

Mechanics of Fracture in Polymeric Solids

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A. Introduction

The intent of the study of the mechanics of fracture in a continuum is to improve the predictability of the crack propagation process; this observation is true regardless of the type of material with which one may be concerned. While this predictability is usually employed to prevent failure by fracture, it may be equally well utilized to determine the optimal conditions for inducing fracture most favorably such as in machining or comminution. Fracture mechanics finds a third use in the description of certain macroscopic, nonlinear constitutive phenomena which are occasioned by the appearance of cracks. With regard to brittle solids we refer here to the compression properties of rocks. In connection with polymers we note that the growth of (surface) cracks can produce macroscopic stress relaxation while the formation of (crack like) crazes in uncrosslinked glassy polymers lead to a time dependent phenomenon which resembles the yielding of metals.

Because of the limits on the length of this paper it is not possible to review here thoroughly the work on polymer fracture from the viewpoint of continuum mechanics. Such a review has been accomplished recently elsewhere [1]⁺. Instead it appears desirable and appropriate in view of a largely non-polymer oriented audience to present a brief exposition of the major similarities and differences between the fracture of polymers, as representatives of strongly rate sensitive solids on the one hand, and of the more conventional engineering materials featuring less rate sensitive - if not totally insensitive - properties, on the other hand. Following that exposition we highlight several developments in the fracture of polymers which use the fracture mechanics of rate-insensitive solids to varying degrees as a point of departure. Against this background we sketch an experimentally and analytically integrated examination of crack propagation in a viscoelastic elastomer.

⁺Numbers in square brackets denote references at the end of the paper.

This is done in the hope that this development provide an illustrative and possibly even useful link between the mechanics of fracture in (some) polymers and those materials which have been regarded conventionally as rate insensitive.

B. Some General Problems in the Continuum Description of Polymer Fracture

The process of fracture in polymers can be understood fundamentally in terms of the interatomic forces that control the cohesion of the material at the tip of a growing crack. An example of which atomistic and molecular parameters may be required for such a description has been given by Zhurkov [2]. Clearly, at this level of detail both the concepts of the fracture process as well as the experimental methods that can be brought to bear on their clarification can differ widely where polymers and metals or ceramics are concerned. On the other hand, if it is permissible to neglect such detailed differences in a more macroscopic approach to fracture which emphasizes the continuity of the non-fracturing part of the solid, the material difference is minimized and the similarities in the fracture of diverse materials emerge. But the molecular and microscopic dissociation of the crack tip material depends, in general, on the stress history transmitted to it via the time-dependently deforming material surrounding the crack tip, which deformations in turn depend on the deformation characteristics of the disintegrating material. Thus a close interaction arises in general between the decomposing crack tip material and the surrounding continuum, whose assessment is complicated by the fact that the macroscopic or average properties of the disintegrating material cannot be measured in a bulk specimen apart from a crack tip. One must therefore supplant this lack of knowledge by assumptions which need to be examined experimentally for their reasonableness; such assumptions, usually called fracture criteria, are thus an essential part of the analytical fracture mechanics of rate sensitive and insensitive solids. However, whether specific criteria that have been found useful in the fracture of rate-insensitive solids are also directly applicable to poly-

mers is not obvious a priori. Polymers may be classified molecularly according to whether they are crosslinked or uncrosslinked, and their mechanical behavior further according to whether they are below the glass transition temperature (T_g) (glassy state) or above (rubbery state). A further distinction is made with regard to the presence or absence of a crystalline phase. This spectrum of molecular structure plus the thermal state engenders a variety of mechanical properties which is also reflected in the fracture behavior. Many elastomers (crosslinked polymers above T_g) sustain large deformations, and some (e. g. natural rubber) form a crystalline structure under high strains due to the parallel orientation of the chain molecules. This strain-induced crystallinity has no direct parallel in metals; its formation and disappearance is time dependent, and if it occurs at the tip of a crack its high reinforcing ability can prevent crack propagation effectively. Sufficiently far below the glass temperature polymers are rigid and their rupture response tends to have the appearance of a brittle solid (like an inorganic glass) except that they exhibit a noticeable rate sensitivity under varying loads. The quasi-brittle behavior is especially pronounced for the crosslinked polymers while uncrosslinked ones may exhibit a time-dependent [3] yield phenomenon caused by the appearance of crazes as mentioned in the introduction [4-7]. In addition to their contribution to the yield-like behavior of certain glassy polymers - which causes also the stress-whitening if the small crazes are numerous - crazed material is found at the tip of cracks [7] and its mechanical properties are distinctly sensitive to the deformation history [8] although any specific dependence on deformation rate is only poorly documented. Thus, like the micro mechanics of plastic deformations in metals crazes introduce microscopically inhomogeneous deformations, represent the behavior of the material at the crack tip and, like plastically deforming metals, introduce characteristics that differ during loading and unloading. To what extent their

time-dependence can be neglected in fracture experiments - if it can be circumvented at all - is not clear at this time.

The rate dependence of polymer properties introduces a further distinction: For rate-insensitive solids one is usually concerned with the problem of whether a crack will or will not propagate at all. If it does propagate its extension rate may be so high that for practical consideration the propagation phase is uninteresting. The same is generally not true for polymers. Speaking in molecular terms, the disintegration of the crack tip material is a continuous function of the applied load history. But from a macroscopic viewpoint it may appear that the crack remains stationary for some initial time span, after which the crack tip material seems to give way to crack propagation, which later may occur only slowly. One speaks thus of a crack speed initiation and of a crack propagation phase. In some solids the initiation phase may take up the major part of a structural life (natural rubber, polystyrene) although this observation may depend strongly on the initial loading history, while in other solids the initiation phase is short and crack propagation consumes by far the major portion of the structural life (e.g. the material studied later in this paper). However, not enough is known about the crack growth characteristics of the various polymers to make general statements in this regard.

