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Recent developments in the kinetic theory of fracture of polymers

By H. H. Kausch von Schmeling

With 4 figures in 5 details

Introduction

The importance of a thorough understanding of fracture processes need not to be emphasized. Costly failures always have and still do attract enough attention to this subject. The obvious aim of the investigator is the prediction of fracture behavior under all kinds of foreseeable conditions or, rather, the formulation of non-fracture conditions. Any predictions will have to be based on experimental results which are linked together through theoretical considerations. The number of theoretical assumptions in combining experimental data varies. There will be many if a large number of material and environmental parameters are taken into consideration. There will be fewer if the response of the material under one set of conditions is taken to be a single process. For instance the time to fracture of a strip of rubber under constant uniaxial load can be viewed as one function of the material and environmental parameters or it can be considered as the complex result of a number of different processes, e. g. crack initiation, slow crack growth, and rapid crack propagation. No matter which philosophy is employed the extrapolation of a function of one parameter into inaccessible regions of this parameter requires a critical check of the validity of all assumptions involved.

In the first section of this paper we will, therefore, briefly discuss the major points of the kinetic theory of fracture, namely the nature of the statistically independent elements, their performance, and how the probabilities for failure of individual elements combine to characterize the behavior of the whole structure.

We will then specify these conditions for the case of oriented polymers in their glassy state under special consideration of all experimental evidence as the ultimate properties at break, their temperature- and time-dependency, the formation of free radicals, and the statistical variability in fracture experiments. In accordance with these conditions a statistico-mechanical model is developed which describes the fracture process until onset of rapid crack propagation. Except for samples with large, pre-existing cracks this covers essentially the total lifetime of a sample. An equation for the time to fracture is derived as a function of orientation and constant uniaxial stress. This equation is discussed and compared with experimental results. Finally it is investigated whether and how the theory may be applied under other than the specified conditions, e. g. for rubbers, and the extensibility to time-dependent loads and multiaxial stress. A fracture criterion is formulated which may be called the kinetic version of *St. Venants* criterion of maximum elastic strain.

Statistical and mechanical models in the kinetic theory of fracture

A theory of fracture usually is called a kinetic theory if it accounts in some way for

time-dependent changes within the material which eventually lead to failure of the sample under consideration. One can even be more specific and say that the time-dependent changes are related to and depend on the fluctuating thermal energy of the atoms, segments, or molecules.

Within this framework the nature of the time-dependent processes can be quite different. *Busse* and his colleagues (4) suggested that *viscous flow* within cotton fibers determines the fatigue life of these fibers and they used *Eyrings* theory of viscosity (13) for interpretation of their data. *Tobolsky* and *Eyring* (45) considered the *"slippage" of secondary bonds* and the net decrease of the number of bonds. They considered the two cases where repair of bonds under stress is either possible or impossible. *Stuart* and *Anderson* (43) discussed a model involving two independent networks and argued that only *fracture within* the first *network with unsymmetrical potential barriers* between broken and unbroken states contributes towards failure of glasses. *Zhurkov* (47, 48) among others suggested that the *breakage of primary bonds* in long-chain molecules may be the dominant cause of failure of a number of different natural and synthetic fibres. *Prevorsek* and *Lyons* (36) emphasized that *nucleation and growth of voids* and flaws can be attributed to the random thermal motion of chain segments even without breakage of any load carrying bonds. The lifetime of a sample would then be determined by the time it takes one flaw to grow to a critical size. Without specification of the nature of the time-dependent process it is sometimes called *damage* (15) or *probability of crack formation* (26).

The mathematical formalism of these various theories can be conveniently compared if we denote by N the number of those elements (bonds, flow steps, nuclei, etc.) whose time-dependent change is considered to determine the lifetime of the sample as a whole. In its general form the equation for the rate of change of N is given as

$$dN/dt = - NK(\sigma, N, T). \qquad [1]$$

where K is the rate of breakage or nucleation, σ the stress tensor[1]), and T the absolute temperature.

The interpretation of K and its formulation is different in the kinetic theories of

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[1]) K is not a functional, σ therefore stands only for its components.

different authors according to the different statistico-mechanical models.

