

Time Dependent Fracture of Polymers

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ABSTRACT

The fracture behavior of polymers is reviewed with emphasis on the time dependent aspects of the problem. Following a delineation of the history of crack propagation investigations in linearly viscoelastic materials, the effects of temperature and solvent environment are examined besides the special effects arising from fatigue loading. These phenomena are examined for both crosslinked and uncrosslinked polymers. Some special consideration is given to the phenomena connected with craze formation in amorphous homopolymers as well as in crystalline materials as exemplified by polyethylene. Finally, status of analytical tools and formulations of fracture problems involving non-linearly viscoelastic material behavior is delineated by means of some examples.

KEYWORDS

Fracture; polymer fracture; time dependence; viscoelasticity; plastics.

INTRODUCTION

The past decade and a half has seen a tremendous increase in the engineering use of polymers in a wide variety of applications. While this march of polymer applications, largely at the expense of the traditional engineering metals, has produced equal volumes of steel and of polymers already several years ago, it is projected (NRC, 1981) that by the turn of the century the weight of polymers produced will equal or exceed that of steel. Although much of these polymers is used in wrapping of commercial products, their varied design advantages over metal applications make them attractive in fields outside of everyday household usage, such as in the automotive and aero-space industries, in civil engineering applications to gas and liquid transport and as coatings in the paint and electronic industries.

The primary drivers in these usages are their generally high resistance to corrosive environments; their ease of manufacture and processing, including exploitation of induced anisotropy for preferential strength orientation; their ease of recycling at costs lower than most traditional materials (containers); and, not least, their generally high strength/weight ratio. The latter is a realistic advantage not only in the aero-space industry, but is also projected to be of cost-saving significance in the civil construction industry; rather than considering the material cost per se - which is usually higher than traditional construction materials - lower cost can result from reduced

use or elimination of heavy construction equipment.

Polymers as a class of materials exhibit a large spectrum of mechanical properties according to the large range of possibilities by which their molecular and supra-molecular morphology can be arranged. These varied molecular conformations are also responsible for a considerable range of failure/fracture behavior. As the synthesis oriented chemist is able to generate seemingly unlimited numbers of polymers with widely differing physical response characteristics, the problem is today more our inability to associate in a unique way the known features of the molecular structure with their failure/fracture behavior.

As outlined in figure 1, one usually distinguishes crosslinked and uncrosslinked (=linear) materials; these are also often referred to as thermosets and thermoplastics, respectively. Thermoplastics occur in either amorphous or in (partially) crystalline form, and those used in structural applications are stiff enough to deserve the name solid, though in principle, depending on the use temperature, they may behave like liquids under (extremely) long time loading. Crystalline polymers are often a mixture of amorphous and crystalline phases, with molecule chains passing between both; for these materials the glass transition temperature of the amorphous phase can be below or above the environmental use temperature and still yield "solids" of considerable stiffness.

Further modifications in polymers are introduced through "mixing" one or more, either physically or at the molecular/chemical level (co-polymers), which, depending on their thermodynamic compatibility, results in microscopically multiphase, seldom or never in molecularly homogeneous

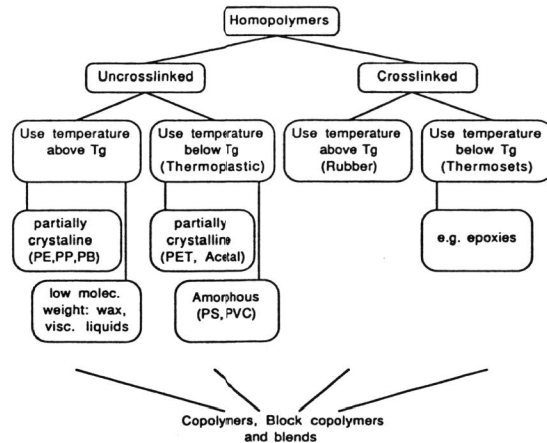


Fig. 1 Polymer classification.

materials. It is clear that with such a palette of properties available it will be not be possible to deal with even the most important of them in detail in this review. Thus, we shall be concerned primarily with reviewing the status of time dependent crack propagation in crosslinked and uncrosslinked polymers; for the former a distinction between rubbery and rigid polymers needs to be made while for the latter differences between amorphous and crystalline materials is in order.

Depending on the use temperature all these materials exhibit viscoelastic characteristics to differing degrees. As a consequence it is generally necessary to consider, in addition to the environmental parameters that influence time dependent failure, the load history in the fracture process much more carefully than is the case with the more traditional, metallic engineering

materials. Accordingly we shall review the influence of the time dependent loading on the failure process to the extent that this behavior is understood today.

The basic question posed in connection with crack propagation in viscoelastic materials is how the time scale of the load application interacts with the intrinsic time (-temperature) scale of the material. Specifically, it is of interest to understand how the instantaneous rate of crack propagation is influenced by the history of applied loads, by the history of the crack propagation and by the intrinsically viscoelastic properties of the material. Often this question can be considered in the context of specific load histories encountered in applications, namely: how is crack propagation influenced under loading that a) varies little or not at all for long periods of time (static fatigue), b) varies monotonically to specimen failure in a relatively short time (laboratory time scale) and c) varies cyclicly in a fatigue type loading. We shall first consider these questions in a somewhat historical review of fracture of crosslinked polymers and elastomers in particular.

CRACK PROPAGATION IN CROSSLINKED POLYMERS

Structural applications of crosslinked polymers may demand that the material possess a glass transition temperature either above or below the use temperature. In the former case we deal with "rigid" thermoset polymers (e.g. epoxies used as adhesives or matrix materials in composites), or with rubbers (e.g. automotive tires, sealants).

Thermosets

Thermosets are generally considered to be rather brittle when used at temperatures well below the glass transition. This characteristic depends, of course, on the degree of crosslinking of the polymer chains, but as a rule of thumb the brittle behavior is typical of these solids. As a consequence, their failure behavior is rather well described in terms of linear fracture mechanics, provided the loading is such as to invoke short term fracture; that situation prevails, for example, when a test specimen or structure is subjected to monotonically increasing load in the laboratory until fracture ensues. This statement may not hold when loading is extended over such long periods of time that relaxation or creep phenomena become apparent. Under such short term loading the mobility of the crosslinked polymer chains in the glassy state is so limited that molecular rearrangement in the macroscopic form of material yield is normally very restricted. Accordingly, if yield like behavior is observed -usually at "elevated" temperatures- it is definitely of the small scale type and thus renders failure largely amenable to analysis by the rules of linear fracture mechanics. Our knowledge of failure due to crack propagation under long term loading derives primarily from our understanding of fracture of these solids when exposed to temperatures above the glass transition (elastomeric behavior) and the understanding that the viscous dissipation accompanying crack propagation is the same as that accompanying crack propagation in elastomers.

Elastomers

Monotonic Loading - Constant rate of crack propagation. The time or rate dependent fracture behavior of these materials is probably the one best understood today of the polymers even though typical large deformations complicate virtually all of the analyses and interpretation of experiments. The reason for this understanding is basically that the complications of highly non-linearly viscoelastic behavior associated with yield-like phenomena are absent in rubbers, if one discounts the special complications introduced in some materials such as natural rubber (NR) and Ethylene-Propylene Rubber (EPR) due to crystallization under high strain.

The first rational treatment of rate sensitive fracture behavior of rubber is associated with investigations at the Natural Rubber Producers Research Association (NRPRA), Welwyn Garden, England.

Following Rivlin and Thomas's observation (Rivlin *et al.*, 1953) that if stress and deformation fields cannot be calculated the fracture behavior of a structure may still be describable in terms of an energy necessary to generate new fracture surface, A.G. Thomas and coworkers embarked on a series of experiments (Thomas, 1955) that demonstrated that such an energy was (reasonably) independent of the test geometry but depended on the (constant) rate of fracture propagation (rate dependent energy release rate). The energy release is computed on the basis of nonlinear, but purely elastic behavior, which relegates the rate sensitive energy dissipation to a small domain about the tip of the crack or tear. No explicit dependence of this fracture energy on the viscoelastic properties of the elastomer were involved or examined and changes in crack speed resulting from transient loadings were not considered in the experiments. The application of this concept to engineering analyses for structural life prediction required the determination of the energy release rate of the fracturing solid as a function of the crack geometry, from which knowledge the appropriate, instantaneous rate of crack propagation could then be determined; from this crack speed history the total failure time could then be calculated (Lake, *et al.*, 1970). This approach to characterizing viscoelastic fracture in elastomers was reviewed by A.G. Thomas at the Brighton ICF2 in 1969.

In order to introduce the explicit dependence of the time dependent fracture behavior on the viscoelastic material behavior Williams had devised an ultimate strain model for time dependent crack growth by discrete jumps (Williams, 1963), along lines of linearized stress analysis for the classical fracture problem for brittle solids. Following a similar approach (discrete jump propagation), but with realistic material behavior and using Irwin's energy balance analysis for the unloading tractions at the tip of an advancing crack, Mueller and Knauss derived a relation (Mueller *et al.*, 1971 a) that explicitly displayed the interaction of the loading, the fracture geometry, the (linearly) viscoelastic material behavior and a postulated, rate-independent or intrinsic fracture energy Γ (Mueller *et al.*, 1971 b). The jump distance, assumed to be a constant (material property), was an essential parameter needed in the viscoelastic characterization of the problem. This model agreed well with experiments and explained the relation of time dependent loading on crack propagation speed; it explained the source of the rate dependent fracture energy $\Gamma \dot{a}$ in the NRPA studies and in particular that it depends on the ratio of the intrinsic fracture energy and on the creep compliance of the fracturing solid¹. Its extension to crack growth with non-constant velocity was documented in (Knauss, 1970) and at the ICF3 in Brighton, England.

This model was improved by replacing discrete jump propagation of the crack with continuous growth through the Barenblatt/Dugdale hypothesis (Barenblatt, 1962, Dugdale, 1960) and was reviewed at the Munich ICF3 (Knauss, 1973). Within experimental accuracy, an energy balance or a crack opening displacement criterion gives the same result. Briefly, the model incorporates rate-insensitive forces not necessarily distributed uniformly in a cohesive zone of size α (c.f. Fig. 2) that is adjusted so as to eliminate any singularity at the crack tip. The model is evaluated in an analysis allowing for general and arbitrary material representations that is exact within the limitations of linearly viscoelastic stress analysis (constant Poisson's ratio) for a steadily propagating crack tip under a constant far field stress intensity factor. With $D(t)$ denoting the uniaxial creep compliance, the model yields an equation that relates the stress intensity factor, K_∞ , the creep compliance and a fracture parameter such as the rate independent fracture energy, Γ or the crack opening displacement, u_0 together with the magnitude of the cohesive forces σ_0 to the speed of crack propagation, \dot{a} :

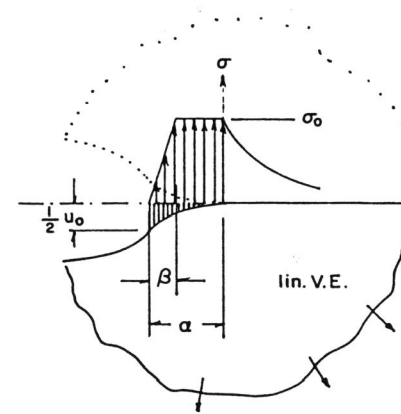


Fig. 2 Crack tip parameters.

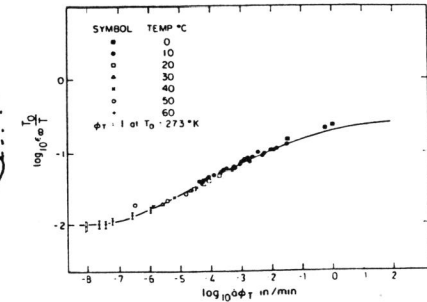


Fig. 3 Master curve of crack-propagation rates obtained on specimens cut from a single sheet.

$$\frac{3}{4} \frac{K^2}{\sigma_0} D_\infty \Theta \left[\frac{\pi K^2}{8 \sigma_0^2 \dot{a}} \right] = u_0 \quad (1a)$$

$$\frac{3}{4} K^2 \Theta \left[\frac{\pi K^2}{8 \sigma_0^2 \dot{a}} \right] = \frac{\Gamma}{D_\infty} \quad (1b)$$

where

$$\Theta = \lim_{R \rightarrow 0} \frac{A(R)}{R} \int_0^R \theta \left[\frac{\alpha}{\dot{a}}, \rho \right] d\rho$$

$$\theta \left[\frac{\alpha}{\dot{a}}, r \right] = \frac{1}{D_\infty} \left\{ D_0 F(r) - \int_r^1 \Delta D \left[\frac{\alpha}{\dot{a}} (\rho - r) \right] F'(\rho) d\rho \right\}$$

and $F(r)$, $A(r)$ are functions arising out of the viscoelastic stress analysis (Knauss, 1973).

