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Fracture mechanics and engineering design in polymers

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Summary

Since polymeric solids do not in general obey classical elasticity theory, they demand a generalised formulation of fracture mechanics. Such a formulation is briefly discussed and then applied to a variety of fracture phenomena in polymers including tensile and creep fracture, dynamic fatigue and stress-corrosion cracking. The amount of data on actual materials is still very limited, but sufficient is available to demonstrate the potential power of fracture mechanics as an engineering design technique. Its exploitation will depend opon our willingness to introduce new materials testing methods (which provide suitable data for fracture mechanics analysis) and upon our surmounting the psychological barrier created for the design engineer by the time and temperature dependence of polymer fracture properties.

Introduction

Polymeric solids (rubbers and plastics) differ from conventional engineering materials in a variety of ways and some of these differences are highly relevant to fracture behaviour. For the purpose of the present paper, in which materials are treated as continuous media, the distinctive characteristics of polymeric solids are as follows.

Relatively low elastic constants
Strong time and temperature dependence of the elastic constants
Non-Hookean elasticity
Visco-elasticity (mechanical losses during cyclic deformation in the 'elastic' range)

In some instances it is possible to ignore the departures from simple elastic/plastic behaviour and thus to employ classical fracture mechanics in a manner completely analagous to that used for metallic materials. Thus glassy polymers such as poly-methylmethacrylate, polystyrene, polycarbonate and natural PVC, together with most thermosetting polymers and some highly crystalline materials can be treated in this way. On the other hand, elastomers (rubbers) and 'soft' crystalline polymers such as polyethylene, together with almost all polymeric materials in their anisotropic forms (e.g. films and fibres) exhibit such strong deviation from classical behaviour that no theory based on classical elasticity and infinitesimal strain assumptions is valid.

The first task in developing the general fracture mechanics of polymers must therefore be to provide a theoretical framework which is sufficiently general to embrace non-classical behaviour. This can then be followed by the second stage of characterising fracture phenomena in polymeric solids in terms of fracture mechanics concepts and by the third and final stage of applying the resulting information to engineering design problems. This paper is subdivided in accordance with this threefold approach.

Before proceeding, however, it must be pointed out that engineering design with polymers is not concerned entirely, or even primarily, with fracture. In many cases the limiting factors on the use of polymeric solids are imposed by processes such as creep deformation, dimensional instability and thermal or ultra-violet degradation. Even in mechanical fatigue, failure can occur by processes which are not, strictly speaking, fracture processes and arise, for example, from 'heat build-up' in poorly conducting specimens subject to mechanical hysteresis. Nevertheless, fracture phenomena involving the initiation and propagation of cracks through the material are frequently the cause of failure in polymeric engineering materials and must impose limitations on design possibilities. Providing non-classical theory is employed where necessary it appears that most fracture phenomena in polymers can be described successfully in fracture mechanics terms, including tensile fracture, fatigue fracture and stress-corrosion cracking.

Formulation of fracture mechanics for 'non-classical' materials

Many polymeric materials are 'non-classical' in the sense that they display non-Hookean elasticity, finite strains and stress-strain irreversibility within the range of recoverable deformation. (See Fig. 1 for examples). It is impossible therefore to define a stress-intensity factor or related parameter in terms of the stress-distribution around a notch or crack calculated using classical elasticity theory. The stress-distribution under these circumstances usually defies calculation, though it has been measured empirically in some non-classical materials (e.g. natural rubber [1]). It was shown by Rivlin and Thomas [2], however, that the energy available to a crack for propagation through such a solid can be calculated in many cases by considering the distribution of stress in regions *remote* from the crack. This is best illustrated by an example.

Consider a sheet specimen having the form [2] shown in Fig. 2. The material is clamped along its long edges as shown and contains a long crack parallel to the clamps. The specimen is stressed by moving the clamps apart perpendicular to their length. The specimen can be divided in four regions as shown. Region A is stress free because it is severed by the crack; region B is in a complex state of stress due to the crack tip; region C is sufficiently remote from the crack tip, and from the free edge of the specimen to be in a state of uniform stress, namely pure shear (because the clamps prevent displacements in the horizontal direction). Region D, finally, includes the free edge and has a complex state of stress. Propagation of the crack by a distance Δc increases region A, and decreases region C, by a volume