In a series of papers *Coleman* (7–9) and *Coleman* and *Marquardt* (10, 11) propose a "theory of breaking kinetics" for fibres. Their approach is completely formal and does not involve any assumptions concerning the microstructure of the fibres. The statistical considerations summarized there for "first order ensembles" obtain new importance, however, when applied to molecular ensembles. Eq. [1] for the rate of decrease of a number N of statistically equal, independent and separately loaded fibers becomes:

$$dN/dt = - N K \qquad [2]$$

and is readily solved with respect to the number $N(t)$ of surviving fibres:

$$N(t) = N_0 \exp \left[- \int_0^t K(\tau)\, d\tau \right], \qquad [3]$$

where N_0 is the initial number of fibres.

The fraction of fibres broken after some time t_b is obviously $1 - N(t_b)/N_0$ and the cumulative distribution function of lifetimes, $Q(t_b)$, therefore, is:

$$Q(t_b) = 1 - \exp \left[- \int_0^{t_b} K(\tau)\, d\tau \right]. \qquad [4]$$

The average lifetime, $\langle t_b \rangle$, is solely determined by K and becomes for constant K:

$$t_b = \frac{1}{N_0} \int_0^\infty t\, N_0\, K \exp(- K t)\, dt = K^{-1}. \qquad [5]$$

It may be noted that in this case the life-expectancy of a surviving fiber is at any time independent of N and t.

Kawabata and *Blatz* (26) developed a simple stochastic theory of creep failure. They argued that the first moments of t_b for an ensemble of ruptured specimens should reveal whether K is independent of time or not. If K depends only on initial load and is independent of N the equation

$$K = (m!/\langle t_b{}^m \rangle)^{1/m} \qquad [6]$$

should hold for any m, that is for any order of moments of t_b. An investigation of the variation of fracture times of a rubber vulcanizate gave excellent agreement with the assumption of a time-independent K (14, 26), i. e. like in eq. [2].

Bueche and *Halpin* (3) have been concerned with fracture of elastomers, which they consider to be the result of the breakage of a large number of filaments within the

stressed specimen. While they still employ the idea of all filaments being equivalent and subjected to practically the same load they introduce two important concepts, the first being that in an area of high stress concentration (crack tip) essentially one small filament is strained until it ruptures at a critical strain λ_c. Only after rupture of the first filament is completed in time t' the rapid straining of the second filament starts etc. The second concept concerns the viscoelastic properties of the filament in comparison with those of the sample as a whole. It is reasoned that the same physical processes are responsible for the creep behavior of a filament and that of the total sample and that it should be possible to deduce the viscoelastic performance of a filament from the observed creep function of the sample. The sample will fracture at a gross strain λ_b after q filaments have been broken in a time $t_b = q\,t'$. The values λ_b and λ_c are connected through the creep function of the material and the stress concentration factor. The theory allows to calculate the elongation at break, λ_b, from the knowledge of the creep function.

We may point out that the theory does not take into consideration any change of the stress concentration factor s with growing crack length or the decrease of t', the time necessary to fracture one filament, with continuing creep of the sample. It is assumed that all filaments will have to be stretched from practically zero elongation to λ_c. That will, in the first place, effect any numerical values of q which may be calculated from fitting experimental failure envelopes. In their calculations *Bueche* and *Halpin* do not make use of the expected statistical variation of fracture times t_b which would lead to additional information concerning q. The time increment t' is not actually constant but will show a variation $Q\,(t')$ in accordance with eq. [4].

A group of q filaments subject to the statistical condition that fracture of one filament may start once the fracture of the preceding one is completed has an average lifetime, $\langle t_b \rangle$, of $q\,t'$ and a *Poisson* distribution of t_b:

$$p\,(t_b)\,dt_b = dt_b/t'\,(t_b/t')^{q-1}\,e^{-t_b/t'}/(q-1)! \qquad [7]$$

The scatter of t_b should be used, therefore, to check the value of q. No matter whether t' is assumed constant or varying around an average the theory leads to a practically constant rate of crack growth for almost the

total length of lifetime followed by a sharp jump to very high crack velocities immediately before failure.

Whenever an ensemble of fibres or elements is strongly interconnected the failure of one element leads to increasing loads for the remaining ones. Whereas the difference is not felt very much at the beginning of the lifetime of a large ensemble, the rates of increase of stress or strain, the fracture development and the remaining lifetime are considerably changed toward the later stages of the lifetime.