It is well known that the rigidity of polymers is a function of their temperature. In the rubbery domain above the glass transition the elasticity is derived largely from entropic processes and the rigidity, say the shear modulus, is then proportional to the absolute temperature⁺. But a change in temperature can cause a much more dramatic change in the relaxation (creep) behavior. In amorphous polymers, for example, a change of 3° C (just above the glass transition temperature) may change the time scale of the relaxation (creep) process by a factor of ten; at other temperatures this sensitivity is usually less. Out of this temperature susceptibility can arise a problem which is (possibly) not paralleled in severity in the fracture of metals, and which

is aggravated by the fact that polymers are generally poor conductors

⁺ Strictly speaking this has been shown valid for the equilibrium behavior of elastomers on the basis of the classical theory of rubber elasticity.

of heat: The deformation of a viscoelastic solid is accompanied by conversion of mechanical work into heat, which conversion is a function of the local deformation rate; this change in the local temperature affects the relaxation (creep) behavior locally, so that the local properties are a function of the local strain history as well as of heat flow from neighboring points. This thermo-mechanical interaction produces thus effectively inhomogeneous material properties at the crack tip. Moreover, the energy dissipation in the crack tip vicinity depends in general on the history of the applied loads as well as on the (generally unknown) history of crack propagation. For repetitive (cyclic) loading it has been demonstrated that heating is not negligible [9, 10] but the conditions, if any, under which this effect can be neglected for crack propagation under monotonic or steady loads has not been delineated satisfactorily to the writer's knowledge.

C. Some Special Problems in the Continuum Description of Polymer Fracture

It has already been mentioned that below the glass transition temperature polymers tend to exhibit brittle fracture behavior, while sufficiently far above that temperature crosslinked polymers exhibit elastic properties, though not necessarily linearly elastic ones. When one considers these two extreme cases of viscoelastic limit behavior it is natural to explore whether in these situations the mechanics of fracture for rate-insensitive solids is able to correlate fracture. If the results were affirmative one could then use this limit behavior as a starting point to investigate the time dependence of polymer fracture. These explorations have been accomplished: In their review of the mechanisms of the fracture of polymers at the Swampscott Meeting in Fracture⁺ Bueche and Berry reported the successful application of brittle fracture theory to glassy PMMA [11]. Much discussion was devoted to the fracture energy and its microstructural origin [12]; additional work on polystyrene reinforced the applicability of the Griffith

⁺ A precursor of the International Conferences on Fracture

theory to glassy polymers [12], although no extensive variations in loading histories were attempted. It was found however [12] that in contrast to the behavior of metals the fracture energy for PMMA increased with decreasing temperature, but the question was not raised what happens when the applied load is less than that producing immediate and brittle fracture and is sustained for a long time. Vincent and Gotham [13] determined on PMMA that under these conditions the crack propagates with a velocity which depends on the magnitude of the applied loads (see also [14]). The energy required for this process was a function of the crack speed (or of the applied loads). It seems to follow therefore, that although a load increasing monotonically to rupture can induce fracture behavior in agreement with the Griffith criterion of brittle fracture, a different load history produces a different fracture history*, in other words, the relation of the fracture energy to the load and crack propagation history remains an open question.

With regard to the fracture of elastomers Rivlin and Thomas pointed out [15] that an energy balance criterion is valid for these solids provided they deform elastically (i. e. a strain energy density function can be defined). It was soon found in tests [16, 17], however, that the energy required per unit new surface increased with the (steady) rate of crack or tear propagation, although the elastomer deformed macroscopically in an apparently elastic manner. This observation prompted the suggestion that like other rate sensitive properties of elastomers this rate dependent fracture energy was a property function of the material. Work on the exploitation of this concept and its application to fracture inducing non-steady crack or tear growth was reported at the first and second International Conferences on Fracture, respectively, by Williams [18] and Lake, Lindley and Thomas [19]. For loading histories which invoke only the elastic response in the bulk of the solid - excepting possibly a small region around the crack tip - a total strain energy of the solid can be defined and its change with unit crack extension can be determined, if necessary, by experimental

means [19]. Equating this change in elastic energy to the rate dependent fracture energy allows the calculation of the instantaneous crack velocity commensurate with the instantaneous change in the elastic energy content of the solid.

When the load history on a cracked structure and its temperature are such that viscoelastic deformations in the bulk of the solid cannot be neglected it is also no longer possible to determine an elastic energy change with crack propagation and the approach proposed in [19] breaks down. One must therefore search for a description of the fracture process which avoids global energy arguments⁺ but concentrates on the local conditions at the crack tip.

An early attempt in that direction was reported by M. L. Williams at the Conference on Fracture at Maple Valley⁺⁺ [20]. Without restriction to any particular material, though motivated by Mullins' work on elastomers [21], Williams considered crack propagation to be the sequential breaking of bundles of polymer molecules at the crack tip. For reasons of analytical simplicity these bundles were assumed to obey a Voigt solid description and were supposed to rupture when they attained a critical (uniaxial) strain. For an infinite sheet under a Heaviside tensile stress, directed normal to the crack, the problem was reduced to the calculation of the time-dependent uniaxial strain in a Voigt solid subjected to a particular stress history. In view of the constantly applied external loads this stress history was the sole consequence of the continuously enlarging crack. The calculations predicted an exponential dependence of the crack speed on the first power of the applied load, a result that was also corroborated by McClintock [22] for a Maxwell material under antiplane shear. A similarly simple model of fracture, but incorporating non-linearly viscoelastic effects, was exploited successfully by Bueche and Haplin [23].

