation of two new surfaces, is

$$2\gamma \; \delta a \quad (3)$$

It was then postulated that the system would be unstable if the energy released were greater than or equal to the energy absorbed, so that

$$\frac{\partial W}{\partial a} \cdot \delta a = 2\gamma \; \delta a \quad (4)$$

gives the critical condition for the onset of unstable fracture, i.e., cracks run when

$$\frac{\partial W}{\partial a} = 2\gamma \quad (5)$$

In fracture mechanics it is assumed that there are always cracks present and that they run at this condition.

Substituting from *Eq 1* gives the familiar result:

$$\frac{\pi \sigma^2 a}{E} = 2\gamma \quad (6)$$

Irwin and others noted, however, that in most real materials, γ was not a true surface energy but contained a large plastic work term because of the high stresses induced at the crack tip, which cause local plastic flow to occur prior to fracture. He suggested that the 2γ term of *Eq 6* be renamed and replaced by an all-embracing parameter, G, and that this be called the "strain energy release rate." At the onset of fracture, G assumes a critical value G_c so that

$$\pi \sigma^2 a = E G_c \quad (7)$$

It is to be noted that the right-hand side of *Eq 7* is concerned solely with material properties while the left-hand side contains only independent variables. Hence a combined material property may be defined as:

$$K_c^2 = E G_c \quad (8)$$

whence

$$K_c^2 = \pi \sigma^2 a \quad (9)$$

This critical parameter, K_c, otherwise known as the stress intensity factor, may be easily found for the simple tension case by testing a range of specimens with varying notch lengths, measuring the stresses to cause failure, and then using *Eq 9* to calculate K_c.

In practical test situations where crack lengths can be large compared with total plate width, the solutions derived above must be modified slightly to account for finite plate effects. The result becomes

$$K_c^2 = Y^2 \sigma^2 a \quad (10)$$

where Y^2 is a function of a/W (the crack length/plate width ratio), which for the case of a plate in tension containing a single-edge crack is:

$$Y^2 = \{1.99 - 0.41(a/W) + 18.7(a/W)^2 - 38.48(a/W)^3 + 53.85(a/W)^4\}^2 \quad (11)$$

Test Program

Essentially viscoelastic, plastics do not always break in a pure brittle manner. With many plastics, total catastrophic failure by fast fracture is often preceded by slow crack propagation. With polymethyl methacrylate and polystyrene, it has been found (8 and 9) that fracture toughness K_c depends on crack speed, which is a measure of the strain rate sensitivity of a material. It is therefore necessary with this type of behavior to measure K_c as a function of crack speed.

Measuring crack speeds also provides a suitable reference scale against which to compare toughness which is obtained by different test methods. Because the environmental stress cracking of polyethylene is a slow crack situation, all results are correlated on a K_c versus crack speed basis.

Low-Density Polyethylenes in Alcohols

As a first study in evaluating the applicability of fracture mechanics to the ESC of polyethylene, a series of tests was carried out on two low-density grades ($\rho = 0.912$) of polyethylene, both of which had high MFI's (7 and 20) and which would therefore be expected to crack in relatively short periods of time in an alcohol environment. To reduce testing variables to a minimum, the simple single-edge notched tension specimen (SEN) was used (inset to *Fig. 1*) for which the solution for K is as given in *Eq 10* and *11*. This specimen is simple to manufacture, and has only one crack length to monitor during crack propagation, a fact which greatly facilitates the taking of speed measurements.

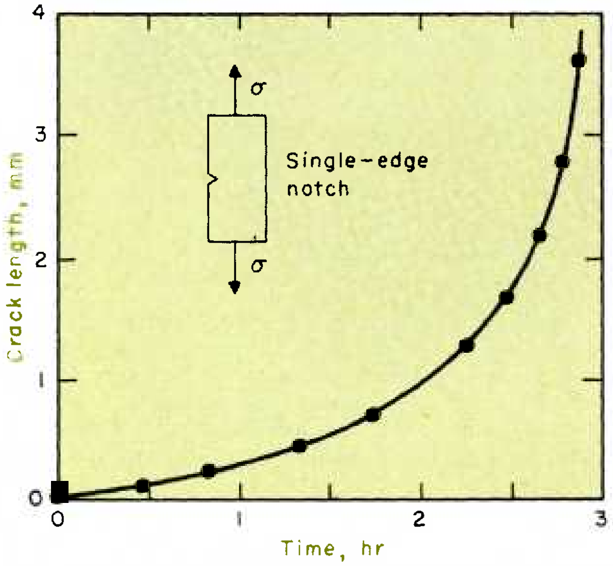

Figure 1. Typical crack length vs time curve developed in the constant load test for low-density polyethylene in a methanol environment. Inset depicts single-edge notch tension specimen.