For reference purposes we note that $\theta(x) \equiv \Theta(x) \equiv D(x/3)/D(\infty)$.

Figure 3 shows the comparison of equations 1a and 1b with experiments on a polyurethane elastomer under conditions of constant crack propagation rates (constant stress intensity), when the stress intensity factor is expressed in terms of the strain appropriate for the experimental test configuration, and under the assumption of a constant cohesive stress, σ_0 .

It is instructive to consider briefly the interaction of loading, geometry and material behavior on

1. This interrelation was discussed at the Brighton ICF2, but the written contribution of that discussion was inexplicably deleted from the proceedings.

crack propagation in this result. The parameter that determines the fracture strength is the intrinsic fracture energy $\Gamma = \sigma_0 u_0$ which has the same meaning as the fracture energy in the Griffith/Irwin energy balance concept. In the present, viscoelastic context it also has the same meaning as the threshold energy estimated in fatigue experiments on elastomers by Lake and Thomas (Lake *et al.*, 1967). Both the loading and the geometry are represented in the far field stress intensity factor while the time or rate dependent material response is embodied in the functions Θ or θ ($\equiv D$).

The velocity of crack growth is determined by the viscosity of the material surrounding the crack tip; while this is, perhaps, self evident, it is interesting to interpret that result in terms of eq. 1a for the COD criterion (Recall that the energy and the COD criteria give essentially the same result): as the viscoelastic bulk material on the crack axis enters the cohesive zone, points just above (and below) the axis begin to move normal to it to form the cusp shaped boundary of the cohesive zone and then the crack boundaries. The amount of this crack-normal displacement depends on the time it takes for the material point to traverse the cohesive zone. If that time is short (high crack speed) the viscoelastic material will allow only a small amount of crack opening unless that displacement is enlarged (multiplied) by a suitably large load (large stress intensity factor). Conversely, if that traverse time is long (slow crack growth) then there is commensurately much time for the viscoelastic material bordering the cohesive zone to creep open and only a small load (stress intensity factor) is needed to supply the COD.

Inasmuch as the creep behavior of the material is subject to the time-temperature trade-off principle (thermorheologically simple behavior) this result also highlights the reason why the failure/fracture behavior of elastomers follows this simple time-temperature behavior. This observation had been made earlier in connection with simple tensile tests (Smith, 1958).

The same model using the energy balance with constant cohesive forces had been proposed (independently) in 1970 by Kostrov and Nikitin (Kostrov *et al.*, 1970) and in 1975 by Schapery in a sequence of papers (Schapery, 1975).

Rate Dependent Fracture Energy. Before considering the growth of a crack under varying stress intensity, it is worthwhile to consider the relation of the above delineated model to the rate dependent energy considered by Thomas and coworkers at the NRPR (Thomas, 1958). This is done recognizing the fact that equations 1a,b apply strictly speaking only to linearly viscoelastic solids while Thomas's work deals with rubber under large deformations at the crack tip and under the assumption of purely elastic material behavior. Within (linearly) elastic theory the energy needed to propagate a crack with constant velocity \dot{a} , $S(\dot{a})$ is given implicitly by (Mueller *et al.*, 1971, Knauss, 1973)

$$S(\dot{a}) \cdot D \left\{ \frac{\pi S(\dot{a}) / \dot{a}}{8 D(\infty) \sigma_0^2} \right\} = \frac{4}{3} \Gamma \quad (2)$$

if constant cohesive forces are appropriate.

We note thus that the "rate dependent" energy is essentially the product of the intrinsic energy Γ and the function Θ^{-1} , which clearly represents the viscoelastic material behavior; inasmuch as the latter is also approximately equal to the time-shifted creep compliance the energy is also approximately given by (Knauss, 1973)

$$S(\dot{a}) \cdot D \left\{ \frac{1}{3} \frac{\pi}{8} \frac{S(\dot{a}) / \dot{a}}{D(\infty) \sigma_0^2} \right\} = \frac{4}{3} \Gamma \cdot D(\infty) \quad (3)$$

This form is important to recognize because it allows the determination of the intrinsic fracture energy as the lower limit of this fracture energy and thus the estimation of the threshold for long-time or slow crack propagation. This value has been estimated from molecular considerations by Lake and Thomas (Lake *et al.*, 1967). In the case of crosslinked materials this lower limit may be determined by eliminating or significantly reducing viscoelastic response by swelling the material in an appropriate solvent (Mueller *et al.* 1971 b). By this means Ahagon and Gent have shown reasonably good agreement between the simple molecular Lake/Thomas model and measured values (Ahagon *et al.*, 1975).

The same fracture and energy considerations apply to the interfacial fracture of elastomeric adhesive bonds, whether the fracture proceeds through the adhesive or along the interface (Knauss, 1971). The characterization of bond strength in terms of a threshold fracture energy is of considerable engineering importance for establishing long-term failure limits on certain engineering designs. In this context the investigations of Ahagon and Gent (Ahagon *et al.*, 1975) are of direct interest.

Variable Crack Propagation Rates. Because the deformation history of the material surrounding the moving crack tip is of prime importance it is clear that changing crack speeds in an arbitrary crack propagation history is also important and that this result, derived for the constant crack speed, is not generally applicable to arbitrarily variable histories of the stress intensity factor. However, it is possible to estimate the error involved when the result for constant crack propagation speeds is applied to situations of varying stress intensity and crack speeds (Knauss, 1976). The result is that when

$$\frac{\dot{K}(t)}{K(t)} < < \frac{\dot{a}(t)}{2\alpha(t)} \quad (4)$$

then the crack propagation laws 1a,1b are applicable to variable stress intensity histories. Physically eq. 4 expresses the fact that constant crack speed conditions prevail approximately as long as the stress intensity factor does not change markedly during the time during which the crack propagates a distance of (two times) the cohesive zone size. With that limitation equation 1a or 1b becomes thus an ordinary nonlinear differential equation for the crack length as a function of the time dependent stress intensity factor.

As an example of the use of (4) consider the fracture of a sheet of viscoelastic material under tension σ_∞ by a centrally growing crack. Making use of the stress intensity factor $K(t) = \sqrt{\pi} a(t) \cdot \sigma_\infty$ and the dependence of α on it one finds for a constant cohesive stress σ_0 that

$$\frac{\sigma_\infty}{\sigma_0} < < 2\sqrt{2} \quad (5)$$

should hold. This inequality is always satisfied. Accordingly, one computes from eq. 1a or 1b (numerically) the crack growth history as a function of time. For a constant far field load this yields crack growth results of the type shown in Fig. 4 for the same material properties associated

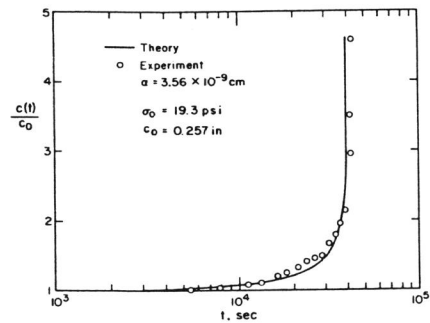


Fig. 4 Crack length as a function of time for initial crack size of 0.26 inch.

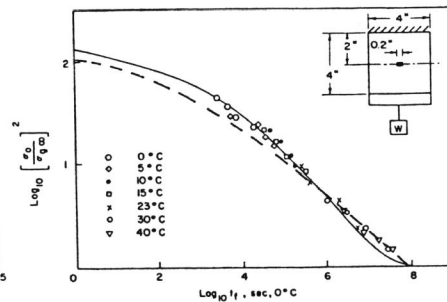


Fig. 5 Failure times as a function of load on a cracked sheet. (dashed curve - Schapery, 1975).

with Fig. 3; if one considers the material sheet to have failed when the rate of crack growth achieves a sufficiently high rate, one can obtain the failure time of the specimen (sheet) as a function of load level and this is illustrated in Fig. 5 in comparison with experimental data. This result is thus an analytical estimate of the "static fatigue" behavior of a viscoelastic material.

Fatigue Loading. Because of their viscoelastic behavior, polymers generate heat under cyclic deformation which raises the temperature if the rate of heat generation exceeds the heat flow to the surroundings. In view of the characteristically high temperature sensitivity of mechanical polymer properties it is clear that such hysteretic heating can have a dominant effect on the failure behavior under cyclic loading. This failure may run the spectrum between excessive softening of the bulk material and ensuing failure by deformation without fracture to the result of localized heating at the tip of a crack accompanied by a redistribution of the stresses and complicated failure characteristics. In the following discussion we shall not address the complications arising from hysteretic heating.

For most engineering materials the failure behavior is characterized in terms of crack growth per cycle. Initial investigations of elastomer fatigue were, therefore, also geared to examinations of cut growth per deformation cycle (Thomas 1958, Gent *et al.*, 1964). This behavior may be appropriate as long as the temperature of the elastomer is well above the glass transition and deformation rates at the crack tip are "somehow small". However, when these rates are comparable to those that give rise to a rate dependent expenditure of fracture energy the question arises whether it is the time spent at elevated stress rather than merely the number of cycles that determine the amount of crack growth. Inasmuch as standard fatigue analysis refers to crack growth as a function of the differential between maximal and minimal stress intensity factor during a cycle one must also ask whether such a characterization is justified for elastomeric solids.

Work at NRPA had shown (Thomas, 1958, Gent *et al.*, 1964) that the tear energy could be used, at least approximately, as a correlator for crack growth under both monotonic or static as well as cyclic load histories, although the effect of cycle frequency was considered to be secondary. In view of the work underlying equations 1a and 1b it was then shown in (Chang, 1983) that crack growth in elastomers is essentially governed by the duration of crack tip load rather than merely the numbers of load cycles, although with sufficiently high frequencies the viscoelastically controlled deformations at the crack tip become increasingly important. Fig. 6 shows crack growth in a polyurethane elastomer under different frequencies, which virtually collapse onto a single curve when plotted against the true rate velocity instead of cyclic growth rate.

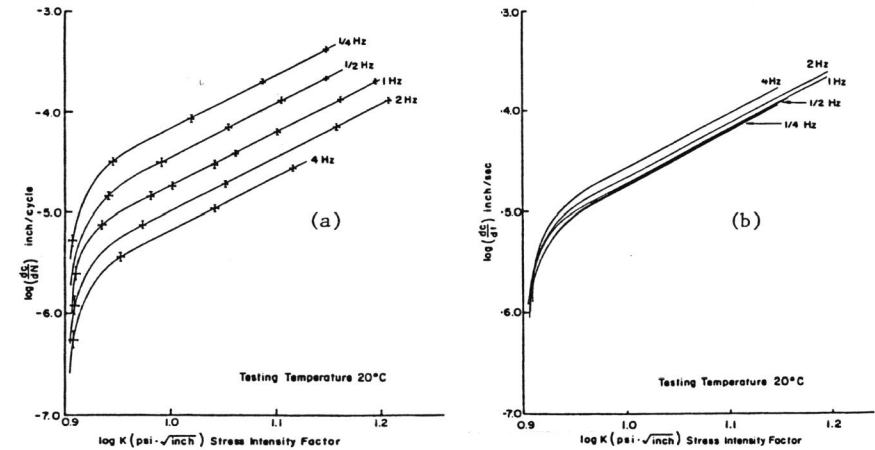


Fig. 6 Crack growth rate in a polyurethane elastomer. a) cyclid growth at different frequencies. b) average velocity $\frac{da}{dt}$.

Similar behavior is not expected when the material is below its glass transition temperature and when nonlinear material behavior occurs that is reminiscent of (metal) yield with significant irreversible deformations that influence the stress redistribution during each load cycle. Inasmuch as crosslinking limits the degree of molecular re-arrangement of molecules in the material around the crack tip one would expect that thermosets propagate fatigue cracks more readily than thermoplastics; that this is indeed the case has been demonstrated by Quereshi (Hertzberg, 1980) on hand of PMMA crosslinked to differing degrees and by Kim (Kim *et al.*, 1978) by means of an epoxy crosslinked to different degrees as shown in Fig. 7. There appears to be no data available that sheds light on the importance of cycle frequency on fatigue crack propagation in thermosets other than the qualitative developments that result from the hysteretic heating mentioned above.