In a separate attempt to describe the time dependence of crack propagation in polymers Barenblatt, Entov and Salganik [24] explored ana-

+ One might argue that the total elastic energy content of a solid can be obtained by subtracting from the work done on the solid the energy dissipated and converted into heat. There is as yet no method of calculating the energy dissipation for a non-linearly viscoelastic solid, and calorimetry seems to be a very arduous way to achieve this goal experimentally.

++ Another precursor of the International Conferences on Fracture.

lytically the rate dependent deterioration of the material at the crack tip which was embedded in an elastic solid. Rather than assume a visco-elastic response for this crack tip material as Williams had done, Barenblatt et al. used Zhurkov's rate theory [25] to calculate the degradation under the stresses imposed by the surrounding (elastic) material. Intended for the analysis of glassy polymers, this model attempts essentially to explain the time dependence of the fracture process by the time dependent molecular processes preceding or accompanying craze formation. Instead of characterizing this process by a constant or rate dependent macroscopically conceived fracture energy this model employs the activation energy of the molecular fracture process as the governing physical parameter. The mathematical difficulties encountered by these researches are, however, formidable and seem surmountable only through numerical methods. So far their results are therefore of a qualitative nature.

We have now considered two approaches to polymer fracture which emphasize either the glassy or the rubbery limits of the relaxation spectrum and which draw primarily on experiments to extend the classical global energy criterion for (linearly) elastic solids to polymers. In addition we have cited two representative attempts to describe the time dependent fracture analytically by considering processes occurring at the tip of the crack. In the next section we review a further crack-tip-related model of viscoelastic fracture under simultaneous consideration of experiments and analysis.

D. Steady crack growth in a linearly viscoelastic solid

It should be stated from the outset that the application of linear viscoelasticity theory to the problem of fracture may lead to an erroneous or inadequate characterization. However, if one considers on the one hand the unresolved state in which the description of non-linear viscoelastic behavior finds itself and the need for clarifying concepts of the time dependence in fracture on the other hand, then it becomes clear that any clarification of thought that can be provided through linearly viscoelastic behavior is (potentially) more informative than no effort at all.

The motivation for the following developments may be stated in the form of several questions: Are the classical criteria (energy criterion, limiting strain or stress criteria) for the fracture of brittle solids also valid for (some) polymers, provided proper account is taken of the material rheology? If an energy criterion is valid, how is the rate-dependent fracture energy [19] related to the rheological properties? How sensitive is a solution of the crack propagation problem to variations of experimental parameters, and what kind of experimental information is needed to predict the speed of crack propagation reasonably accurately?

Answers to these questions must be resolved ultimately through experiments. Building on the encouraging results of earlier investigations [26-28] we report therefore further experiments and analysis. It is clearly beyond the scope of a review paper such as this to present these developments in any detail. Because of this limitation on writing space we record therefore only the salient points and refer the reader to a more comprehensive treatment in reference [29].

a) Material properties and crack propagation experiments. We precede the analysis by a description of the physical properties of the elastomer which is to serve as the test material. We use an optically clear and highly birefringent polyurethane elastomer called Solithane 113⁺. Its distinguishing features are that under small deformations it is thermorheologically simple and that it breaks under relatively small strains (see later in this section)*; this latter property nourishes the hope of correlating a linearly viscoelastic analysis with experiments. The material exhibits a fracture surface at any of the crack speeds encountered which is mirrorlike as for inorganic glasses and featureless under the scanning electron microscope [30]. This latter property indicates that the mechanism of fracture at the crack tip is (possibly)

⁺The equivoluminal composition of the two component system as supplied by the manufacturer, The Thiokol Chemical Corporation. The birefringence was used to determine the crack tip stress-free condition; glass transition temperature $T_g = -18^{\circ} \text{C}$.

insensitive to the crack speed or the applied loads, and it provides a valuable upper bound estimate on the surface roughness produced in the fracture process.

The material is produced in sheets 12 x 12 x 1/32 inches. After an initial high temperature cure (2 hrs. at 140° C) the sheets post cure for several weeks at room temperature and change their properties at a steadily decreasing rate until after some time they are constant for practical purposes. In order to avoid changes during the weeks of experimental work the material was first stored for one year over silica gel. In spite of careful production methods the mechanical properties vary from sheet to sheet. To account for this variation the creep compliance of each sheet was measured and the results are summarized in figure 1; numbers in circles denote sheet identifications. Although the shapes of the curves vary somewhat, only a normalization with respect to time was made: Upon bringing the different creep compliances to an average coincidence by shifting along the log-time scale and by using sheets ① and ⑤ as a norm, time scale corrections were obtained which were later applied to the crack propagation data. All tests on any one sheet were concluded within a time span of two to three weeks.

The creep compliance was measured under constant tensile load, with a linearly variable differential transformer, allowing strains on the order of two-to-three percent. The creep specimens (0.5 x 6 x 1/32 inches) were cut from the crack propagation specimens after the latter had been used and broken.