$$ld\Delta c$$

where l is the separation of the clamps and d the sheet thickness. Regions B and D remain unchanged since they are defined solely by the geometry of the stress fields around the tip and free edge respectively. The loss in total elastic energy $\mathscr{E}$ consequent upon crack propagation is therefore given simply by

$$-\Delta\mathscr{E} = ld\Delta c \times W$$

where W is the stored energy density in pure shear i.e. in region C. The clamps remain stationary during propagation so that no external work is done. The energy loss per area, A, of fresh crack, and thus the energy available for propagation in the absence of external work is, finally, given by the limit,

$$-\frac{\partial\mathscr{E}}{\partial A} = \tfrac{1}{2}Wl \qquad (1)$$

since

$$A = 2cd \text{ (two surfaces)}$$

Explicit values of $-\partial\mathscr{E}/\partial A$ can be obtained as a function of the measured strain in region C either from theoretical stress-strain relationships if known, or otherwise from experimental tests on the material in pure shear. No assumptions about Hookean behaviour or infinitesimal strain are involved. Conversely, however, the classical result for such a test-piece is obtained as a special case by substituting the classical value for W (in terms of strain or stress) into equation (1).

Similar calculations can be carried out for a number of specimen geometries and further details will be found in the paper by Lake, Lindley and Thomas (this Conference, paper No.). Of perhaps widest general importance is the solution for an edge crack in an infinite sheet under uniaxial tension (Fig. 3), which takes the form

$$-\frac{\partial\mathscr{E}}{\partial A} = kcW \qquad (2)$$

where c is the crack length, W the stored energy density in the bulk of the specimen and k is an undetermined constant. In a 'classical' material of Young's modulus E under uniaxial stress σ,

$$W = \sigma^2/2E$$

and

$$-\frac{\partial \mathscr{E}}{\partial A} = kc\sigma^2/2E$$

Comparing this with the Griffith solution [3] (treating an edge crack as half the Griffith crack) it is clear that k has the value π for a classically elastic solid, and that the classical solution for an edge crack is a special case of equation (2). Greensmith [4] measured the value of k for rubber and found that it is not, in fact, constant with strain. It decreases from its classical value at small strains to a value around unity at strains of several hundred per cent. Recently Andrews and Walker [5] have found by a quite different method, that k also decreases threefold with increasing strain (or stress) in polyethylene. This decrease is not simply a finite strain effect since in polyethylene the reduction of k occurs over a bulk strain range of under 50% compared with a range of several hundred per cent in rubber.

So far we have considered materials which are 'non-classical' in the sense that they exhibit finite strain and non-Hookean behaviour. It has so far been assumed that the stored energy density W is uniquely defined i.e. that the material is reversibly elastic. Many polymers, however, display marked mechanical hysteresis and it becomes difficult to define the quantity W. The study already cited [5] on polyethylene provides an empirical answer to this problem since it was found that crack growth data could only be satisfactorily correlated using a value of W calculated from the extension phase of the stress-strain loop (see Fig. 1) and not from the retraction phase. This is, at first sight, an unexpected result since the retraction curve alone indicates the energy elastically *recoverable* from the system and it is only recoverable energy which can participate in an energy balance between bulk and crack. However it must be remembered that crack growth occurs *continuously* during extension of the specimen whereas the retraction curve characterises the energy recoverable *after* the maximum deformation in the cycle has been achieved. The continuously recoverable energy will be much closer to the total input energy.

This raises the question of the physical validity of the energy balance concept, as opposed to its formal or mathematical usefulness. The latter, as we shall see, is unquestionable, but in *physical* terms it is probable that the parameter $(-\partial \mathscr{E}/\partial A)$ is best viewed as a stress field determinant. As we have seen, the stress field at a crack in a 'non-classical' material cannot be calculated, so that no stress field parameter (such as K of classical fracture mechanics) can be defined directly. The energy balance approach provides us with an indirect method of defining such a parameter and it has been shown empirically for at least one 'non-classical' material [1] that the stress field (intensity and geometry) around a crack is governed by the quantity $(-\partial \mathscr{E}/\partial A)$.