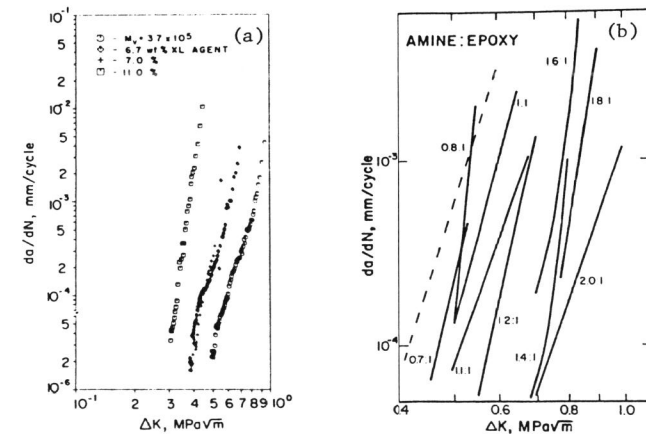


Fig. 7 Effect of crosslinking on fatigue crack growth; increased crosslinking moves curves to lower δk .

a) PMMA (Hertzberg, 1980) b) Epoxy (Kim *et al.*, 1978)

In terms of production volume uncrosslinked thermoplastic polymers outrank crosslinked ones by a considerable margin. The latter tend to be used as high strength or other specialty polymers while the former gain their advantage through the ease with which they can be formed and shaped economically. Uncrosslinked polymers divide into two large classes of polymers as outlined in the introduction, namely amorphous and (partially) crystalline materials. Typical examples of the former are Polymethyl methacrylate (PMMA), Polystyrene (PS), Polyvinyl Chloride (PVC)² and Polycarbonate (PC) while the latter are exemplified by the Nylons, the Teflons, high and low density polyethylene (HDPE and LDPE), polypropylene (PP), polybutene (PB) and polyethyleneterephthalate (PET; = Mylar in biaxially stretched form) as well as copolymers like eg. the Acetals Delrin (Dupont) or Celcon (Celanese). The crystalline polymers are translucent because the size of the crystallites is typically on the order of the wavelength of visible light. Since this fact makes the observation of small scale fracture processes much more difficult than in amorphous materials which are optically clear, it may be at least in part responsible for the relatively smaller body of information on the details of the fracture process in these kinds of polymers.

It is generally accepted, however, that fracture of uncrosslinked polymers is intricately associated with the development of "crazed material" as a precursor to fracture (Kambour, 1965, 1966) forming either from the bulk solid or at the tip of a crack, and that the fracture growth process consists of the failure of this crazed material. The craze process was studied first in connection with amorphous polymers at temperatures considerably below the glass transition. It refers to the development of a very thin zone of mechanically transformed material, the zone being oriented normal to the maximum tension and of a thickness in the tension direction that is on the order of (sub)microns and a lateral extent that is several orders (about three or more) of magnitude larger in the direction transverse to the tension. The transformation consists of development of submicron sized cavities and fibrillar material oriented in the tension direction, possessing an average density of about half that of the bulk material.

In crystalline polymers a similar phenomenon is observed, however on a considerably larger scale. No doubt the size scale determined by the amorphous and crystalline regions determine this size feature as well as the fact that the amorphous material is above or close to the glass transition which has a strong influence on the deformability of the material and on the instability process associated with the void formation and growth process. It is customary to refer to either process as crazing, regardless of the size scale as long as a fibrillar structure is formed (at the crack tip). Accordingly, the fracture behavior of uncrosslinked polymers is largely studied in terms of craze formation, growth and disintegration.

One should thus distinguish between the fracture processes in amorphous homopolymers, on the one hand, and in crystalline homopolymers and in copolymers, on the other. Certain aspects of the failure process are common to all of these like the development of such line- or wedge-like craze zones, others are not sufficiently explored today to allow a clear distinction on the basis of micromorphology, while still other features are clearly different as, for example, the response under changes in temperature and environment. In the following we shall first discuss those characteristics in homopolymers and crystalline/block co-polymers that deserve separate mention and then consider the more common elements for which clear differences are not yet established.

2. Although PVC contains about 5% of a crystalline phase that is too small to be normally considered as a crystalline polymer.

In view of the importance of crazing to the failure of (rigid) polymers much work on the behavior of crazes and its influence on failure has been performed. There arise several basic questions which we shall discuss briefly here in terms of results developed by several authors, but primarily by Kambour, Kramer, Argon, Doell and J.G. Williams.

Development of microvoids in the craze. The transformation of bulk into crazed material occurs apparently through a Taylor type instability associated with the unstable motion of the meniscus in a viscous liquid in a duct (Argon *et al.*, 1976). This process requires the possibility of viscous flow which is provided in the bulk polymer at points of high stress concentrations (dust particles; crack tips) where the local dilatation reduces its (glassy) viscosity to a level much lower than the local temperature would indicate (Gent, 1970) through the strong effect of the free volume on polymer rheology (Emri *et al.*, 1981, Knauss *et al.*, 1987). This process develops what is called a primordial craze (Lauterwasser, *et al.*, 1979). The voiding/instability process allows a reduction of the local stress so that the front of the primordial craze is located on or near a locus of maximum stress (Argon *et al.*, 1983).

Craze Growth and Thickening. As a result of the now locally inhomogeneous stress distribution the primordial craze material, with microfibrils oriented molecularly to the strength of the polymeric backbone chain, draws polymer from the surrounding bulk material in the direction of the locally maximum tension; while stretching these fibrils become more oriented and, simultaneously, draw more amorphous material from the bulk as they become incorporated deeper into the growing craze. These processes are clearly time dependent, though our knowledge of the laws governing that deformation-rate sensitivity does not go much beyond a qualitative understanding.

Failure Process of the Craze Fibrils. This process, and particularly its time dependent aspect, is as poorly understood as the balance between fibril stretching and drawing from the bulk discussed under Craze growth and thickening. However, on the basis of continuum analyses and measurements of craze boundary profiles (Lauterwasser, *et al.*, 1979, Ungsuwarungsri, *et al.*, 1988) it appears clear that the molecular orientation in the fibrils within/and/or outside of the primordial craze becomes so high that maximal strength is achieved, giving rise to a second peak in the stress distribution at the end of a propagating craze, i.e. at the crack tip.

Effect of the Viscoelasticity of the Parent Material Surrounding the Craze. That these processes cannot occur independently of the (time dependent) deformation of the surrounding material is self evident, for it is this part of the solid which must be in local force equilibrium with the crazed material. In this regard it is usually assumed that the bulk solid is in an elastic state because the relaxation or creep behavior is weak; however, it is clear that this assumption cannot be correct in principle, because crazes are observed to grow in a time dependent manner, their growth depending on the applied loading. This topic will be addressed more in a later section. All these questions need to be understood in the framework of the load history to which the failing material is subjected, i.e. essentially monotonic as opposed to fatigue type loading.

In this context it is also of great interest to understand whether the growth of crazes, and with them cracks, takes place in a manner that is continuous or discontinuous on the scale typical of the fibrils so as to occur by (nearly) simultaneous failure of a large number of them. While in crystalline polymers both kinds of crack growth appear under monotonic or steady loading, discontinuous growth is apparently mentioned only in the context of fatigue in amorphous polymers; it is possible of course that the amount of discontinuous growth is so small that it evades inspection techniques normally used. This would be particularly relevant if discontinuous growth occurs under low intensity loading so that both the craze size and the growth rate are small. One notable exception to continuous crack growth has been reported by Hull (Hull, 1970) who noted that under high-speed, dynamic conditions a crack in polystyrene would propagate apparently discontinuously under formation of groups of crazes (craze bunches) on either side of the fracture path. However, this phenomenon appears to be of a different nature than the discontinuous growth resulting from fibril creep we have in mind here and which is noted under slow growth conditions in crystalline and blockcopolymers. In this dynamic situation the discontinuity seems strongly coupled with the inertial stress field exterior to the main craze in producing a whole field of crazes next to the crack axis.

The crack speed of moving cracks is usually measured as a function of the stress intensity factor as in the case of elastomer fracture, assuming continuous crack propagation. A typical plot collected by Doell (Doell, 1983) from different authors for PMMA at room temperature is shown in Fig. 8. One notes that the range of the stress intensity (about half a decade) is small compared to the range of resulting velocities (which range over about 8 decades). We shall return to this observation in connection with modeling time dependent crack propagation with rate sensitive cohesive forces in a later section. Doell has shown successful correlation of the crack propagation behavior of crack tip crazes by modeling the latter with the Barenblatt/Dugdale model assuming that the cohesive stress is constant along the craze but varies, as it turns out, by only a factor of about two over the range of crack speeds in Fig. 8 (cf Fig. 12a in Doell, 1983). While the dependence of this fracture behavior on molecular weight is beyond the scope of this written account, we nevertheless note that this topic is a very important aspect of fracture characterization. One of the goals of fracture mechanics is to provide a framework in which the similarities and the differences of various materials can be characterized. Moreover, it is important to understand from a polymer synthesis point of view what controls the fracture process and how sensitively so. In this regard Doell has provided some of the few data that speak to this materials related fracture issue (Doell, 1983); matters would be helped greatly, if more material systems could be investigated in this manner.

The data collected in Fig. 8 derived from a variety of test geometries and under conditions of variable crack speed under changing stress intensity. Recall the earlier discussion on variable crack propagation rates in elastomers. One would argue in the present context similarly, namely, that the relation between crack speed and stress intensity factor is valid instantaneously and that, therefore, data such as presented in Fig. 8 defines the crack propagation speed as long as the stress intensity factor is a known function of the crack length in any given geometry. If we denote then the data in Fig. 8 formally by

$$K(a) = f(\dot{a}) \quad (6)$$

then eq. 6 is a (nonlinear) differential equation for the crack length a , for which the failure time for complete failure of a specimen may be determined just as was accomplished in connection with Figs. 4 and 5 for elastomeric fracture.

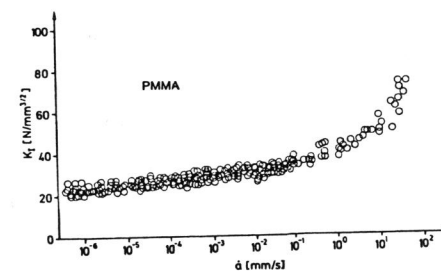


Fig. 8 Fracture toughness K_I and crack speed in PMMA (Doell, 1983).

Fracture of Crystalline and Copolymers

The fracture behavior of these materials is more difficult to understand because of their multiphase nature. One could also include in this discussion the effect of inert phase additions, but we shall limit ourselves primarily to the behavior of crystalline materials. Polymeric crystals undergo phase transformations at their boundary under load and under temperature changes in a manner not understood very well quantitatively. Therefore, some of the phenomena observed in their fracture behavior are not explicable in a straight forward manner.

Of particular interest is the phenomenon of discontinuous crack growth under monotonic or steady loading. An example of this behavior is given in the work of N. Brown on the long term fracture behavior of polyethylene (Brown *et al.*, 1988) a very widespread crystalline polymer in the piping industry. In following the time dependence of the COD and the crack tip position under the microscope Brown and his colleagues determined that the crack tip would come nearly to rest and then propagate in essentially a jump manner to a new rest position. Moreover, each one of these "jumps" is then associated with a "rest marking" or "arrest line" that, at least to date, appears to be indistinguishable from a striation band developed in fatigue (see discussion below).

Another feature of significance for long term failure prediction is the occurrence of different "mechanisms" of crack growth under low and high loads. In order to study or predict long term failure it is, by definition, necessary to conduct accelerated tests by performing failure measurements at elevated temperatures or elevated loads or both. A continuous worry is the possibility that under such "acceleration procedures" the material fails by a different mechanism than that which would be operating under long-term, low-load conditions. Brown and coworkers have shown that such can be indeed the case in polyethylene in that fracture can occur in what is termed a "ductile" or "brittle" fashion.

The term "brittle" is derived from the fact that the material surrounding the crack tip does not apparently undergo significant permanent "plasticity-like" deformation. Under appropriately low loading a (carefully prepared) crack tip will develop a craze. In contrast to the craze in an amorphous homopolymer the craze in the crystalline material is much larger (tens of microns in the former as compared to hundreds of microns in the latter) and presents a much coarser internal structure so that it is feasible to observe it with optical microscopy. The "brittle" failure consists in the gradual destruction of this coarse craze to provide discontinuous crack propagation. A section through a "brittle" crack tip is shown in Fig. 9a.