The crack propagation specimen is dimensioned in figure 2: Application of a constant and uniform strain ϵ_{∞} across dimension $2b$ (cf figure 2) produces a constant rate of crack propagation, provided the time of observation is longer than the longest significant relaxation time (1 min at 0° C). Excepting three cases, all strains ϵ_{∞} were chosen to produce crack speeds lower than one inch per minute, primarily to eliminate or reduce possible crack tip heating. Both the creep compliance and the crack propagation data shown in figure 3 were obtained at different

temperatures and then shifted along the log-time axis to produce master curves. All data sets were shifted independently of each other with the corresponding shift factors recorded in figure 4. We point out that the raw shift factors for the crack propagation data are shown as the dotted symbols in figure 4; they were further corrected in accordance with a temperature factor occasioned by the test method as described later in the analysis discussion. The master curves for the crack propagation data for all tests are shown in figure 5, while figure 6 displays data obtained for one sheet only, in order to provide an assessment of how influential the sheet-to-sheet variations were.

b) Fracture criteria and conditions at the crack tip. We investigate two criteria applied at the crack tip: One is based on an energy argument, while the other relates to an ultimate strain which the material can sustain. To this end we employ a crack tip cohesive force model. The motivation for the use of this model comes from the observation that many polymers produce a filamentous structure at the crack tip while the latter moves or is stationary [4-6, 31]. This filamentous structure can occur macroscopically as an open "foam" - or (sub) microscopically in an equivalent form - and provides cohesive forces on the newly forming crack surfaces. For a steadily moving crack these forces should attain a maximum somewhere within or at the end of the cohesive zone and drop to zero continuously at the point which we would define as the crack tip. In figure 7 we show an idealized force distribution with the crack tip located at $\bar{X} = 0$. Several comments are in order in lieu of a more logical and complete development of the crack tip model: First, the model assumes that the mechanical disintegration of the crack tip material occurs in a vanishingly thin strip along the crack axis. Second, the dissociating material possesses no viscoelastic or elastic properties of its own and does not therefore enter an interaction with the bulk of the fracturing solid,

except through providing cohesion forces. For the present we need not assume that the forces are independent of the crack speed with regard to both distribution and magnitude since we are interested in steady crack propagation; experiments only can and will show whether such an assumption is called for. The time dependence of the fracture process is thus implicitly dependent only on the viscoelastic response of the continuum surrounding the crack tip.⁺ Third, we prefer the use of the bilinear cohesive force distribution ($\beta \neq 0$ in figure 7) over the conventional constant distribution representing "yielding" for two reasons: On the one hand a steadily moving crack demands a continuous rather than discontinuous force distribution for physical consistency. On the other hand a discontinuous distribution associated with a "constant yield stress" assumption engenders mathematical difficulties which are resolved easily by resorting to a continuous distribution, from which the result for a discontinuous one is obtained as a limit ($\beta \rightarrow 0$) - if desired. Fourth, and finally, we remark that the present model differs from the Dugdale slit model, beyond the minor distinction concerning the force distribution, by the physical phenomenon underlying the rupture process. The cohesive forces are not the result of a yielding mode induced by the crack tip in a thin sheet⁺⁺ but it is a consequence of the manner in which the material is believed to come apart, regardless of whether the solid represents a thick or a thin section. In terms of the proposed line-fracture model the ultimate strain criterion is expressed more appropriately as a crack opening displacement criterion; With reference to figure 7 we require thus for the ultimate strain criterion, with u_0 a constant and \dot{a} the crack tip speed

$$u_y(0, 0, \dot{a}) = u_0 \quad (1)$$

⁺ We recall in this context the computations by Barenblatt et al. [24] who assumed that the time dependence of fracture derived from the rate processes within the domain of disintegrating material.

⁺⁺ We shall see that in spite of the small sheet thickness in the present experiments (1/32") the conditions at the crack tip are not those appropriate to generalized plane stress since the cohesive zone is smaller than the thickness by several orders of magnitude.

For the energy criterion we ask whether the work done per unit crack extension by the tractions in the cohesive zone is a constant, which constant may possibly be interpreted as the energy required to rupture the chemical bonds of the polymer [28]. Denoting by $\dot{u}_y(x, 0, \dot{a})$ the velocity component of the crack boundary normal to the crack axis, by T_n the normal tractions and by Γ the constant fracture energy, one writes the energy criterion as

$$\int_0^\alpha T_n(x) \cdot \dot{u}_y(x, 0, \dot{a}) dx = \Gamma \dot{a} \quad (2)$$

For a constant crack propagation speed the time derivative is readily converted to a spatial derivative, whereafter integration by parts yields, in view of $T_n(0) = 0$, $u_y(\alpha, 0, \dot{a}) = 0$ and the definition of the function T_n in figure 7

$$\int_0^\beta u_y(x, 0, \dot{a}) dx = \frac{\beta \Gamma}{\sigma_0} \quad (3)$$

It is evident from (1) and (3) that if Γ and σ_0 are constant (or $\Gamma/\sigma_0 = \text{const}$) then for $\beta \rightarrow 0$ the two criteria are equivalent⁺ and independently so of the crack speed \dot{a} .

c) The viscoelastic boundary value problem representing the moving crack and the form of the fracture criteria. We restrict our attention to the case when the size of the disintegration zone α is small compared to any other (in-plane) dimension of the solid. This restriction allows us to work only with the dominant part of the stress field in the crack tip vicinity. We confine ourselves furthermore to conditions which cause only growth along the crack axis.