This concludes our brief formulation of 'non-classical' fracture mechanics except for a few definitions. The fracture parameter will be written as $(-\partial \mathscr{E}/\partial A)$ under general conditions. At some values of $(-\partial \mathscr{E}/\partial A)$ crack propagation will occur and under these conditions the parameter will be represented by the symbol $\mathscr{T}$. Thus $\mathscr{T}$ is a value of $(-\partial \mathscr{E}/\partial A)$ for which the crack propagates. This value is not unique, however, since in many fracture phenomena in polymers (e.g. stress corrosion) propagation occurs at different speeds over a wide range of $(-\partial \mathscr{E}/\partial A)$. Finally, it is sometimes useful to define some particular value of $\mathscr{T}$ which characterises some particular event, e.g. the lowest value of $(-\partial \mathscr{E}/\partial A)$ at which propagation occurs or the value of $\mathscr{T}$ at which some change in propagation (e.g. slow to rapid) takes place. Such special values of $\mathscr{T}$ will be designated $\mathscr{T}_c$.

Finally it must be repeated that some plastics are sufficiently 'classical' in their behaviour to be treated in terms of normal fracture mechanics. Under these conditions $\mathscr{T}$ is equivalent to the 'surface work' term usually denoted G and the normally defined 'fracture toughnesses' K_c (plane stress) and K_{1c} (plane strain) can be employed.

Fracture phenomena in polymeric solids

A wide range of fracture phenomena in polymeric solids can be characterised in fracture mechanics terms. These include tensile fracture, other 'direct loading' fracture behaviour, creep fracture or static fatigue, dynamic fatigue and stress-corrosion cracking. In some cases there is still insufficient data available, but some of these areas are briefly reviewed below.

(a) Tensile fracture and non-corrosive creep fracture

The stored energy W_f at fracture in a tensile specimen is related to the length c of the largest suitably oriented edge crack in the specimen by equation (2) which can now be re-written,

$$W_f = \mathscr{T}/kc \tag{3}$$

In accordance with this, model experiments on a wide range of materials containing intentional flaws show that $\mathscr{T}$ has a tolerably constant value for each material providing the temperature and rate of testing are constant. For glassy plastics, for example,

$$\mathscr{T}_c \sim 10^5 \text{ to } 10^6 \text{ erg cm}^{-2}$$

Closer inspection of results, however, show that the situation is rather complicated. The value of $\mathscr{T}$ determined in straightforward tensile tests on pre-cracked specimens is the value for the onset of catastrophic failure. At much lower values of $\mathcal{T}$ slow crack propagation is often observed and can eventually lead to fracture of the specimen. Two situations can occur.

(*i*) $\mathcal{T}$ is a determinable function of the rate of crack propagation and of temperature. This frequently occurs in visco-elastic materials where the energy dissipated at the tip of the propagating crack is directly related to the rate of deformation and, thus, to crack velocity. Under these conditions $\mathcal{T}$ increases with the rate of propagation but decreases with rising temperature. Unfilled elastomers often display this behaviour (Fig. 4) though similar effects of much smaller magnitude have been observed in polymethylmethacrylate [6]. If propagation achieves such velocities that adiabatic conditions obtain, local temperature rise can offset the rate effects leading to velocity instability and catastrophic rupture.

(*ii*) The slow growth occurring at low $\mathcal{T}$ can, alternatively, become self-inhibited so that a small amount of propagation takes place but then ceases until the specimen is further strained. Since the amount of growth is usually small it has little effect upon tensile fracture, but it is fundamental to fatigue fracture.
In these cases tensile fracture occurs at fairly well defined $\mathcal{T}$ and thus corresponds more closely to the simple ideas of fracture mechanics. This behaviour is observed in natural rubber and polyethylene.

It is clear that whilst simple fracture mechanics calculations can be carried out for the latter cases, the application of these ideas to materials in the former category could be very dangerous. In practice one is faced with the problem of 'static fatigue', i.e. fracture under steady applied load after an interval of time. This problem is amenable to treatment provided $\mathcal{T}$ is known as a function of propagation rate. Suppose that the known function $\mathcal{T}(\dot{c})$ can be expressed (as is usually the case) as

$$\mathcal{T}^m = P\left(\frac{dc}{dt}\right) \tag{4}$$

P and m ($m > 1$) are constants at a fixed temperature. For an edge or surface crack

$$\mathcal{T}^m = (kcW)^m$$

So that, rearranging

$$\int_{c_0}^{c} \frac{dc}{(kc)^m} = P\int_0^t W^m dt$$

where c_0 is the intrinsic flaw size

$$\frac{c^{-m+1} - c_0^{-m+1}}{k^m(1-m)} = P\int_0^t W^m dt \tag{5}$$

provided $m \neq 1$.