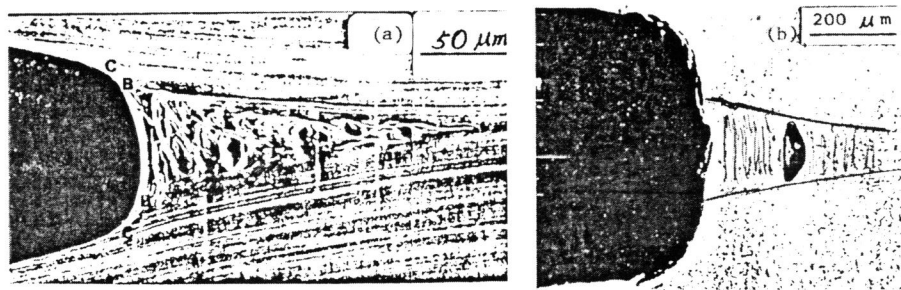


Fig. 9 Appearance of craze associated with "brittle" (a) and "ductile" (b) fracture.

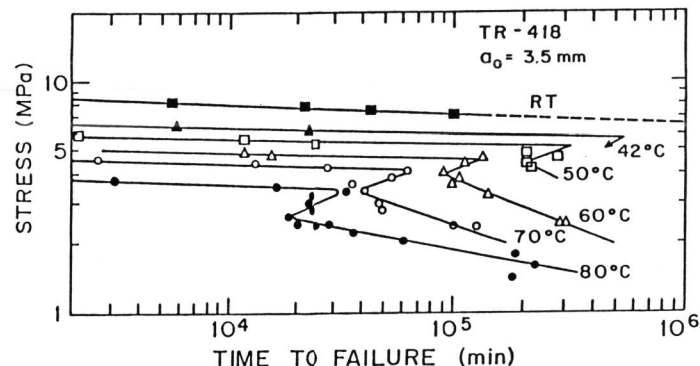


Fig. 10 Failure times as a function of load in pE, differentiated by "ductile" and "brittle" behavior. (Brown *et al.*, 1988).

When an appropriately high load is applied to the material the oriented craze material provides sufficient strength to elevate the bulk material adjacent to the crack tip to such stress levels that stress-augmented and accelerated creep occurs which results in plastically deforming the crack flanks ("ductile" behavior) A section through this type of craze is shown in Fig. 9b for comparison with a "brittle" configuration.

In Fig. 10 the failure times in a notched tensile specimen as a function of load is shown with the upper branch of the z-shaped curves corresponding to the "ductile" mode and the lower branch to the "brittle" one. There is a clear and systematic transition from one mode to the other. Also evident is that the projection of failure on the basis of the ductile mode to long times would be clearly non-conservative.

This differentiated fracture behavior is the result of (nonlinear) viscoelasticity and the deformation history at the tip of the crack: Clearly, to reach the load levels associated with the "ductile" fracture the craze material at the crack tip has to pass through stress levels at which failure would occur in a brittle manner over long periods of time. The differentiation is then a competition between the rate of disintegration/creep of the oriented fibrillar material and the nonlinearly viscoelastic creep/relaxation process occurring in the bulk at the crack tip. It appears that there is no a priori knowledge as to which materials sustain such a competitive behavior, though

crystalline materials seem good candidates for it; however, there is no reason why amorphous homopolymers could not exhibit similar behavior, but that information is not yet available.

Effect of Temperature. J.G. Williams and his associates have studied the effect of temperature changes on the propagation of cracks and associated crazes in a number of polymers of different morphology. As experience has well demonstrated, temperature change affects polymers by accelerating deformation processes, including those that control the fracture process. We have noted already that in the case of elastomer fracture the temperature effect is felt primarily through a multiplicative factor on the crack speed with a relatively minor adjustment possible in the load if the long term rubbery modulus is involved.

Crack propagation tests on Polymethylmethacrylate (PMMA) and Polycarbonate (PC) show clearly a crack speed increase at constant stress intensity factor with a raise in the environmental temperature. However, it is also clear from the example in Fig. 11 taken from the work of J.G. Williams (Parvin *et al.*, 1975) that a mere multiplication of the crack speed by a temperature dependent function (shift function) will not allow these curves to be brought into superposition: Therefore, temperature must enter into the problem in more than merely the thermorheologically simple manner, as it enters the elastomer fracture.

The stress intensity factor may not be the most efficient way to characterize time and temperature dependent fracture in these kinds of materials; instead, it appears more appropriate to characterize time/temperature sensitive fracture in terms of the crack opening displacement, at least in an approximate manner. The motivation for this thought comes from two considerations. First, we have seen that in the case of elastomer fracture the process can well be represented by a COD criterion, provided the ultimate stress is considered to be a material constant; the second, and perhaps more telling thought derives from the observation (Doell, 1983) that the crack opening displacement at the trailing end of the craze in a homopolymer is nearly constant (2.5 μm to 3.2 μm) over many (about 10) decades of crack speed. See also reference (Parvin *et al.*, 1975) Using the Barenblatt/Dugdale model we find for the $COD = U_0$

$$U_0 = \frac{\kappa + 1}{8} \frac{K^2}{\mu \sigma_y} \quad (7)$$

where κ depends on Poisson's ratio, μ is the shear modulus and σ_y the yield stress. If we allow, for purposes of making an engineering estimate, that the shear modulus and the yield stress are proportional to each other as a function of temperature we find that the COD is proportional to $(K / \sigma_y)^2$. The yield stress σ_y (as determined in a constant strain rate experiment) decreases with temperature as also reported (Parvin *et al.*, 1975). Thus if one normalizes the stress intensity factor in Fig. 11a by the temperature dependent yield stress one obtains a quantity that is proportional to the square root of the COD. This normalization has been accomplished in Fig. 11b which shows that now the mismatch of the curves obtained at different temperatures is small or minor. However, that mismatch can be further improved by allowing for a small amount of shifting along the $\log(\dot{a})$ speed axis in accordance with the normal time-temperature superposition to render the composite or master curve in Fig. 11c. While there are certainly unknowns in this evaluation for the crack/craze propagation analysis it appears that at least approximately the COD criterion merits consideration for studying crack propagation in amorphous homopolymers³.

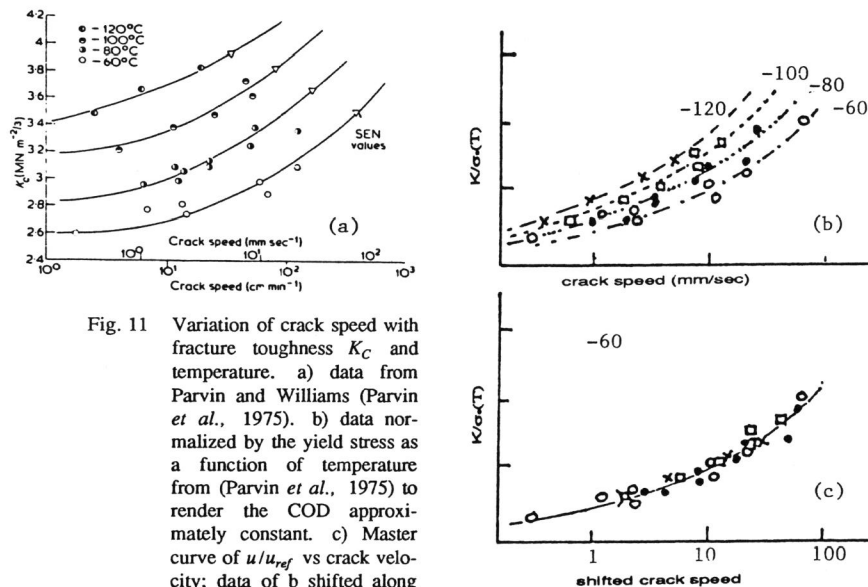


Fig. 11 Variation of crack speed with fracture toughness K_C and temperature. a) data from Parvin and Williams (Parvin *et al.*, 1975). b) data normalized by the yield stress as a function of temperature from (Parvin *et al.*, 1975) to render the COD approximately constant. c) Master curve of u/u_{ref} vs crack velocity; data of b shifted along the log time axis.

It will be recalled that we discussed in the beginning that fracture on polymers may be accompanied by crazes and or plasticity-like shear flow. The latter is enhanced by increasing temperatures so that in some homopolymers an increase in toughness is experienced with rising temperature: this increase derives from the fact that increased shear deformability enhances the formation of shear (flow) lips corresponding to the plane stress deformations in sheet metal. While this plane stress/plane strain feature is bound to develop if the temperature rises high enough, it appears to be particularly relevant in the initiation of crack propagation, and somewhat less so in the propagation problem and to be particularly prone to occur in crystalline homopolymers as well as composite polymers (Parvin *et al.*, 1976, Mai *et al.*, 1977).

Effect of Environment. Although polymers offer resistance to corrosive environments as one distinct advantage over metals, there are many situations in a varied industrial environment where solvents or other chemically degrading liquids are present in a fracture sustaining configuration. Of particular concern in engineering applications is the effect of the environment that can transform a normally very ductile polymer into a nearly brittle type to fail by slow crack propagation under very small load levels. We shall not deal here with the coupled chemistry problem of stress induced reactions in a chemical environment (bona fide corrosion-augmented fracture) but consider only the effect of solvents insofar as these liquids aid the formation and disintegration of the craze material at the tip of a crack.

3. The data available for this estimate is too sketchy to allow a reasonable deduction of the appropriate shift factor. The data precision as determined from a journal article and the lack of a more direct knowledge of the temperature dependent modulus does not seem to allow a more determined deduction given if one ignores the fact that both the modulus and the yield data would have to encompass viscoelasticity effect if one were to drive this development to the final conclusion.
4. A brother of the conductor Otto Klemperer.

For craze-forming polymers residual stresses left over from the manufacturing process can be sufficient to generate crazes if exposed to a suitable solvent or, preferentially, its fumes. Thus Klemperer⁴ (Klemperer, 1941) seems to have been the first who was concerned with the formation of crazes on polycarbonate windshields for aircraft after cleaning with fluids containing alcohol. While Kambour used solvents to generate large crazes for experimental studies, J.G. Williams and coworkers have examined the physics of diffusion into the craze and its effect on craze growth more intensely and examined the craze/crack behavior in terms of fracture mechanics parameters.

One result of these investigations was that under sufficiently small stresses the growth of the craze was a function of the initial stress intensity factor (Marshall *et al.*, 1970, Williams *et al.*, 1975). Under the low stress the craze would form in a plate specimen with the faces of the plate remaining uncrazed because the near-surface plane stress state promoted plastic flow rather than dilatation induced crazing, so that the craze constituted a relatively long channel on the inside of the specimen plate. This result is interpreted to indicate that the flow of the solvent medium is set up materially by the conditions existing initially at the crack tip: They determine the porosity of the craze material which in turn controls the flow rate of the penetrating medium.

Fatigue.

Crack growth behavior under cyclic loads is a very important topic in engineering applications. For this reason considerable interest has been devoted to this topic and comprehensive reviews on it exist; one of these (Hertzberg *et al.*, 1980) deals thoroughly with the existing knowledge of fatigue failure in the contexts of standard fracture mechanics parlance, while the other (Doell, 1983) addresses the physical behavior of the craze in more depth, augmenting chapter 4 in (Hertzberg, *et al.*, 1980). Four topics are of interest here; they comprise the differentiation between continuous and discontinuous growth, the effect of temperature changes, of frequency and of the loading range.

Effect of Loading Range. Because "rigid" polymers exhibit nonlinear material response that is, macroscopically, similar to metal plasticity it has been found that crack propagation behavior can be correlated through plots of δK vs da/dN . As in crosslinked polymers below the glass transition temperature these two quantities can be related, at least approximately, by a power law with rather high exponents.

Frequency Dependence. In contrast to the behavior of elastomers the frequency does not have a strong influence on the growth rate per cycle unless it is so high that dissipative heating plays a role. For example, Figs. 12 a and 12b show the same data plotted against per-cycle and per-time propagation rate (We note that the maximum crack tip opening plotted here is proportional to the square of the stress intensity factor). It is clear that the crack speed on a time basis is very nearly proportional to the frequency.

Discontinuous crack propagation. While this is not the place to discuss the fatigue crack propagation of particular polymeric materials it is important to point out that the crack growth behavior in polymers can be quite different compared to metals. In the latter, the crack propagates a certain distance with each cycle depending on the stress intensity range. In polymers the crack may not propagate for many cycles - on the order of one or several hundred- but then jump ahead by a given amount which depends on the size of the stress intensity (range). The fracture surfaces then leave a marking in the form of a band that indicates the width of the discontinuous crack advance.