Consider then the problem for a linearly viscoelastic half space which is loaded at infinity by as yet unspecified tractions, and on the surface $y = 0$ by the normal tractions

$$T_n = \begin{cases} 0 & x - \dot{a}t \leq 0 \\ \sigma_0 \frac{x - \dot{a}t}{\beta} & 0 < x - \dot{a}t \leq \beta \\ \sigma_0 & \beta < x - \dot{a}t \leq \alpha \end{cases} \quad (4)$$

⁺ Assuming that u_y is continuous at the crack tip for $\beta \rightarrow 0$

with the shear stress $\tau_{xy} = 0$ on $-\infty < x - \dot{a}t < \infty$. The prescription on the normal displacement of the crack surface is

$$u_y(x, 0, \dot{a}t) = 0 \quad \alpha \leq x - \dot{a}t \quad (5)$$

To the requirements (4) we add that of finite stresses at $x - \dot{a}t = \alpha$. For the exploitation of (1) and (3) we need the displacement $u_y(x, 0, \dot{a}t)$. The solution may be obtained by several methods [29, 32-34] but the presentation of any exceeds the writing space available. Therefore only the essential results are stated below (for an incompressible solid); more detail may be found in [29]. Let the far field stresses produce a singular stress field characterized by a stress intensity factor K in the absence of tractions on the crack surface (including the segment $\alpha \leq x \leq \alpha$), and of body forces. Let, furthermore,

$$X = x - \dot{a}t \quad \rho = X(t)/\alpha \quad r = X(\xi)/\alpha$$

$$R = \beta/\alpha$$

$$c = (1-R)^{1/2}$$

$$c_0 = (1-R)^{1/2}$$

$$A(R) = \left\{ [1 - c_0 - \frac{1}{3}(1 - c_0^3)]/R + c_0 \right\}^{-1}$$

$$F(\rho) = c_0 + \frac{A(R)}{2} \left[\frac{R-\rho}{2} \ln \left| \frac{c+c_0}{c-c_0} \right| - c_0 \rho \right] + \frac{A(R)}{4R} \left[\frac{R^2-\rho^2}{2} \ln \left| \frac{c-c_0}{c+c_0} \right| - \frac{\rho^2}{2} \ln \left| \frac{c+1}{c-1} \right| - (1-c_0)(1+\rho)c + \frac{1}{3}(1-c_0^3)c \right]$$

$$D(t) = \text{tensile creep compliance, } D_0 = D(0)$$

$$\Delta D(t) = D(t) - D_0$$

Then the normal crack surface displacement $u_y(\rho, \dot{a}t, a)$ for $\rho < 1$ can be written for $K = \text{const.}$ as

$$u_y(\rho, 0, a) = \frac{4K\sqrt{\alpha}}{\sqrt{2\pi}} \left\{ D_0 F(\rho) - \int_{\rho}^1 \Delta D \left[\frac{\alpha}{a} \cdot (r-\rho) \right] F^{\rho}(r) dr \right\} \quad (6)$$

to which one must adjoin the condition on the finiteness of the stresses as stated following equation (5); this condition requires the interdependence of K , α , β and σ_0 through

$$\sigma_0 = \frac{1}{2} \cdot \sqrt{\frac{\pi}{2}} \cdot \frac{K}{\sqrt{\alpha}} A(R) \quad (7)$$

We note in passing that for a uniform cohesive stress ($\beta=0$) and for a rate insensitive solid ($\Delta D(t)=0$) (6) and (7) reduce to the familiar result obtained for the slit model of plastic fracture [35].

So far α , β or σ_0 were not specified. There seems to be no a priori dependence for them on crack speed (i. e. on the applied loads) as long as the finiteness condition (7) is satisfied. Disregarding the variation of β for reasons that become clear later, we can consider two extremes which may bound the experimental crack propagation behavior: If we allow α to remain constant, then σ_0 has to increase with increasing crack tip stresses (increasing K). Since increasing K results usually in a crack velocity increase, an increase in σ_0 would be associated with an increase in crack propagation rate; such a possibility would be reasonable for a viscoelastic solid and in keeping with Zhurkov's reaction rate model as presented by Barenblatt et al [24]. On the other hand one may consider σ_0 to be independent of the crack speed, but then α increases with increasing stress intensity K . In accordance with these two extremes the two criteria (1) and (2) provide four limit relations. Let us use the notation

$$\mathcal{D}\left(\frac{\alpha}{a}, \rho\right) = E_{\infty} \left\{ D_0 F(\rho) - \int_{\rho}^1 \Delta D \left[\frac{\alpha}{a} (r-\rho) \right] F^{\rho}(r) dr \right\} \quad (8)$$

$$\Theta_R\left(\frac{\alpha}{a}\right) = \frac{A(R)}{R} \int_0^R \mathcal{D}\left(\frac{\alpha}{a}, \rho\right) d\rho$$

and particularize the problem to the long-time or relaxed conditions experienced in the crack propagation experiments described in section B. Since the stress intensity for the geometry in figure 2 is then $K = E_{\infty} \epsilon_{\infty} (4b/3)^{1/2}$, ($\nu = 1/2$), we obtain, upon using the further notational definition

$$Q = \frac{\pi b E_{\infty}^2 A^2(R)}{6 \sigma_0^2} \quad (9)$$

for the ultimate strain criterion

$$e_{\infty} \mathcal{D}\left(\frac{\alpha_0}{a}, 0\right) = \frac{\sqrt{6\pi}}{8} \frac{u_0}{\sqrt{b\alpha_0}} \quad \alpha_0 = \text{const.} \quad (10)$$

$$e_{\infty}^2 \mathcal{D}\left(Q \frac{\epsilon_{\infty}^2}{a}, 0\right) = \frac{3 \sigma_0 u_0}{4 E_{\infty} b A(R)} \quad \sigma_0 = \text{const.} \quad (11)$$

and for the energy criterion

$$\epsilon_{\infty}^2 \Theta_R \left(\frac{\alpha_0}{\dot{a}} \right) = \frac{3\Gamma}{4E_{\infty}b} \quad \alpha_0 = \text{const.} \quad (12)$$

$$\epsilon_{\infty}^2 \Theta_R \left(Q \frac{\epsilon_{\infty}^2}{\dot{a}} \right) = \frac{3\Gamma}{4E_{\infty}b} \quad \sigma_0 = \text{const.} \quad (13)^+$$