The main test series was carried out under constant loading conditions, dead-weight loads being applied through a simple lever arm system to the specimens, which were totally immersed in methanol baths. Other tests involving the measurement of crack initiation as a function of straining rate were also conducted on an Instron testing machine at a number of different cross-head rates.

Specimen dimensions were generally 150 by 50 by 1.5 mm, although a sub-series of tests was made on 3 and 4.5 mm thick material to evaluate the effect of specimen thickness on the results. All specimens were pre-notched with razor blades, initial crack lengths being varied in the 2-12 mm range so as to assess the influence of variation in notch length on K_c values. (It is fundamental to the theory that results shall be independent of notch geometry above all else!)

In the constant load tests, the crack growth under load was measured by a microscope, and a running plot of crack length vs time was made for each test. A typical example is shown in *Fig. 1*, where it can be seen that crack growth rate increases throughout the test, in a manner reminiscent of slow crack growth in other, more brittle plastics such as polymethyl methacrylate (8) and polystyrene (9). Crack speeds were found by taking slopes at selected points on the crack length vs time curve; K_c values were also evaluated at these points by using the current value of crack length together with the loading parameters to calculate K from *Eq 10*.

By carrying out this procedure on tests loaded to give a wide range of crack speeds, a plot of K_c vs crack speed was made for each grade of material, as shown in *Fig. 2*. The data from many different tests is seen to fall together to give a single curve, the scatter being of the order of ±10%, which is very acceptable for any form of fracture test and which compares well with the scatter of ±15% obtained on similar tests with polymethyl methacrylate in air. It is certainly far better than the precision of any other type of stress cracking test. *Figure 2* shows that within testing limits, a unique relationship does exist for each material, although there are certain limitations. In other tests, not reported here, it became apparent that the uniqueness of the K_c vs crack speed relationship breaks down when comparatively large gross stresses are applied to specimens having large a/W ratios. This phenomenon would appear to be a result of a large net section stress leading to the eventual breakdown of the basic equations as plasticity and finite plate effects become predominant. For a/W ratios below 0.4, the results shown in *Fig. 2* are all valid and, indeed, appear to indicate that the ESC failure mode is totally brittle. Casual examination of the fractures produced would also lead to the same conclusion since there was no sign of ductility on the macro scale. For those tests where high net section stresses and finite plate effects had invalidated the results, the amount of ductility increased markedly and was readily apparent at fairly low magnifications (50 times).

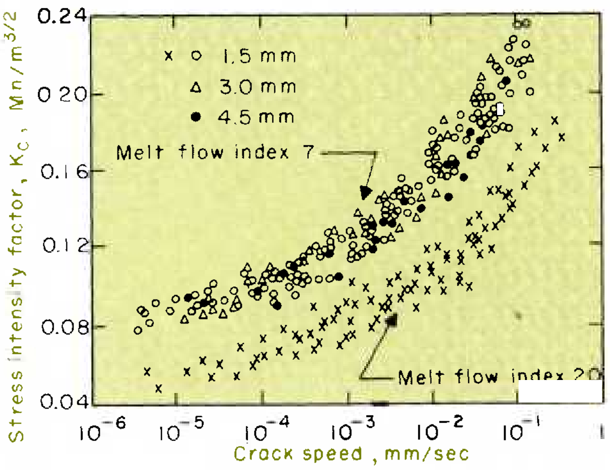

Figure 2. Effect of varying thickness and melt flow index on crack propagation in a methanol environment. Within certain limits there is a unique relationship for each material.