Various situations can now be treated [7], including a simple tensile test at a known rate of loading (so that $W(t)$ is known) and a creep fracture test in which W is independent of time. Taking the latter example, the time to fracture is found by setting $t = t_f$ and c, the upper limit of crack length equal to infinity. Then equation (5) becomes, since $m > 1$,

$$\{PW^m c_0^{m-1} k^m (m-1)\}^{-1} = t_f \tag{6}$$

Alternately, equation (4) may apply up to some (known) value $\mathcal{T} = \mathcal{T}_c$ for catastrophic fracture. In this case a critical flaw size c_c would be defined for a given value of W

$$c_c = \mathcal{T}_c / kW$$

and used instead of infinity as the upper limit for the integration.

The only indeterminate constant in equation (6) is c_0 so that a value for this quantity is obtained by fitting equation (6) to experimental data.

(*b*) *Dynamic fatigue*

Fatigue failure in polymers can occur as a result of processes such as heat build-up which do not involve the propagation of fatigue cracks, but under moderate loading conditions crack initiation and propagation are the predominant mechanisms of failure. A full treatment [8] of fatigue in polymers has been given elsewhere by the author and only the fracture mechanics aspects can be included here.

Since $(-\partial\mathcal{E}/\partial A)$ can be viewed as a stress field parameter, it is not surprising that the incremental crack growth which takes place each fatigue cycle can be related directly to it. For a wide range of materials, including many metals, glassy plastics, natural rubber and polyethylene, a law of the following form applies:

$$\frac{dc}{dN} = B\mathcal{T}^n \tag{7}$$

N is the number of stress cycles and B and n are constants. Here $\mathcal{T}$ refers to the maximum value in the cycle. Assuming, as before, the existence of intrinsic flaws of maximum length c_0, equation (7) can be integrated to predict fatigue life N_f. Again the edge-crack value can be taken for $\mathcal{T}$ so that,

$$\int_{c_0}^{c} \frac{dc}{B(kcW)} n = \int_{0}^{N_f} dN \tag{8}$$

In a simple fatigue test W is constant, so that

$$\frac{1}{Bk^n W^n} \int_{c_0}^{c} \frac{dc}{c^n} = N_f$$

And if $c_f \gg c_0$, and provided $n > 1$,

$$\{Bk^n W^n (n-1) c_0^{\,n-1}\}^{-1} = N_f \tag{9}$$

This calculation is complicated by the fact that the 'constants' B and n in Equation (7) may only be constant over certain ranges of dc/dN and it may be necessary to define several sets of values (B, n) to cover the whole range. This is true for natural rubber where two ranges, having $n = 1$ and $n = 2$ respectively, must be defined. In polyethylene the situation is illustrated in Fig. 5, which shows log (dc/dN) plotted against log $\mathcal{T}$ for a particular material. Two distinct linear plots appear joined by a transition range. The transition from one characteristic to the other is stress and temperature dependent and corresponds to a change from quasi-brittle to ductile fracture.

This means that the integration of equations (7) to (9) must be carried out in stages corresponding, in polyethylene, to the quasi-brittle, transition and ductile regions respectively, and the resulting partial N_f values summed. This was done for a variety of polyethylenes to give a theoretical fatigue curve (in terms of W against N_f) for comparison with fatigue curves obtained on un-notched specimens [5]. The only 'fitting constant' available is c_0, and some results are shown in Fig. 6. Here the experimental data for fatigue are shown as points on the graph and the theoretical values for three choices of c_0 (3, 4 and 5×10^{-3} cm) by the curves. A remarkably good fit is obtained which also defines the value of c_0 to within 25%. This value is found to correlate closely with the spherulite (or 'grain') size in the material suggesting that c_0 has a real physical significance for polyethylene at least. Similar agreement between fatigue curves and theoretical predictions from crack growth data had previously been obtained by workers on rubber [9], results which stimulated the polyethylene investigations. The value of c_0 required to fit the data in rubber is fairly constant at about 0·003 cm. The intrinsic flaw in rubber is probably a surface ozone crack. No actual

predictions of fatigue data appear to have been made for polymethylmethacrylate but its crack growth behaviour [10] certainly follows equation (7).