If the material is thermorheologically simple one sees with the aid of (6) that a change in temperature affects the time scale through a shift factor ϕ_T which multiplies the velocity \dot{a} . Moreover, on the basis of the classical theory of rubber elasticity the equilibrium modulus is proportional to the absolute temperature T ; in (11) and (13) E_{∞}^2 enters the argument of Θ or Θ_R through Q (see equation 9). If we write thus the temperature dependent equivalent of (13), for example, we obtain, with T_0 as a reference (here 273°K) and with E_* the equilibrium modulus at T_0 ,

$$\epsilon_{\infty}^2 \Theta_R \left[\frac{\pi b E_*^2 A^2(R)}{6 \sigma_0^2} \frac{\epsilon_{\infty}^2}{\alpha} \frac{T^2}{T_0^2 \phi_T} \right] = \frac{3\Gamma T_0}{4E_* \Gamma b} \quad (14)$$

Thus the crack velocity data need not necessarily time-temperature shift according to the shift law for thermorheologically simple solids but may involve further temperature corrections. Moreover, these possible corrections as evidenced in (14) are occasioned by the test method since they result from the prescription of the load in the form of displacements (strain) rather than tractions.

We add here a brief observation on the relation of the rate dependent fracture energy mentioned in section B; let this energy be denoted by $S(\dot{a})$. For the strip geometry in figure 2 this quantity can be expressed for constant temperature by [28]

$$S(\dot{a}) = \frac{4}{3} E_{\infty} \epsilon_{\infty}^2 b \quad (15)$$

Substituting, for example (15) into (12) yields

$$S(\dot{a}) = \frac{\Gamma}{\Theta_R \left(\frac{\alpha_0}{\dot{a}} \right)} \quad (= 2\Gamma; \dot{a} \rightarrow 0) \quad (16)$$

+ For the limit of $\beta \rightarrow 0$ equation (13) reduces to the result given in [36]. While equation (13) - as well as (10-12) - apply strictly only to steady crack propagation due to assumptions incorporated into (6), the result in [36] is derived with the intent to treat a general crack speed history.

Thus the rate dependent fracture energy [19] is the product of the intrinsic fracture energy Γ , presumably of molecular origin, and a non-dimensional function $[\Theta_R(\alpha_0/\dot{a})]^{-1}$ which embodies the (viscoelastic) rheology of the material surrounding the crack tip. This result contradicts the suggestion in ref [18] that the rate dependent fracture energy be the sum of the intrinsic fracture energy (surface energy) and of the viscous contribution. Finally, if (15) is combined with (13) instead of (12) a less simple relation results, namely

$$S(\dot{a}) \Theta_R \left[\frac{\pi}{8} \frac{E_{\infty} A(R)}{\sigma_0^2} \frac{S(\dot{a})}{\dot{a}} \right] = \Gamma \quad (17)$$

The relations (10-13) are plotted in figure 8 in such a way that they coincide for $\dot{a} \rightarrow 0$; this adjustment affects only the right hand sides of these equations which await yet experimental interpretation. These results were obtained by integrating (8) numerically with the material properties recorded in figure 1 (sheets ④ and ⑤). A variation of R from zero to unity had no significant effect on the shapes of these curves; $R = \frac{1}{2}$ was therefore used.

It is perhaps surprising that the ultimate strain and the energy criteria for $\sigma_0 = \text{const.}$ agree so well over the whole velocity range displayed. The agreement is not one in principle but a consequence of the fact that the maximum of the log-log slope of the creep compliance in figure 1 is not any greater. It is thus a consequence of the material properties, and it can be shown that for a standard linear solid possessing the same short-and long-time properties as those in figure 1 the two criteria predict different results, though not markedly so. However, many materials exhibit log-log slopes smaller than those shown in figure 1; since the present material is more representative of other materials than the standard linear solid, one can argue that for practical purposes the ultimate strain and the energy criteria lead to the same result, provided the maximum cohesive stress remains independent of the crack speed.

d. Experimental Evaluation: We have yet to examine whether the relations (10-13) are able to correlate the experimental results in figures 4 and 5. In each one of these criteria there are two unknown pa-

rameters: the possible pairs are (u_0, α_0) , (u_0, σ_0) for the ultimate strain criterion and (Γ, α_0) , (Γ, σ_0) for the energy criterion. The quantities u_0 or Γ may be chosen so that the proper limit is obtained as $\dot{a} \rightarrow 0$. The parameters α_0 or σ_0 are obtained by matching the theoretical and experimental velocity scales.

The best fit of the data was obtained with the ultimate strain and energy criteria for which $\sigma_0 = \text{const}$. These relations, (11) and (13) are shown as the solid lines in figures 5 and 6. In view of the marked difference for the criteria (10) and (12) exhibited in figure 8 the data clearly favor the criteria (11) and (13).