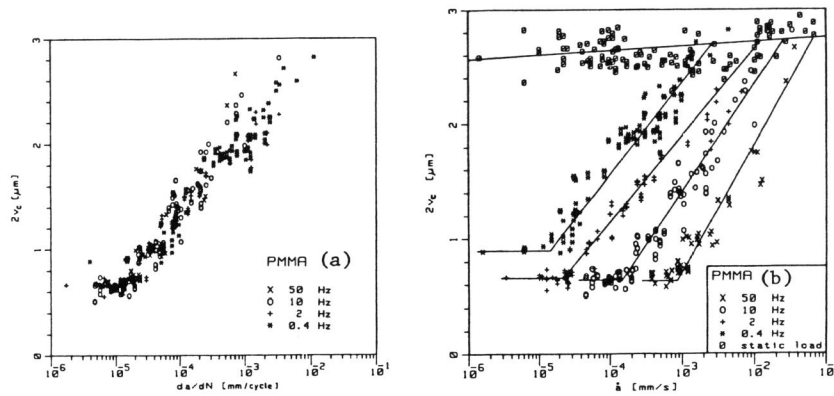


Fig. 12 Fatigue crack propagation data for PMMA at 23°C. a) Max COD vs growth per cycle b) Max COD vs timerate of growth (also known continuous growth of the crack in top of the graph) (Doell, 1983).

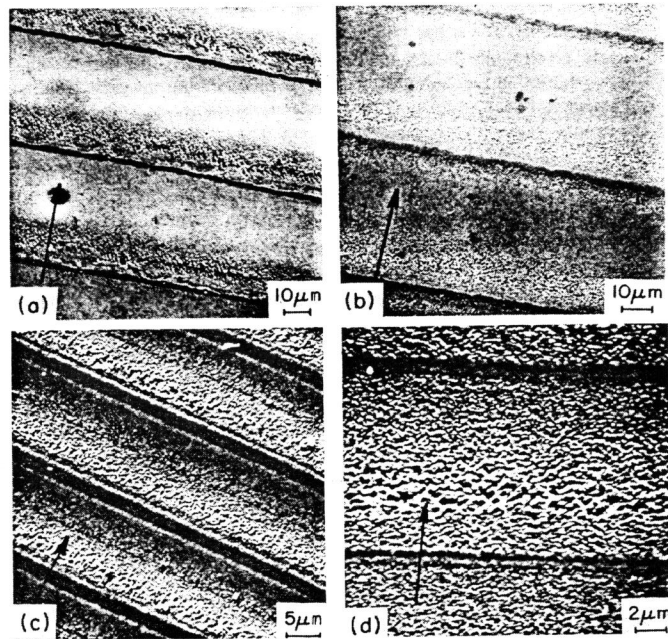


Fig. 13 Growth bands resulting from fatigue crack propagation in (Skibo, et al., 1977), a) PVC; b) PS; c) PS; d) PC

Examples of this behavior are shown in Fig. 13 taken from reference (Skibo *et al.*, 1977). On the other hand at higher load levels, such that the steady rate of crack propagation under monotonic loading is approached, the propagation manner changes over gradually to "growth per cycle". Thus the appearance of "striations" is not necessarily an indication of the rate of crack growth or of the magnitude of the load on the structure. Indeed, at sufficiently small load levels fatigue crack propagation can occur without any periodic markings on the fracture surfaces, leading to a mirror like and featureless surface as continuous crack growth would produce.

NON-LINEARLY VISCOELASTIC ANALYSES

It is clear from the foregoing that, although at times rough engineering estimates can be made by treating rigid polymers as elastic solids, a realistic and successful analysis requires the incorporation of non-linearly viscoelastic material description. Two issues present themselves in this context, namely the determination of the stress and displacement field surrounding the crack tip and the establishing of a failure or initiation/propagation criterion.

A Path Independent Integral:

For hyperelastic solids the non-linear aspects of initial crack propagation have been well formulated in terms of the path independent J-integral, which for plastic-type dissipative behavior has been used successfully as an approximate criterion for fracture. Schapery has examined the consequences of a certain type of approximation for non-linearly viscoelastic behavior that leads to a path independent integral (Schapery, 1986, 1988).a

Many polymers exhibit creep or relaxation behavior for linearly viscoelastic behavior that vary slowly on a log-log time representation in the sense that the maximum slope is less than about $1/4 (d(\cdot)/d \log t < 1$ or $d^2(\cdot)/d(\log t)^2 < 1$) For those materials it is possible to determine the stress distribution resulting from step load histories (and also some monotonic load histories) approximately by starting with the elastic analogue problem and by simply replacing the elastic material constants with their viscoelastic counterparts as functions of time. Such a procedure has become known as the "quasi-elastic" (estimation) method.

Considering nonlinearly viscoelastic behavior of the ageing type (relaxation times change with time in some specified way) it is assumed that there can be found approximately a potential function Ψ like that for a hyperelastic solid defined in terms of time independent strains ϵ^{ijR} , which lead to time-independent stresses τ_{ij}^R and time-independent displacements U_i^R . Suppose that there exists a non-linearly elastic relation between the components of the stress τ_{ij}^R (R denotes an elastic solution to a reference BV problem)

$$\tau_{ij}^R = \tau_{ij}^R(E_{ij}^R, x, t) \quad (8a)$$

derived from elastic displacements U_i^R such that

$$E_{ij}^R = \frac{1}{2} (U_{i,j}^R + U_{j,i}^R) \quad (8b)$$

which satisfy the equilibrium equations

$$\tau_{ij,j}^R = 0 \quad (9)$$

If the constitutive law is governed by a single hereditary function (e.g. Poisson's ratio is a constant for linearly viscoelastic behavior) the stresses for the non-linearly viscoelastic problem are equal to the non-linearly elastic values, but the strains ϵ_{ij} and displacements U_i are then time dependent according to the convolutions (for this correspondence rule see Schapery, 1986)

$$E_{ij} = E_R \int_{0^-}^t D(t-\zeta, t) dE_{ij}^R \quad (10a)$$

$$U_i = E_R \int_{0^-}^t D(t-\zeta, t) dU_i^R \quad (10b)$$

where E^R is a reference modulus, $D(t-\zeta, t)$ is the uniaxial creep compliance, conjugate to the relaxation modulus $E(t-\zeta, t)$ via (Schapery, 1986, 1988)

$$\int_{\zeta_0}^t D(t-\zeta, \tau) \frac{\partial}{\partial \zeta} E(\zeta-\zeta_0, \zeta) d\zeta = H(t-\zeta_0) \quad (11)$$

with $H(t)$ denoting the Heaviside step function and $\zeta_0 \geq 0$. Analogy to nonlinearly elastic behavior renders then the quantity

$$J_v = \int_{C_1} \left\{ \Psi dx_2 - T_i \frac{\partial U_i^R}{\partial x_1} ds \right\} \quad (12)$$

independent of the path C_1 as long as the path surrounds the crack tip in the appropriate manner and the crack faces are traction free. Here the $T_i = \tau_{ij} v_j$ are the Cauchy tractions on the contour C_1 having locally the outer normal v , and the U_i^R are determined by the inverse of (10b) as

$$E_R U_i^R = \int_{0^-}^t E(t-\tau, t) dU_i \quad (13)$$

Applications of the integral (12) to crack initiation and propagation will be discussed in the lecture.

Effect of non-linearly viscoelastic behavior based on free volume

In closing we shall discuss two exploratory models of crack tip response when the rate of creep or relaxation of the viscoelastic material behavior is controlled by the local dilatation. We consider as a first problem the time dependent deformation and stress field in a sheet containing a central crack that has been subjected to a sudden far field stress normal to the crack axis ⁵.

As a second example we consider the companion problem to that exemplified in the section on Elastomers in that here the cohesive forces are prescribed through a nonlinearly viscoelastic

5. The computations for this work have been carried out by B.Moran, now at Northwestern University.

constitutive law, incorporating an at least rudimentary law for damage accumulation to failure ⁶.

The non-linearly viscoelastic material description follows the outline in reference (Emri, *et al.*, 1981, Knauss, 1987). The material model draws on the idea that when a polymer is dilated, whether by temperature, stress or solvents, its relaxation times shorten in a very sensitive manner. This idea also underlies Gent's observation (Gent, 1970) that the material instability leading to craze formation results from the development of rapid creep/relaxation at the craze initiation site under a locally high stress concentration (dust particle); it also accounts for the raising of the glass transition temperature under pressure. The model accounts for linearly viscoelastic behavior under sufficiently small stress: The constitutive behavior is governed by the following equations between the stress components τ_{ij} , small strains ϵ_{ij} with S_{ij} and e_{ij} denoting deviator stresses and strains, respectively. One has, then

$$S_{ij} = 2 \int_{-\infty}^t \mu(\zeta - \zeta') \frac{\partial e_{ij}(t')}{\partial t'} dt' \quad (14a)$$

$$\tau_{kk} = 3 \int_{-\infty}^t K(\zeta - \zeta') \frac{\partial \epsilon_{kk}(t')}{\partial t'} dt' \quad (14b)$$

$$\zeta = \zeta(t) = \int_0^t \frac{du}{\Phi[T(u), \epsilon_{kk}(u)]} \quad (14c)$$

where, $\mu(t)$ and $K(t)$ are the shear and bulk relaxation moduli for the isotropic material, and Φ is a shift factor that controls the relaxation spectrum according to

$$\log_{10} \Phi = \frac{b}{2.303} \left[\frac{1}{f} - \frac{1}{f_0} \right] \quad (15a)$$

$$f = f_0 + A \cdot \alpha(t) * dT + B \epsilon_{kk} \quad (15b)$$

with f denoting the fractional free volume and f_0 a reference value thereof. For illustrative purposes the thermal dilatation

$$\alpha * dT = \int_{-\infty}^t \alpha(\zeta - \zeta') \frac{\partial T(x, t')}{\partial t'} dt' \quad (16)$$

has been included in terms of a convolution of the temperature with a time dependent thermal volume expansion characteristic $\alpha(t)$. A and B and b are experimentally determined constants. The volume strain ϵ_{kk} is given by the inverse of (14b) as

$$\epsilon_{kk} = \int_{-\infty}^t M(\zeta - \zeta') \frac{\partial \tau_{kk}(x, t')}{\partial t'} dt' \quad (17)$$

6. This study has been performed by G. Losi, Graduate Student, Graduate Aeronautical Laboratories, Caltech.

where $M(\tau)$ is the creep compliance in bulk. An example of this constitutive law for a simple strain history is presented in Fig. 14 (Emri, *et al.*, 1987, Knauss *et al.*, 1988). A particularly interesting feature of this constitutive behavior is the capability of the model to produce rate dependent strain softening in uniaxial tension, a feature that is often associated with certain flow instabilities in rate insensitive materials.

A Stationary Crack in a Sheet Under Sudden Load. The problem is plane-strain modeled in terms of finite elements on a square domain containing a central crack of a size that is 1/100 of the square side. The crack tip is configured as a notch of radius 1/1000 of the half crack length and the smallest element has dimensions about 1/5 of the notch radius. The radius and the finite elements are so small that a singularity field becomes recognizably established, yet it makes sense to consider a stress concentration as a measure for the stress intensity magnitude.

An initial investigation using a Maxwell body for both shear and bulk in (14) and (15) (relaxation time for shear and bulk = 1 second, glassy uniaxial tension modulus $E_0 = 1$ Pa and Poisson's ratio = 0.3) along with $f_0 = 0.01$, $b = 0.05$, $A = 0$ and $B = 1.0$ renders, for example, the crack-normal stress ahead of the crack at different times as shown in Fig. 15 when the applied stress is 0.1% of the glassy modulus. Also shown for comparison is the line representing a square root singular behavior. While the model is very simple, it provides insight into the time dependence of the crack tip stress field: At zero time the stresses are elastic-like with a typical elastic singularity, but these abate quickly because the high dilatational stresses cause accelerated relaxation there. Since overall equilibrium must be obeyed the stress drop at the crack tip must be equilibrated elsewhere and a "stress hump" develops which travels away from the crack tip with a rate that depends on the relaxation time of the material. During this time the square root singularity gives way to a different field not readily characterized in standard terms except asymptotically in the case of a mathematically sharp crack, since for infinite dilatational stresses the crack tip becomes established there as a totally relaxed material (in case the material were rubbery elastic for large times). The "traveling stress hump" eventually moves to the edge of the sheet and passes out of it with the consequence of further redistribution of stresses which then produces a rise in the crack tip stresses again that become now higher than those encountered there initially. This crack tip stress history is indicated in Fig. 16 as the maximum normalized stress versus time. In Fig. 17 crack opening profiles are illustrated for three different times: It is clear that the non-linear feature produces not only acceleration in crack opening but generates considerable crack blunting reminiscent of the "ductile" deformation pattern observed in the Polyethylene work of N. Brown and collaborators (see the section on Fracture of Crystalline and Copolymers).