(c) *Stress-corrosion cracking*

In common with other materials, polymeric solids are prone to cracking under stress in certain environments. Examples are the ozone cracking of unsaturated hydrocarbon elastomers, the cracking of polyethylene in the presence of surface active liquids and the cracking of glassy polymers in contact with organic solvents (vapour or liquid). Braden and Gent [11] showed that ozone cracking in rubbers obeys a fracture mechanics criterion, i.e. the crack only propagates when,

$$-\frac{\partial \mathcal{E}}{\partial A} > \mathcal{T}_c$$

the critical value $\mathcal{T}_c$ being independent of ozone concentration and having a value approaching 50 ergs/cm^2. Andrews and Braden [12] subsequently showed that this probably represents the true surface energy S of an ozone degraded layer. The behaviour of the rate of crack propagation with increasing $\mathcal{T} > \mathcal{T}_c$ is shown in Fig. 7 (a). The rate of growth is a constant, independent of $\mathcal{T}(>\mathcal{T}_c)$ but is proportional to the ozone concentration and also varies with temperature. Thus,

$$\left.\begin{aligned} \frac{dc}{dt} &= B(T)Z && \text{for } \mathcal{T} > \mathcal{T}_c \\ &= O && \text{for } \mathcal{T} < \mathcal{T}_c \end{aligned}\right\} \tag{10}$$

where $B(T)$ is a function of temperature and z is the ozone concentration. The time to fracture of a specimen is thus given, very simply by

$$t_f = B(T)Zl \tag{11}$$

where l is the width of the sepcimen which must be severed by the crack.

Andrews and Bevan [13] found that the cracking of a glassy plastic, polymethylmethacrylate, in alcohols also obeyed the fracture mechanics criterion, propagation only occurring for

$$-\frac{\partial \mathcal{E}}{\partial A} > \mathcal{T}_c$$

The behaviour of $\mathcal{T}_c$ with temperature has the form shown in Fig. 7 (b). The value of $\mathcal{T}_c$ was fairly constant above some critical temperature T_c and, whilst not as low as $\mathcal{T}_c$ for ozone cracking, was two orders of magnitude smaller than $\mathcal{T}_c$ for catastrophic fracture in the absence of solvent (of the order of 10^3 ergs/cm^2 compared with $\sim 10^5$ ergs/cm^2).

The velocity of crack propagation is not constant with $\mathscr{T}$ above $\mathscr{T}_c$ but increases in such a way that

$$\frac{dc}{dt} = \mathscr{F}_1\,(\mathscr{T} - \mathscr{T}_c)\mathscr{F}_2\,(T - T_c) \tag{12}$$

where $\mathscr{F}_1$ and $\mathscr{F}_2$ are functions. Over quite a wide range of data these functions are nearly linear for some cases so far investigated. If the corrosion crack grows from an edge crack, for which $\mathscr{T} = kcW$, equation (12) becomes for linear $\mathscr{F}_1$,

$$\frac{dc}{dt} = B(T)\,(kcW - C) \tag{13}$$

where $B(T)$ and C are constants. This equation can clearly be integrated to predict lifetime under stress in terms of the intrinsic flaw size, as was done previously for other fracture processes. Insufficient data is yet available however to provide examples.

Application to design

The application of the foregoing information to engineering design is potential rather than actual. This is, firstly, because it is only recently that data on actual materials has become available in a suitable form (rubber is perhaps an exception to this statement) and secondly, because engineering design of any kind with polymeric solids is a relatively new art. A great deal of work remains to be done in characterising polymer fracture phenomena in terms of fracture mechanics before comprehensive design calculations become feasible. For example, the extremely promising predictions of fatigue lifetime have so far been limited to fatigue in tension without compression. In rubber it is safe to assume that a compressive phase in the fatigue cycle does not affect the process at all, but this would not be true for glassy or crystalline plastics where plastic deformation occurs at the crack tip. The effects of mean stress level, interrupted loading and temperature will all have to be investigated before design calculations of any generality can be carried out.