The parameters which one extracts from fitting to the data are

$$\begin{aligned}\Gamma &= 0.018 \text{ lb/in} \\ \sigma_0 &= 1.7 \text{ to } 2.5 \cdot 10^4 \text{ psi} \\ u_0 &= 1.3 \cdot 10^{-6} \text{ inch (300 \AA)} \\ \alpha &= 2.5 \text{ to } 1.3 \cdot 10^{-4} \epsilon_\infty^2 \text{ inch} \\ &= 6.3 \text{ to } 3.1 \cdot 10^4 \epsilon_\infty^2 \text{ \AA}\end{aligned}$$

where the range in σ_0 and α corresponds to the solid curves in figures 5 and 6. The intrinsic fracture energy is of the same order of magnitude as that determined earlier on nominally the same material but with a different pretest history [28]. To our knowledge there exists no good estimate for the magnitude of σ_0 . If the material were a crystal one would expect a value on the order of ten percent of the elastic modulus. The fact that the above range of σ_0 is between seven and ten percent of the glassy modulus (2.5×10^5 psi) may be significant, but could equally well be fortuitous if one considers the amorphous molecular structure of the material and the large deformations which this structure experiences at the crack tip. With regard to the size of the cohesive zone we recall the appearance of the fracture surface, whose glassy and mirror-like smoothness indicates roughness below a quarter of a wavelength of light. Using, for example, 5000 \AA as an indicative wavelength one finds that the roughness should be below 1200 \AA , although the cohesive zone might be larger. For a strain of $\epsilon_\infty = 0.1$ one finds $\alpha \approx 600 (300 \text{ \AA})^2$ while at the limit of $\dot{a} \rightarrow 0$ for $\epsilon_\infty = 0.01$, $\alpha \approx 6 (3) \text{ \AA}^2$. On the

average the value of α is acceptable in the light of the upper bound provided by the smoothness of the crack surface, but for $\dot{a} \rightarrow 0$ the zone represents clearly molecular rather than continuum mechanical dimensions. In looking at these small values of α critically we must not forget, that this datum (and the value of σ_0) is the result of matching the theoretical velocity scale to the experimental one which was, in turn assembled by a none-too-accurate time-temperature shift factor. In addition we recall that we have not accounted for the non-linearly viscoelastic response of the highly deformed material at the crack tip. If the large strains⁺ at the crack tip have the effect of shifting the relaxation spectrum to longer times then this would result, for the present developments, in a value of α which is erroneously too small. The meaning of u_0 is probably more strongly dependent on the mechanical model of fracture (a slit zone of zero thickness) than any of the other ones, but it affords a rough estimate of the shape of the deformed cohesive region at small strains ϵ_∞ ($\epsilon_\infty = 0.01$, $u_0 = 300 \text{ \AA}$, $\alpha = 6 \text{ \AA}^2$) as well as larger ones ($\epsilon_\infty = 0.1$, $u_0 = 300 \text{ \AA}$, $\alpha = 600 \text{ \AA}^2$). Finally we must be aware of the possibility that the parameter α does not literally correspond to the size of the zone in which fracture occurs actually in the experiments. It could possibly also stand for the size in which the molecules reach their ultimate extensibility. If this were so then β would have to be considered as the actual length over which the material breaks down. However, α would probably still determine the local size scale in the crack tip region which measures the domain in which the most significant portion of viscous energy dissipation occurs.

E. Concluding remarks

We have attempted to review briefly the major problems in the macroscopic description of crack propagation in polymers. In addition we have presented an experimentally and analytically integrated investigation of a fracturing viscoelastic solid, which investigation suffers probably most from an inadequate assessment of non-linearly viscoelastic

⁺ We deal here potentially with strains so large that they induce crystallization in natural rubber.

constitutive behavior. Such shortcomings notwithstanding the relatively simple model for crack propagation is able to correlate the steady crack growth of a low strength elastomer rather adequately. It was found that either an ultimate strain (crack opening displacement) criterion or an energy criterion describes the fracture growth of the particular polyurethane elastomer studied, provided that in either case the maximal crack tip stress was independent of the crack speed. It was found also that for thermorheologically simple solids the time-temperature shift of crack propagation data need not necessarily be precisely the same as that obtained from the reduction of relaxation or creep data. Furthermore, the parameters describing the average properties of the cohesive material at the crack tip are reasonable when measured against the little information that is available for an estimate apart from the curve fitting procedure. Finally we emphasize that we have investigated only steady crack propagation and that on the basis of past experience, but not on the strength of this analysis, the results may be applicable also with good approximation for monotonically increasing stress intensities. However, for decreasing stress intensities one must resolve how the properties of the cohesive material influence the crack tip stress field in the unloading process.

In conclusion we hope that this study can clarify concepts of fracture in some viscoelastic solids. Since we know already of some elastomers to which this model does not apply we expect that the results presented here aid nevertheless in posing new questions on the fracture of other materials in a rational manner.

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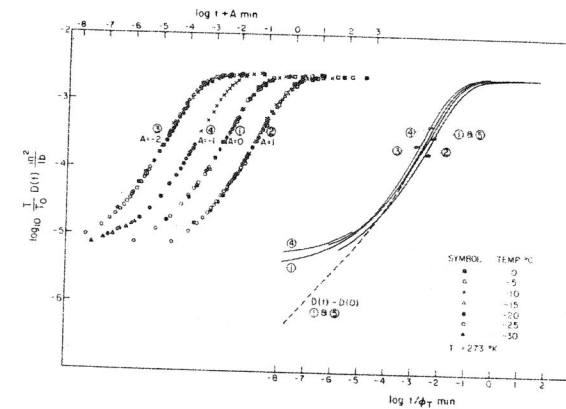


Figure 1: Master curves of the creep compliances for different sheets of Solithane 113 (equivoluminal composition).