Results obtained with the 3 and 4.5 mm thick material are shown plotted on the MFI 7 curve and show clearly that they are unaffected by thickness and that fractures occur under essentially plane strain conditions. The two curves also show the influence of MFI on ESC fairly clearly, the higher molecular weight material having a definitely greater resistance to environmental attack. This was also found to be true for similar tests in an ethanol environment, the toughness ratios between the two materials being the same for each environment.

Test results suggested that enough information had been obtained to demonstrate that fracture mechanics could describe environmental cracking of polyolefins and that the tests should give sufficiently precise data by which to compare the behavior of different materials. It was felt at the time, however, that a more severe test would be provided by testing materials of greater commercial significance than those chosen for the preliminary series and hence a test program looking at the environmental stress cracking of higher density, low MFI materials has now been inaugurated and some preliminary results are now presented.

ESC of Low MFI Polyethylenes

Two different grades of material were tested, one a medium-density ($\rho = 0.935$) homopolymer of MFI = 0.2 and the other a high-density ($\rho = 0.954$) copolymer of MFI = 0.2. Tests on both materials in methanol indicated that cracking would take too long to occur and hence all tests were conducted in an "Adinol" liquid detergent environment. All tests were carried out in a controlled atmosphere at a temperature of 20 ± 0.5°C.

The first series of tests was again conducted with SEN specimens, initial notches being made with a razor blade, as before. Examples of crack length vs time curves for these materials under dead-weight loads are shown in *Fig. 3*. Even on this basis, it is readily apparent that the copolymer is much more resistant to cracking than the homopolymer, even though the MFI's are not appreciably different. In both cases, as was expected, cracking rates were very much slower than with the low-density material. A long-term test with either of the high-density materials could be as long as 2000 hr (*Fig. 3*) as compared with 20 hr for the low-density material.

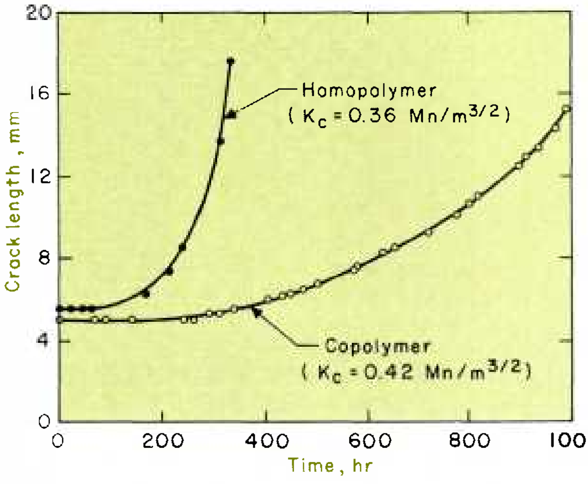

Figure 3. Typical crack length vs. time curves for high-density polyethylene under dead-weight loads. Copolymer is much more crack resistant than the homopolymer.

Values of K_c and crack speed were calculated from the crack length vs time curves, giving results similar to those in *Fig. 2*, except for the speed range, the copolymer data points being above those for the homopolymer. The amount of data available is necessarily less than for the high MFI materials, but there is enough of it to show that the curve is independent of loading and crack length as before, within the confidence limits of ±10%, provided, once again, the applied stresses are not too high. For high stress and long crack length combinations, extended plasticity was observed at the crack tips and the cracks tended to tunnel down the central section of the specimen, leaving the surface regions uncracked (see *Fig. 4*). These surface regions yield, and slow down the cracking. This process is a demonstration of the plane strain susceptibility of polyethylene undergoing ESC; the plane stress regions at the walls of the specimen remain uncracked by the environment. This yielded region occurs on all crack edges, but for slow-speed cracking it is only visible under a microscope and its effect is considered negligible. *Figure 5* is a scanning electron microscope photograph showing the apparent brittle nature of the majority of a crack surface at high magnification (200 times). It can be seen that there is only a marginal amount of microductility.

Figure 4. Fracture surface showing the tunneling effect created by high strength and long crack length combinations. Surface regions yield and slow down cracking.