Another example, this time for standard linear solid representations in shear and bulk is given in Fig. 18 and 19 for some time after initial loading as further evidence of the non-traditional distribution of stress at the crack tip. Fig. 18a shows the distribution of the effective stress on the size scale of the crack while Fig. 18b illustrates the finer detail close to the crack tip. We note in particular that in Fig. 18b the effective stress is at a minimum in a lance shaped domain ahead of and disconnected from the crack tip. Fig. 19 shows contours of the average dilatational strain to develop an elongated domain which only close-in resembles contours of the typical elastic strain field.

A feature worth mentioning here that arises out of these, as well as more detailed studies not documented here, is that the strain softening exhibited by this material model does not automatically

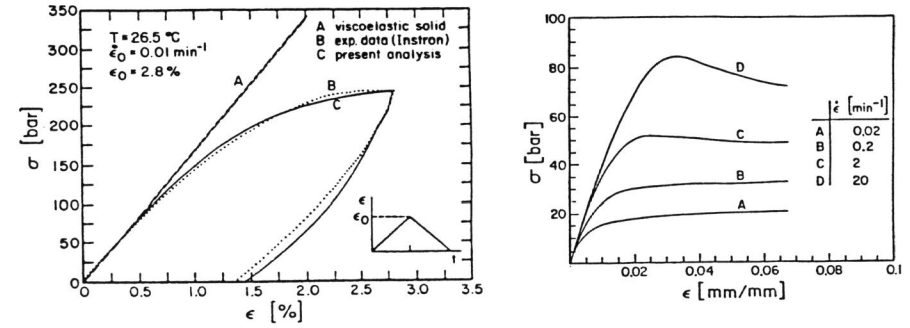


Fig. 14 Nonlinearity viscoelastic response in uniaxial extension according to the free volume model. (Knauss *et al.*, 1987).

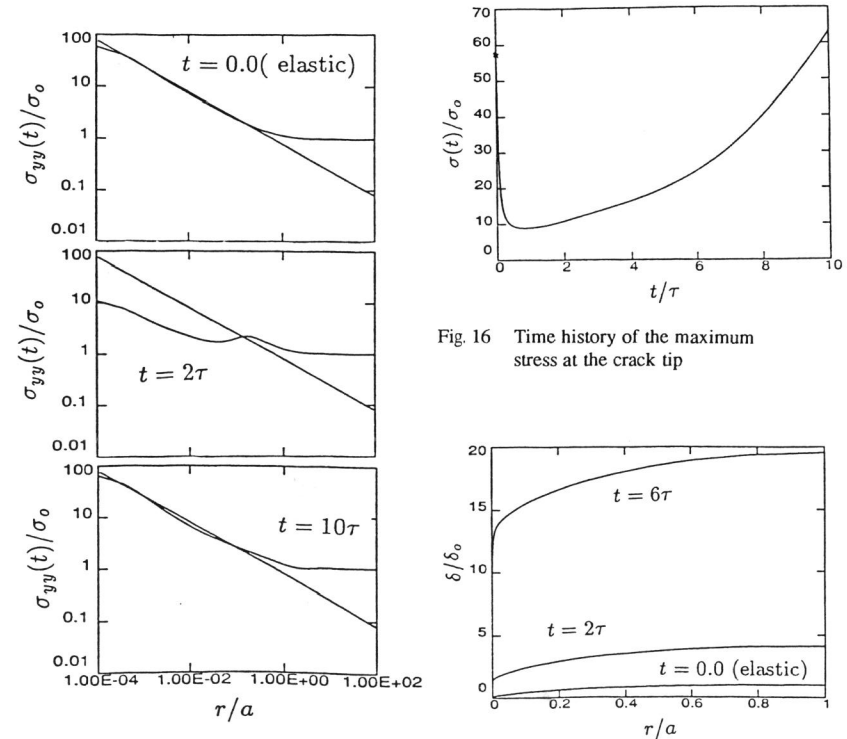


Fig. 15 The crack-normal stress ahead of the crack for a nonlinear Maxwell body at different times (τ = relaxation time)

Fig. 17 Crack opening profiles for nonlinear Maxwell solid.

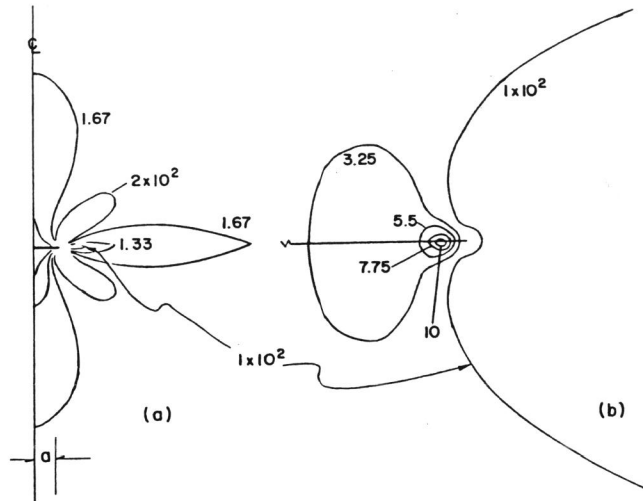


Fig. 18 Effective stress contours $\bar{\tau} = \{3/2 S_{ij} S_{ij}\}^{1/2}$ for nonlinear "standard solid"; a) large field b) detail near crack tip "a" = half crack length

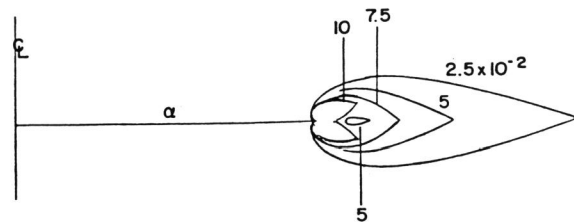


Fig. 19 Contours of average dilatation $\frac{1}{3} E_{kk}$ a = half crack length

lead to shear band instabilities although the elongated features of crack tip stress/strain contours remind us of the development of craze like line features along the crack axis. It appears so far that the mere existence of strain softening is not sufficient for shear banding to occur but that the rate of softening is equally important in developing instability of the stress/strain field as the viscosity controlled deformations progress in time or with loading.

A Viscoelastic Craze-like Problem. The motivation for this problem arises out of considerations of the discussion in Crack Propagation in Crosslinked Polymers where the linearly viscoelastic model had been described as one for which the energy of fracture is assumed to be a material constant. In view of the discussion of the craze problem it is clear however that in general such an assumption may be too restrictive and that the energy required for crack propagation should be a function of the rate-dependent cohesive forces and deformations. It seems appropriate,

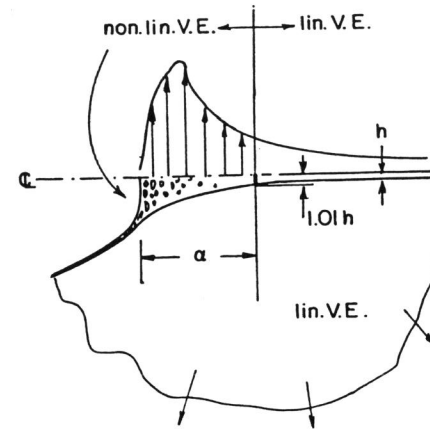


Fig. 20 Crack tip model with division into linearly and nonlinearly viscoelastic domains

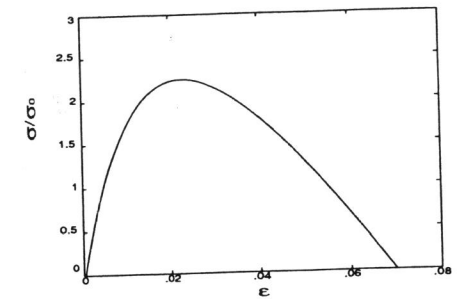


Fig. 21 Schematic of damage induced stress-strain response function

therefore, to consider the problem in which the cohesive forces are determined as a function of the rate dependent deformations in the cohesive zone instead of prescribing them (arbitrarily?) in an a priori manner.

This example is best introduced with the help of Fig. 20 which depicts the tip of a crack at which nonlinearly viscoelastic and damage behavior occurs in a thin zone along the crack axis. The bulk of the material is considered to be linearly viscoelastic while the cohesive forces are modeled by the nonlinearly viscoelastic law in (14-17). The increasing damage accumulation encountered as the crack tip (trailing end of the "craze") is approached is accounted for by a nonlinear function of strain determined experimentally for Polyvinylacetate (PVAc) (Parvin, *et al.*, 1988). The linearly and nonlinearly viscoelastic properties are chosen as those of PVAc also.

The strain dependent damage function is shown schematically in Fig. 21 and the cohesive forces are taken as the nonlinearly viscoelastic description of equations (14-17) multiplied by the value of this function corresponding to the strain across the cohesive zone. Thus the failure at the crack tip occurs, de facto, by a strain criterion by virtue of this approximation. However, the size of the cohesive zone and the distribution of the stress within the zone is self adjust in equilibrium with the outer viscoelastic domain. The beginning of the cohesive zone is defined as the point where the strain on the crack axis reaches a fixed value so as to warrant description in the cohesive zone in terms of nonlinear rather than linearly viscoelastic behavior. For the present illustration this value was taken to be one per cent.

The solution to the problem is formulated in terms of the superposition of linearly viscoelastic problems as illustrated in Crack Propagation in Crosslinked Polymers for the outer domain such that an arbitrary distribution of cohesive stresses results in the "craze zone". The cohesive forces follow the nonlinearly viscoelastic/damage law in uniaxial tension across the "craze" and

are adjusted so that these strains provide displacements that match those of the linearly viscoelastic outer bulk material along the interface between the two domains. The problem leads to a highly nonlinear integral equation which is solved essentially iteratively for a fixed velocity under the constraint that singularity stresses must vanish at the tip of the craze. Inasmuch as only a crack tip stress field is used with a "far-field stress intensity factor" as the prescribed load there is no other geometric size scale than that determined by the cohesive zone.

Fig. 22 illustrates typical results at a single temperature (23°C; it should be noted that such a large range of crack velocities cannot be observed at any one temperature in real experiments; nor has an analysis been performed along the lines mentioned in the Effect of Temperature in Fracture of Crystalline and Copolymers to account for an adjustment of the stress intensity factor according to temperature. The cohesive stress distribution is not readily summarized in a single graphical form since it passes through a maximum in the cohesive zone such that the value of the maximum apart from the distribution does not convey any apparently new or distinguishing features. However, it is clear that essentially two different kinds of fracture responses develop, depending on whether the crack moves in a "near-rigid" polymer (crack speed > 1m/min) or in a strongly viscoelastic material (crack speed < 1m/min).

In the "near-rigid" phase the stress intensity factor tends to vary very little as observed in connection with crack/craze propagation by Doell. The response of the crack speed to the stress intensity factor depends to some degree on the strain at the craze tip which determines the change over from linear to non-linear material description. This range of crack behavior is characterized by a very nearly elastic response of the bulk solid outside of the line-craze zone. Virtually all the time dependence of the crack propagation derives from the nonlinearly viscoelastic behavior that is controlled by the free volume effect. The cohesive zone size in this region is essentially constant or slightly decreasing with increasing crack speed; this result is not in keeping with results from observations on crazes, and most likely the consequence of the simplified interaction between nonlinearly viscoelastic behavior and damage in the cohesive zone.

For low crack speeds the fully viscoelastic response of the bulk material comes into play. This fact is evident through the generally low stress levels commensurate with the long term elastic (rubbery) behavior at one extreme. This behavior is also characterized by a strong variation in the cohesive zone size which in the limit as $\dot{a} \rightarrow 0$ achieves a constant value. There is clearly a lower limit to the stress intensity below which no crack propagation occurs which is in agreement with the earlier discussion of the linearly viscoelastic model. Assuming that this lower limit corresponds to that case there are shown also, for comparison purposes, the limit cases of the linearly viscoelastic crack propagation problem as indicated in the caption of the figure.

To summarize the information gathered from this example it becomes thus clear that the time and rate dependent sensitivity of the cohesive material can have a strong influence on the dependence of the crack propagation speed on the stress intensity factor. Further investigations along this line need to be carried out in order to better relate the failure characteristics to the micro-morphology of polymers which controls the material behavior in the cohesive zone.