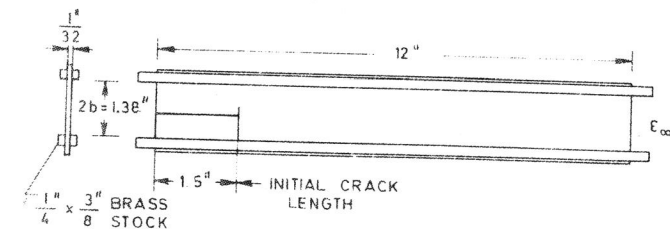


Figure 2: Crack propagation specimen (pure shear specimen) Brass stock was joined to elastomer with Eastman 910 adhesive.

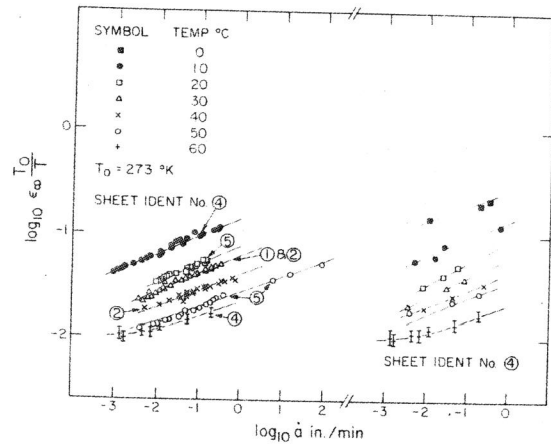


Figure 3: Crack propagation rates at different strains ϵ_{∞} and different temperatures. Left set of data from various sheets, right set from one sheet only to assess the effect of sheet-to-sheet variability in properties.

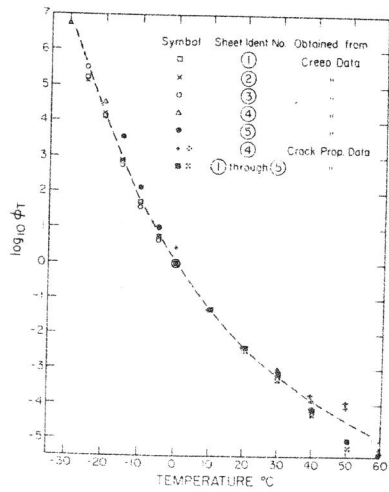


Figure 4: Time-temperature shift factors for figures 1, 5 and 6

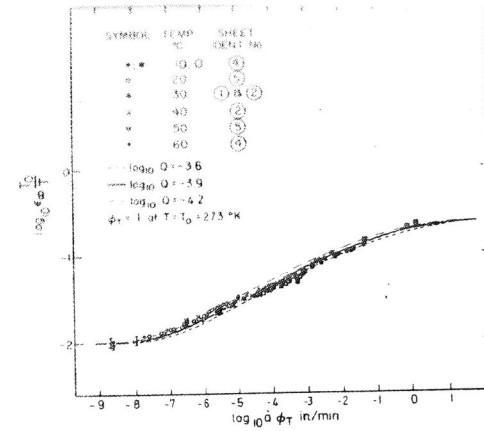


Figure 5: Master curve of crack propagation rates obtained on various sheets

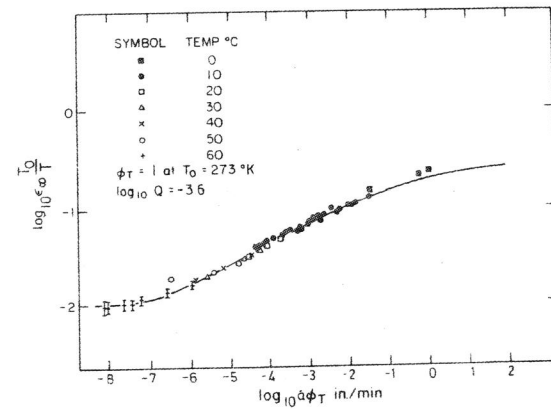


Figure 6: Master curve of crack propagation rates obtained on specimens cut from a single sheet.

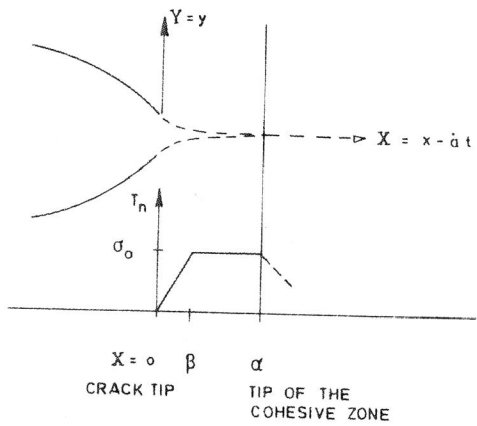


Figure 7: Definition of crack tip parameters and geometry.

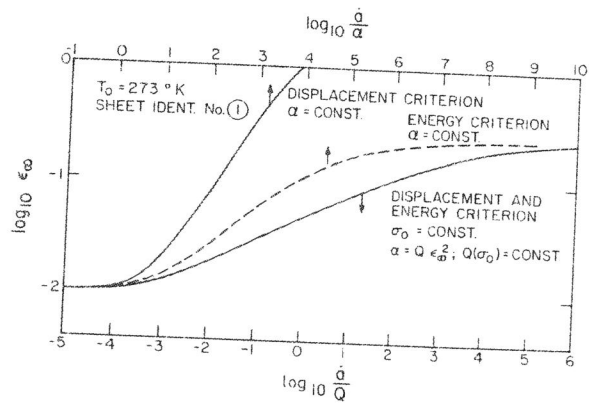


Figure 8: Comparison of the ultimate strain and energy criteria for constant α and σ_0 ; creep properties of figure 1. Parameters u_0 and Γ adjusted so that $\dot{a} \rightarrow 0$ for $\epsilon_\infty = 0.01$