As a further check upon the validity of the application of fracture mechanics to ESC, it was considered necessary to further investigate the effect of changes in specimen geometry. A number of tests on specimens with widths from 30-100 mm were performed and the results were found to be in good agreement, and so for a more rigorous appraisal a test series was carried out using centrally notched plate specimens (CN) (see

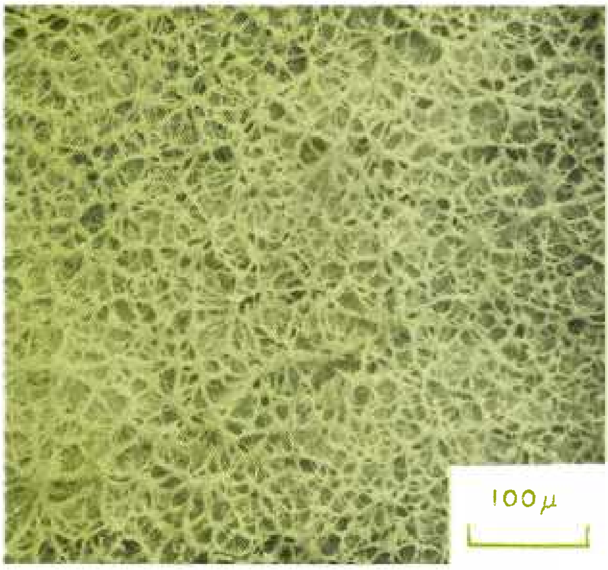

Figure 5. Scanning electron micrograph of a fracture surface at 200 times magnification shows apparent brittle nature of the majority of a crack surface.

inset to *Fig. 6*). In these tests the bending effect caused by finite plasticity is reduced, so that the results might be expected to be slightly different at the fast crack speed range but should provide a check on the validity of the test during slow cracking. The results for one material are shown in *Fig. 6*, plotted on a K_c vs crack speed basis. It is readily apparent that there is very little difference between results and that the points for center-notch specimens lie within the scatter band obtained with the SEN specimens. What is not apparent is the great stability of the symmetry of cracking, which makes testing of CN specimens a good practical proposition.

The validity of these results suggests that the test may now be used to consider the variables in ESC. Since the materials are commercial products, little can be said about them because of their complexity, and so our considerations have turned to the effects of temperature and environment.

The "normal" procedure for accelerating ESC tests on especially tough materials usually involves heating the environment to around 50°C when the environmental attack becomes more severe. There are hidden dangers in this procedure, however, since it is always possible that the "order of merit" observed at lower temperatures may well change with temperature and there is the additional problem of deducing exactly what changes occur in the material itself because of the heating. A series of tests undertaken at different temperatures shows that testing at moderate temperatures could well be valid as regards "order of merit," so that there is now a tendency towards testing at above ambient temperatures because the test time scale is more acceptable.

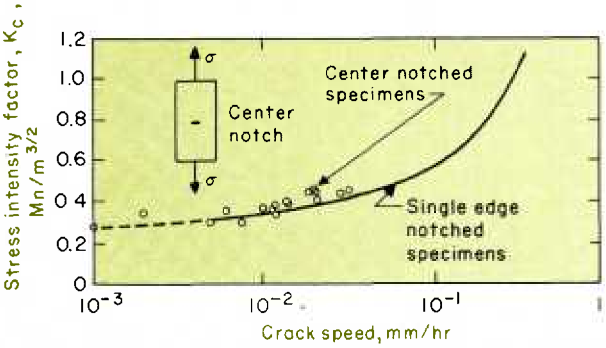

Figure 6. Comparison of single-edge and center-notched specimens shows very little difference in test results.

The other variable is the environment and a number of ideas have been put forward regarding aggressiveness. These include the effects of viscosity, surface tension, film forming ability, and molecular size of the environment. Some work has been done on this problem using fracture mechanics. The K_c vs crack speed curve shown in *Fig. 7* is for the copolymer considered in two detergents and in air. (The effect of air is known as oxidative stress cracking but this distinction is not considered necessary here.) It can be seen from the graph that environment has a greater effect at high cracking speeds, and that at low K_c values there appears to be little difference. This low K_c region is the one important to practical applications, since this is where the serious long-term failures can occur; and it does seem that if a sharp notch can be initiated, perhaps in the presence of a surfactant environment, then this crack may well grow even after the environment has been removed.