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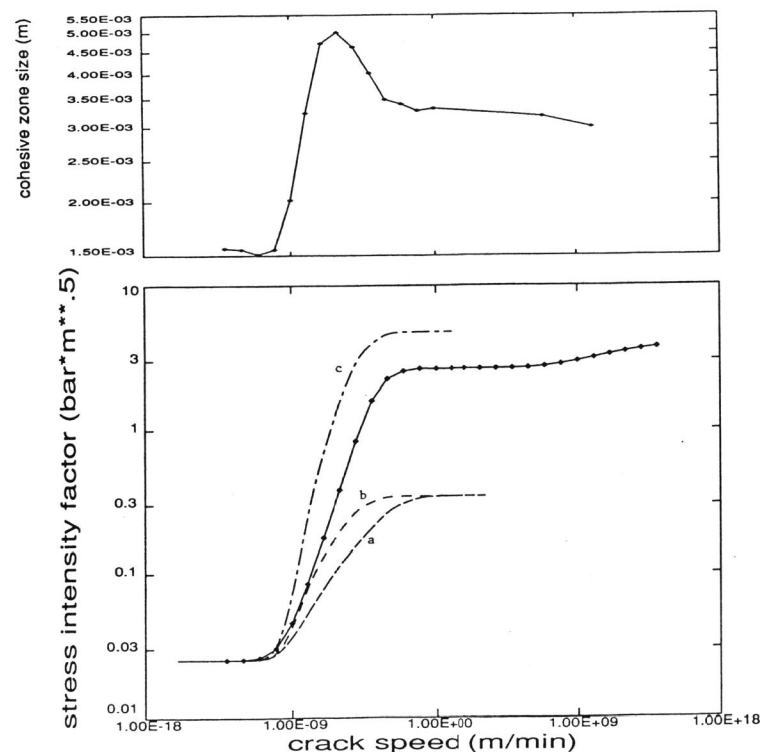


Fig. 22 Relation between stress intensity factor and crack speed for non-linearly viscoelastic "craze" problems (solid curve) and corresponding cohesive zone size (upper). Comparison with linearly VE model a) Energy or COD criterion with constant cohesive stress b) Energy criterion with constant cohesive zone size c) COD criterion with constant cohesive zone size.

REFERENCES

- National Research Council (NRC) (1981), Polymer Science and Engineering: Challenges, Needs, and Opportunities, *National Academy Press* Washington, DC.
- Ahagon, A. and A.N. Gent (1975). Threshold Fracture Energies for Elastomers. *J. Polymer Sci.*, 13, 1903.
- Argon, A.S. and M. Salama (1976). The Mechanism of Fracture in Glassy Materials Capable of some Inelastic Deformation. *Mat. Sci. and Eng.*, 23, 219.
- Argon, A.S., R.E. Cohen, O.S. Gebizlioglu and C.E. Schrier (1983). Crazing in Block Copolymers and Blends. In: *Advances in Polymer Science* (H. Kansch, ed.), Vol. 52/53, p. 275. Springer, Berlin.
- Barenblatt, G.I. (1962). The Mathematical Theory of Equilibrium Cracks in Brittle In: *Advances in Applied Mechanics*, Vol. 7, p. 55. Academic Press, New York.
- Brown, N. and X. Lu (1988). First Annual Report GRI Grant No. 5087-260-1468, Department of Materials Sci. and Eng., University of Pennsylvania, Philadelphia.

- Chang, J.K.Y. (1983). Crack Propagation in Viscoelastic Materials under Transient Loading with Application to Adhesively Bonded Structures. Aeron. Eng. Thesis. California Institute of Technology, Pasadena.
- Doell (1983). Optical Interference Measurements and Fracture Mechanics Analysis of Crack Tip Craze Zones. In: *Advances in Polymer Science* (H. Kansch, ed.), Vol. 52/53, p. 105. Springer, Berlin.
- Dugdale, D.S. (1960). Yielding in Steel Sheets Containing Slits *J. Mech. Phys. Solids*, 8, 100.
- Emri, I.J. and W.G. Knauss (1987). Volume Change and the Nonlinear Thermo-Viscoelasticity Constitution of Polymers. *Polymer Eng. and Sci.*, 27, 86.
- Gent, A.N., P.B. Lindley and A.G. Thomas (1964). Cut Growth and Fatigue of Rubbers I. The Relationship between Cut Growth and Fatigue. *J. Appl. Polymer Sci.*, 8, 455.
- Gent, A.N. (1970). Hypothetical Mechanism of Crazing in Glassy Plastics. *J. Mat. Sci.*, 5, 925.
- Greensmith, H.W. and A.G. Thomas (1955). Rupture of Rubber III. Determination of Tear Properties. *J. Polymer Sci.*, 18, 189.
- Greensmith, H.W. (1956). Rupture of Rubber IV. Tear Properties of Vulcanizates Containing Carbon Black. *J. Polymer Sci.*, 21, 175.
- Greensmith, H.W., L. Mullins and A.G. Thomas (1960). Rupture of Rubber. *Transact. Soc. Rheology*, 4, 179.
- Greensmith, H.W. (1964). Rupture of Rubber XI. Tensile Rupture and Crack Growth in a Noncrystallizing Rubber. *J. Appl. Polymer Sci.*, 8, 1113.
- Hertzberg, R.W. and J.A. Manson (1980). *Fatigue of Engineering Plastics*. Academic Press, New York.
- Hull, D. (1970). Effect of Crazes on the Propagation of Cracks in Polystyrene. *J. Mat. Sci.*, 5, 357.
- Kambour, R.P. (1965). Mechanism of fracture in glassy polymers, I. Fracture surfaces in polymethyl methacrylate. *J. Polymer Sci. Part A*, 3, 1713.
- Kambour, R.P. (1966a). Mechanism of fracture in glassy polymers, II. Survey of crazing response during crack propagation in several polymers. *J. Polymer Sci. Part A-2*, 4, 17.
- Kambour, R.P. (1966b). Mechanism of fracture in glassy polymers, III. Direct observation of the craze ahead of the propagation crack in poly(methyl methacrylate) and polystyrene. *J. Polymer Sci. Part A-2*, 4, 349.
- Kim, S.L., M.D. Skibo, J.A. Manson, R.W. Hertzberg and J. Jenisewski (1978). Tensile, Impact and Fatigue Behavior of an Amine-Cured Epoxy Resin. *Polymer Eng. Sci.*, 18, 1093.
- Klemperer, W.B. (1941). Stress Pattern Crazing. In: *T. von Karman Anniversary Volume*, p. 328. California Institute of Technology, Pasadena.
- Knauss, W.G. (1970). Delayed Failure - The Griffith Problem for Linearly Viscoelastic Materials. *Int. J. Fract. Mech.*, 6, 7.
- Knauss, W.G. (1971). Fracture Mechanics and the Time Dependent Strength of Adhesive Joints. *J. Composite Mat.*, 5, 176.
- Knauss, W.G. (1970)a. Delayed Failure - The Griffith Problem for Linearly Viscoelastic Materials. *Int. J. Fract. Mech.*, 6, 7.
- Knauss, W.G. (1971)b. Fracture Mechanics and the Time Dependent Strength of Adhesive Joints. *J. Composite Mat.*, 5, 176.
- Knauss, W.G. (1976). Fracture of Solids Possessing Deformation Rate Sensitive Material Properties. In: *The Mechanics of Fracture* (F. Erdogan, ed.). AMD-Vol. 19, American Society of Mechanical Engineers, New York, p. 69.
- Knauss, W.G. and I.J. Emri (1981). Non-linear viscoelasticity based on free volume consideration. *Computers and Structures*, 13, 123.
- Kostrov, B.V. and L.V. Nikitin (1970). Some General Problems of Mechanics of Brittle Fracture. *Archivum Mechaniki Stosowanej*, 22, No. 6, Engl. version, 749.
- Lake, G.J. and A.G. Thomas (1967). The strength of highly elastic materials. In: *Proc. Roy. Soc. London, Series A, Math. and Phys. Sci.*, Vol. 300 (1460), p. 108.
- Lake, G.J. and B.E. Clapson (1970). Truck tire groove cracking, theory and practice. *Rubber Journal*, 12, 36.
- Lauterwasser, B.D. and E.J. Kramer (1979). Microscopic mechanisms and mechanics of craze growth and fracture. *Phil. Mag.*, A Vol. 39, 469.
- Mai, Y.W. and J.G. Williams (1977). The effect of temperature on the fracture of two partially crystalline polymers; polypropylene and nylon. *J. Mat. Sci.*, 12, 1376.
- Marshall, G.P., L.E. Culver and J.G. Williams (1970). Craze growth in polymethylmethacrylate: a fracture mechanics approach. *Proc. Roy. Soc. London, A* Vol. 319, 165.
- Mueller, H.K. and W.G. Knauss (1971a). Crack propagation in a linearly viscoelastic strip. *J. Appl. Mech.*, 38, Series E No. 21, 483.
- Mueller, H.K. and W.G. Knauss (1971b). The Fracture Energy and Some Mechanical Properties of a Polyurethane Elastomer. *Trans. Soc. Rheology*, 15, 217.
- Parvin, M. and J.G. Williams (1975). The effect of temperature on the fracture of polycarbonate. *J. Mat. Sci.*, 10, 1883.
- Parvin, M. and J.G. Williams (1976). The effect of temperature on the fracture of rubber modified polystyrene. *J. Mat. Sci.*, 11, 2045.
- Parvin, M. and W.G. Knauss (1988). Advances in Nonlinear Fracture Mechanics. In: *Proc. of a IUTAM Meeting on Advances in Nonlinear Fracture Mechanics*. California Institute of Technology, Pasadena. To appear in *Int. J. Fract.*
- Rivlin, R.S. and A.G. Thomas (1953). Rupture of Rubber - I. Characteristic energy for tearing. *J. Polymer Sci.*, 10, 291.
- Schaperly, R.A. (1975a). A theory of crack initiation and growth in viscoelastic media, I. Theoretical development. *Int. J. Fract.*, 11, 141.
- Schaperly, R.A. (1975b)II. Approximate methods of analysis. *Int. J. Fract.*, 11, 369.
- Schaperly, R.A. (1975c)III. Analysis of continuous growth. *Int. J. Fract.*, 11, 549.
- Schaperly, R.A. (1986). TITLE. In: *Encyclopedia of Materials Science and Engineering*, p. 5043. Pergamon Press, Ltd., Oxford.
- Schaperly, R.A. (1988). On some path independent integrals and their use in fracture of nonlinear viscoelastic media. In: *Proc. of a IUTAM Meeting on Advances in Nonlinear Fracture Mechanics*. California Institute of Technology, Pasadena. To appear in *Int. J. Fract.*
- Skibo, M.D., R.W. Hertzberg, J.A. Manson and S. Kim (1977). On the generality of discontinuous fatigue crack growth in glassy polymers. *J. Mat. Sci.*, 12, 531.
- Smith, T.L. (1958). Dependence of the Ultimate Properties of a GR-S Rubber on Strain Rate and Temperature. *J. Pol. Sci.*, 32, 99.
- Thomas, A.G. (1955). Rupture of Rubber - II. The strain concentration at an incision. *J. Polymer Sci.*, 18, 177.
- Thomas, A.G. (1958). Rupture of Rubber - V. Cut Growth in Natural Rubber Vulcanizates. *J. Polymer Sci.*, 31, 467.
- Thomas, A.G. (1960). Rupture of Rubber - VI. Further Experiments on the Tear Criterion. *J. Appl. Polymer Sci.*, 3, 175.
- Ungsuwarungsri, T. and W.G. Knauss (1988). A Nonlinear Analysis of an Equilibrium Craze: Part I - Problem Formulation and Solution. Part II - Simulations of Craze and Crack Growth. *JAM*, 55, pp. 44, 52.
- Williams, J.G. and G.P. Marshall (1975). Environmental crack and craze growth phenomena in polymers. In: *Proc. Roy. Soc. Lond.*, A Vol. 342, 55.
- Williams, M.L. (1963). The Fracture of Viscoelastic Material. In: *Fracture of Solids* (Drucker and Gilman, eds.), p. 157. Interscience Publishers

In the current standards for the determination of fracture toughness of metals, ASTM E399-81 and ASTM E813-87, a fatigue precrack is required to guarantee a sufficiently sharp root radius at the crack tip to give a minimum value of fracture toughness. However, in polymeric materials, crack tip root radii as sharp as fatigue precracks can sometimes be achieved using methods requiring less time and specialized equipment. Such methods include pressing a new razor blade into the notch, or natural cracks obtained via pop-in on materials exhibiting brittle behavior.

Mandell *et al.* (1983) compared the use of razor sharpened notches with those obtained with the use of a sharpened blade on a milling machine on polyethylene pipe materials and suggested that pressing a razor blade into the pre-existing notch provides adequate sharpness. In another comparison between fatigue precracking and razor notching of polyethylene pipe material, Jones and Bradley (1988) determined that razor notching gave a value of J_{Ic} which was 33% higher than that measured in fatigue precracked specimens.

Darwish *et al.* (1981) and Mandell *et al.* (1982) found on poly(vinylchloride) that specimens containing a notch that was sharpened with a razor blade to a controlled depth gave adequate crack sharpness when compared with other methods such as fatigue precracks and natural cracks grown at low temperatures.