In spite of this, however, it is clear that a modified form of fracture mechanics, which is not limited to classically elastic materials, is accessible to us and that, given sufficient material data, fracture behaviour may be predicted under a variety of circumstances. If these exciting possibilities are to be realised and exploited two things must be done. Firstly, those responsible for the testing and physical evaluation of polymeric materials must recognise the importance of characterising fracture phenomena in terms amenable to fracture mechanics treatment. This means that a variety of unconventional measurements must be made, and some conventional measurements recognised as completely

unsatisfactory. Crack growth data under fatigue conditions, for example, must supplement traditional fatigue testing, and corrosion crack propagation rates must replace the usual, but almost meaningless standard tests for solvent stress cracking. This re-evaluation of test methods is probably the most important step to be taken if design against fracture is to become a practical proposition.

The second requirement, of course, is that the engineer should, as far as possible, use the methods of fracture mechanics to supplement traditional techniques. The time and temperature dependence of polymer properties present a psychological as well as a practical barrier to such usage, but I hope that the brief survey given in the preceding pages will encourage engineers to believe that the problem is not insuperable.

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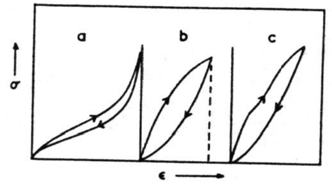

Fig. 1. Stress-strain loops for some 'non-classical' elastic materials; (a) natural rubber; (b) polyethylene (below yield); (c) a synthetic fibre.

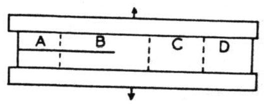

Fig. 2. 'Pure-shear' testpiece. (After Rivlin and Thomas [1].)

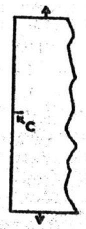

Fig. 3. Edge crack in a semi-infinite, uniformly stressed lamina.

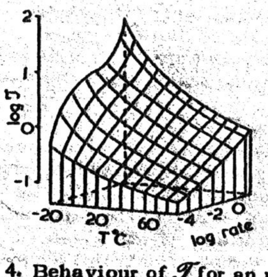

Fig. 4. Behaviour of $\mathcal{T}$ for an unfilled elastomer (SBR). $\mathcal{T}$ is in units of 10^6 ergs cm^{-2} and rate in cm s^{-1} (After Greensmith and Thomas, *J. Polymer Sci.*, vol. 18, p. 189, 1955).

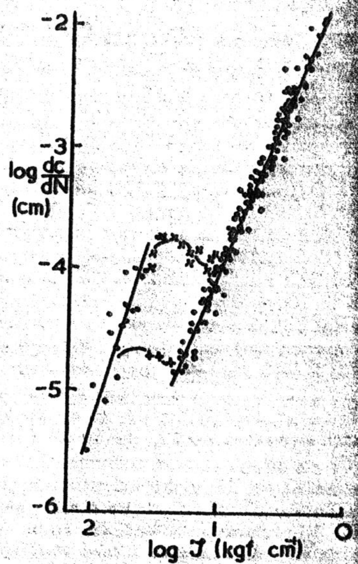

Fig. 5. Crack growth characteristics a particular grade of low density polyethylene. The two transition ranges relate to different stress levels in th specimen. (After Andrews and Walker [5].)

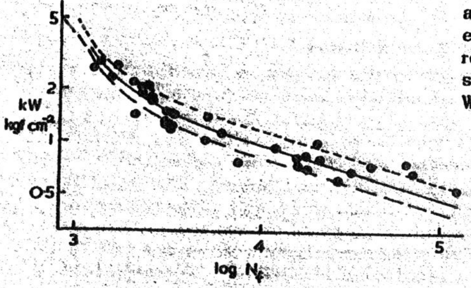

Fig. 6. Fatigue data on the same polyethylene as Fig. 5. Points are experimental results, lines are predicted from crack growth data, using c_0 values of $3\cdot10^{-3}$ cm (short dashes), $4\cdot10^{-3}$ (solid line) and $5\cdot10^{-3}$ (long dashes). (After Andrews and Walker [5].)

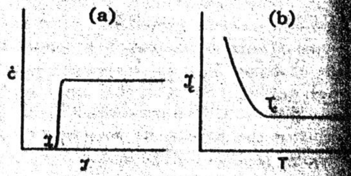

Fig. 7. Stress-corrosion cracking behaviour (schematic), (a) velocit of ozone cracks in rubber as a function of $\mathcal{T}$. (b) dependence of upon temperature for solvent stres cracking in polymethylmethacrylat