Results

The most pleasing aspect of these tests is their consistency in all cases, proving that the K_c vs crack speed approach provides a sensitive measure of ways in which environmentally induced cracks grow in polyethylene. It is particularly noteworthy that results on the two higher density grades follow the same general pattern established previously for the low-density non-commercial grades. Even though cracking times in these tougher materials are exceedingly long and results are taken from tests run for several weeks, there is no inconsistency in the data. Using stress intensity factor K as the controlling parameter rather than adopting the traditional polymer fracture approach of measuring "surface energies" circumvents the difficulties involved in assessing the values of modulus E over the long terms, since all material parameters are accommodated in K. The rate at which material creeps will obviously affect results; but in the present case, viscoelastic responses are shown up in the rates of crack growth and the general shape of the K_c vs crack speed curves. Materials with small viscoelastic response generally do not produce much slow crack growth—if indeed any at all (e.g., thermosetting resins)—whereas materials such as polyethylene do give this wide speed spectrum shown in *Figs. 2, 5,* and *6.*

That the toughness measure, K_c, increases with crack speed is not really surprising, since such behavior is common in other, more glassy plastics (8 and 9). Williams (12) has produced an analysis of the K_c vs crack speed curve for polymethyl methacrylate by converting crack speeds to strain rates. He has shown that curve shape can be predicted using time dependent modulus and yield stress behavior, since increasing the crack speed is effectively the same as increasing the strain rate at the crack tip—hence producing changes in modulus and yield stress.

It is possible that when sufficient data is available a similar analysis will satisfactorily explain the shapes of polyethylene curves and will be able to account for the ways in which different grades react to different environmental systems.

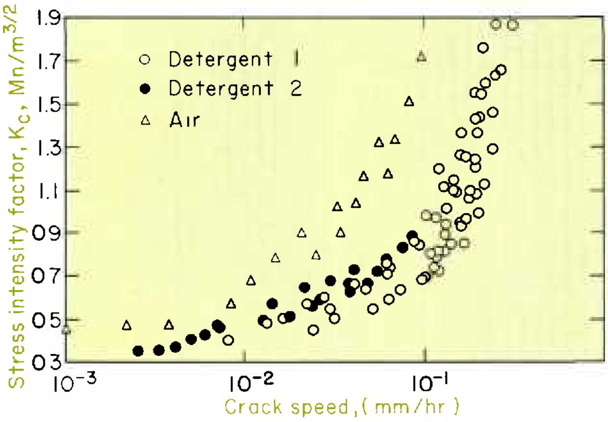

Figure 7. Effects of different environments: two detergents and air. The effect of environment is seen to be greatest at high cracking speeds.

Relevance of the Fracture Mechanics Approach to ESC

The main practical conclusion to be drawn from the results so far is that fracture mechanics parameter K is a sensitive measure of polyethylene resistance to environmental stress cracking. The use of K_c and other allied parameters to explain and describe fracture processes is now standard practice in the metals field and is rapidly becoming accepted in the analysis of fracture in the more brittle glassy plastics. When more results are available on polyethylene, similar advances can be made in the stress cracking of polyolefins.

Because the data is much more sensitive than time to failure data commonly measured in other tests, it is thought that even now, SEN and center-notched tests, are of more use in ranking ESC resistance of polyethylenes—when data is compared on a crack speed basis!

Notched specimens are seen to work very well, since no discrepancy is introduced by materials having a different degree of surface finish. In tests with unnotched specimens, the results necessarily depend to a large extent on surface conditions and will therefore be liable to huge scatter of results, especially where different molds or dies, etc., are used to make test samples. The very nature of the present tests always assumes the existence of flaws in the material and that from these inhomogeneities, cracks grow to produce eventual failure. It is arguable that different materials may have built-in structural differences that make crack initiation less likely, but it is still maintained that even in these cases the K_c vs crack speed curve is a much more sensitive measure of material performance, since structural characteristics which produce toughening would still be manifested in the crack propagation data, i.e., materials with 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 (1) and the minimum K_c value obtained from the K_c vs 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 value into *Eq 10*. Changes in the production process could affect this quantity and by careful tests it should be possible to identify sources of flaw generation.

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