Williams (1984) found on polymethylmethacrylate (PMMA) that cracks can be extended from fine saw cuts in the specimen by pressing a razor into the end of the slot which causes a crack to run slightly ahead of the blade. However, it is noted that this procedure must be exercised with care since any blunting can lead to either a blunt crack tip or a multiple crazed crack tip.

Marshall *et al.* (1973) used three methods to precrack polystyrene (PS) which included slow razor notching, impact razor notching, and fatigue precracking. It was determined both razor notching techniques produced craze bundles at the tip of the crack causing higher initiation values of toughness where fatigue precracking led to a single craze at the crack tip and hence a lower limit on fracture toughness (Williams, 1984).

The objective in this study has been to determine which techniques used to produce a precrack on polycarbonate would give sufficiently low residual stresses and an adequately sharp crack tip radii necessary to give a true minimum in K_{Ic} . Polycarbonate was chosen for use in this study because of its biofringent character which gives a convenient way to examine the extent of residual stresses introduced by the various crack starter methods.

EXPERIMENTAL PROCEDURES

Machining of Specimens

Standard 1/2-T compact tension specimens were machined with the same orientation from a single plaque of Lexan polycarbonate. The plaque was free of an indication of residual stresses using a photoelastic birefringence technique. This technique is accomplished by viewing a photoelastic material between two polarized filters backed by fluorescent lighting. Specimens were machined with either a chevron notch or with a straight across notch parallel to the thickness direction.

Fatigue Precracking

Chevron notched specimens were fatigue precracked on a closed loop servo-hydraulic materials testing system at various levels of the critical stress intensity, K_{Ic} , of the material. The fatigue precracking loads were calculated using ASTM E399-81.

Razor - Notch Guillotine

In this method, the starter crack is attained by pressing a new razor blade directly into the specimen perpendicular to the thickness dimension. This technique which utilized specimens containing both chevron and standard machined notches. In the case of the chevron notch, a new razor blade was pushed to a depth just past the trailing edge of the chevron into a region of constant thickness. The specimens containing a straight machined notch were first slotted parallel to the machined notch on an Accutom cut-off wheel using a 0.254mm thick, 88.9mm outer diameter jeweler's slotting saw. The saw blade thickness is equivalent to that of a standard razor blade. The angular velocity of the saw blade was set at 500 rpm with a table displacement rate setting of approximately 0.2 mm/min.

Razor - sawing

The idea behind this technique is that the notching would be accomplished by actually cutting the material in a sawing motion parallel to the thickness dimension of the specimen in an attempt to minimize the amount of compressive residual stresses induced into the crack tip region. Prior to razor sawing, these specimens which also contained a standard (non-chevroned) machined notch, were slotted with the jeweler's slotting saw, as previously described.

RESULTS AND DISCUSSION

Extent of Residual Stresses Introduced During Precracking

A photoelastic birefringence technique was again used to give a qualitative assessment of the extent of residual stresses being induced ahead of the crack tip by the various notching techniques. Figure 1 shows a comparison of the damage zones introduced by the initial specimen machining alone. Note that the specimen containing the chevron is free of damage ahead of the notch, while that of the specimen which was notched straight across exhibits a large region of compressive residual stress ahead of the notch. Therefore, the machining of specimens alone may induce varying degrees of residual stresses adjacent to the notch prior to the final notch sharpening.

Fatigue precracking can create varying degrees of damage prior to testing depending on the level of loading. Figure 2 shows the results of fatigue precracking at 40%, 30%, and 10% of the load necessary to fracture the specimen, as determined in subsequent testing. However, it should be noted that the crack tip is located at the end of the butterfly zones shown in Fig. 2, and hence, the material ahead of the crack tip is free of residual stresses.

The razor-notching using a guillotine was utilized in two methods. The first involved pressing the razor blade directly into a chevron notched specimen with the use of the

- Chang, J.K.Y. (1983). Crack Propagation in Viscoelastic Materials under Transient Loading with Application to Adhesively Bonded Structures. Aeron. Eng. Thesis. California Institute of Technology, Pasadena.
- Doell (1983). Optical Interference Measurements and Fracture Mechanics Analysis of Crack Tip Craze Zones. In: *Advances in Polymer Science* (H. Kansch, ed.), Vol. 52/53, p. 105. Springer, Berlin.
- Dugdale, D.S. (1960). Yielding in Steel Sheets Containing Slits *J. Mech. Phys. Solids*, 8, 100.
- Emri, I.J. and W.G. Knauss (1987). Volume Change and the Nonlinear Thermo-Viscoelasticity Constitution of Polymers. *Polymer Eng. and Sci.*, 27, 86.
- Gent, A.N., P.B. Lindley and A.G. Thomas (1964). Cut Growth and Fatigue of Rubbers I. The Relationship between Cut Growth and Fatigue. *J. Appl. Polymer Sci.*, 8, 455.
- Gent, A.N. (1970). Hypothetical Mechanism of Cracking in Glassy Plastics. *J. Mat. Sci.*, 5, 925.
- Greensmith, H.W. and A.G. Thomas (1955). Rupture of Rubber III. Determination of Tear Properties. *J. Polymer Sci.*, 18, 189.
- Greensmith, H.W. (1956). Rupture of Rubber IV. Tear Properties of Vulcanizates Containing Carbon Black. *J. Polymer Sci.*, 21, 175.
- Greensmith, H.W., L. Mullins and A.G. Thomas (1960). Rupture of Rubber. *Transact. Soc. Rheology*, 4, 179.
- Greensmith, H.W. (1964). Rupture of Rubber XI. Tensile Rupture and Crack Growth in a Noncrystallizing Rubber. *J. Appl. Polymer Sci.*, 8, 1113.
- Hertzberg, R.W. and J.A. Manson (1980). *Fatigue of Engineering Plastics*. Academic Press, New York.
- Hull, D. (1970). Effect of Crazes on the Propagation of Cracks in Polystyrene. *J. Mat. Sci.*, 5, 357.
- Kambour, R.P. (1965). Mechanism of fracture in glassy polymers, I. Fracture surfaces in polymethyl methacrylate. *J. Polymer Sci. Part A*, 3, 1713.
- Kambour, R.P. (1966a). Mechanism of fracture in glassy polymers, II. Survey of crazing response during crack propagation in several polymers. *J. Polymer Sci. Part A-2*, 4, 17.
- Kambour, R.P. (1966b). Mechanism of fracture in glassy polymers, III. Direct observation of the craze ahead of the propagation crack in poly(methyl methacrylate) and polystyrene. *J. Polymer Sci. Part A-2*, 4, 349.
- Kim, S.L., M.D. Skibo, J.A. Manson, R.W. Hertzberg and J. Jenisewski (1978). Tensile, Impact and Fatigue Behavior of an Amine-Cured Epoxy Resin. *Polymer Eng. Sci.*, 18, 1093.
- Klemperer, W.B. (1941). Stress Pattern Crazing. In: *T. von Karman Anniversary Volume*, p. 328. California Institute of Technology, Pasadena.
- Knauss, W.G. (1970). Delayed Failure - The Griffith Problem for Linearly Viscoelastic Materials. *Int. J. Fract. Mech.*, 6, 7.
- Knauss, W.G. (1971). Fracture Mechanics and the Time Dependent Strength of Adhesive Joints. *J. Composite Mat.*, 5, 176.
- Knauss, W.G. (1970a). Delayed Failure - The Griffith Problem for Linearly Viscoelastic Materials. *Int. J. Fract. Mech.*, 6, 7.
- Knauss, W.G. (1971b). Fracture Mechanics and the Time Dependent Strength of Adhesive Joints. *J. Composite Mat.*, 5, 176.
- Knauss, W.G. (1976). Fracture of Solids Possessing Deformation Rate Sensitive Material Properties. In: *The Mechanics of Fracture* (F. Erdogan, ed.). AMD-Vol. 19, American Society of Mechanical Engineers, New York, p. 69.
- Knauss, W.G. and I.J. Emri (1981). Non-linear viscoelasticity based on free volume consideration. *Computers and Structures*, 13, 123.
- Kostrov, B.V. and L.V. Nikitin (1970). Some General Problems of Mechanics of Brittle Fracture. *Archivum Mechaniki Stosowanej*, 22, No. 6, Engl. version, 749.
- Lake, G.J. and A.G. Thomas (1967). The strength of highly elastic materials. In: *Proc. Roy. Soc. London, Series A, Math. and Phys. Sci.*, Vol. 300 (1460), p. 108.
- Lake, G.J. and B.E. Clapson (1970). Truck tire groove cracking, theory and practice. *Rubber Journal*, 12, 36.
- Lauterwasser, B.D. and E.J. Kramer (1979). Microscopic mechanisms and mechanics of craze growth and fracture. *Phil. Mag.*, A Vol. 39, 469.
- Mai, Y.W. and J.G. Williams (1977). The effect of temperature on the fracture of two partially crystalline polymers; polypropylene and nylon. *J. Mat. Sci.*, 12, 1376.
- Marshall, G.P., L.E. Culver and J.G. Williams (1970). Craze growth in polymethylmethacrylate: a fracture mechanics approach. *Proc. Roy. Soc. London, A* Vol. 319, 165.
- Mueller, H.K. and W.G. Knauss (1971a). Crack propagation in a linearly viscoelastic strip. *J. Appl. Mech.*, 38, Series E No. 21, 483.
- Mueller, H.K. and W.G. Knauss (1971b). The Fracture Energy and Some Mechanical Properties of a Polyurethane Elastomer. *Trans. Soc. Rheology*, 15, 217.
- Parvin, M. and J.G. Williams (1975). The effect of temperature on the fracture of polycarbonate. *J. Mat. Sci.*, 10, 1883.
- Parvin, M. and J.G. Williams (1976). The effect of temperature on the fracture of rubber modified polystyrene. *J. Mat. Sci.*, 11, 2045.
- Parvin, M. and W.G. Knauss (1988). Advances in Nonlinear Fracture Mechanics. In: *Proc. of a IUTAM Meeting on Advances in Nonlinear Fracture Mechanics*. California Institute of Technology, Pasadena. To appear in *Int. J. Fract.*
- Rivlin, R.S. and A.G. Thomas (1953). Rupture of Rubber - I. Characteristic energy for tearing. *J. Polymer Sci.*, 10, 291.
- Schaperly, R.A. (1975a). A theory of crack initiation and growth in viscoelastic media, I. Theoretical development. *Int. J. Fract.*, 11, 141.
- Schaperly, R.A. (1975b)II. Approximate methods of analysis. *Int. J. Fract.*, 11, 369.
- Schaperly, R.A. (1975c)III. Analysis of continuous growth. *Int. J. Fract.*, 11, 549.
- Schaperly, R.A. (1986). TITLE. In: *Encyclopedia of Materials Science and Engineering*, p. 5043. Pergamon Press, Ltd., Oxford.
- Schaperly, R.A. (1988). On some path independent integrals and their use in fracture of nonlinear viscoelastic media. In: *Proc. of a IUTAM Meeting on Advances in Nonlinear Fracture Mechanics*. California Institute of Technology, Pasadena. To appear in *Int. J. Fract.*
- Skibo, M.D., R.W. Hertzberg, J.A. Manson and S. Kim (1977). On the generality of discontinuous fatigue crack growth in glassy polymers. *J. Mat. Sci.*, 12, 531.
- Smith, T.L. (1958). Dependence of the Ultimate Properties of a GR-S Rubber on Strain Rate and Temperature. *J. Pol. Sci.*, 32, 99.
- Thomas, A.G. (1955). Rupture of Rubber - II. The strain concentration at an incision. *J. Polymer Sci.*, 18, 177.
- Thomas, A.G. (1958). Rupture of Rubber - V. Cut Growth in Natural Rubber Vulcanizates. *J. Polymer Sci.*, 31, 467.
- Thomas, A.G. (1960). Rupture of Rubber - VI. Further Experiments on the Tear Criterion. *J. Appl. Polymer Sci.*, 3, 175.
- Ungsuwarungsi, T. and W.G. Knauss (1988). A Nonlinear Analysis of an Equilibrium Craze: Part I - Problem Formulation and Solution. Part II - Simulations of Craze and Crack Growth. *JAM*, 55, pp. 44, 52.
- Williams, J.G. and G.P. Marshall (1975). Environmental crack and craze growth phenomena in polymers. In: *Proc. Roy. Soc. Lond.*, A Vol. 342, 55.
- Williams, M.L. (1963). The Fracture of Viscoelastic Material. In: *Fracture of Solids* (Drucker and Gilman, eds.), p. 157. Interscience Publishers