The "ideal bundle" (9) is a very good realization of this concept. The rate equation is changed now into:

$$dN/dt = -\,N\,K\,(\sigma/N)\,. \qquad [8]$$

Without any information on the rate function K this equation cannot be integrated. We will, therefore, briefly turn our attention to some experiments revealing the stress dependency of K. We may recall that for one value of uniaxial stress K can be determined from the breaking times of a set of single fibres under separate identical constant loads. The variation of these breaking times reveals whether K is constant with time (26). If so, K is just the inverse of the average lifetime (eq. [6]). From a series of experiments under different loads, σ_0, the function $K(\sigma_0)$ can be obtained. Uniaxial loading experiments have been carried out for a large number of natural (4, 30, 31, 47) and synthetic (2, 7, 27, 36, 39, 48) fibres, for glasses (43), SBR-vulcanizates (16, 26), and metals (39, 48).

The results from all these experiments show that a plot of $\log t_b$ versus σ_0 is sort of a sigmoidal curve with an extended linear central section and portions of increasing slope at higher and smaller stresses respectively (29). The same results are often plotted as stress versus the duration of the experiment, if the *strength* of the material is considered to be the dependent variable. In fig. 1 both representations are compared. A closer examination shows that the assumption of K independent of time holds for the linear central section only. It follows for this section immediately that K is an exponential function of σ_0:

$$K = \omega_b \exp\,(\beta\,\sigma_0)\,, \qquad [9]$$

where ω_b and β are constant with respect to time and uniaxial stress, σ_0. We may now return to the ideal bundle or a time-dependent number of primary or secondary bonds

which *share* a *constant* stress σ_0. The stress experienced by each surviving element is $N_0 \sigma_0/N(t)$ and the rate equation becomes:

$$dN/dt = -N \omega_b \exp [N_0 \beta \sigma_0/N(t)] . \qquad [10]$$

This equation may be solved in terms of the exponential integral[2]) for constant σ_0:

$$\langle \omega_b t_b \rangle = \int_{\beta \sigma_0}^{\infty} \frac{e^{-x}}{x} dx \equiv -E i (-\beta \sigma_0) . \qquad [11]$$

In eq. [11] the average of t_b appears since eq. [10] is a deterministic equation. The time intervals Δt necessary to produce a change ΔN of N are subject to statistical variation. It is seen from a comparison of eqs. [5], [9] and [11] that the average lifetime of a bundle of fibers deviates from the lifetime of a single fibre by a factor $-E i (-\beta \sigma_0)/\exp (-\beta \sigma_0)$, which is equal to $1/\beta \sigma_0$ if $\beta \sigma_0 \gg 1$. The statistical concept of coupling the performance of many elements, which causes the mentioned decrease in $\langle t_b \rangle$ also reduces the second moment of t_b, $M_2(t_b)$. *Coleman* calculated (9) that the coefficient of variation of the lifetimes,

$$(\langle t_b^2 \rangle - \langle t_b \rangle^2)^{1/2}/\langle t_b \rangle$$

is proportional to $N_0^{-1/2}$ and thus approaches zero if there are a large number (N_0) of elements per bundle or subvolume.

So far we have discussed kinetic theories in which crack initiation and propagation are governed by the same principle, namely a rate controlled irreversible decrease of load carrying elements. In accordance with the derivation of kinetic theories of fracture from the theory of absolute reaction-rates the earliest approaches accounted for changes in both directions, that is for the breakage as well as for the reformation of bonds (45). Eq. [1] then has to be formulated as:

$$dN/dt = -N K_b + (N_0 - N) K_r \qquad [12]$$

using separate rate functions for the breaking (K_b) as well as for the reforming process (K_r). If it were attempted to interpret this situation in terms of just one rate function K as in eq. [1], K would become highly time-dependent even though K_b and K_r may be constant with respect to time. On the basis of this theory *Stuart* and *Anderson* (43) explained the fatigue life of glasses over 16 decades of temperature-reduced timescale.

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[2]) The above exponential integral $-E i (-\beta \sigma_0)$ is for positive arguments often also abbreviated as $E_1 (\beta \sigma_0)$.

The author has previously discussed (22) the stress-lifetime curves resulting for different time-dependent rate functions K_b and K_r and also the existence of dynamic equilibria which lead to infinite lifetimes. It was pointed out that the assumption of reforming processes would conveniently explain the non-linear slope of the sigmoidal stress-lifetime curve (fig. 1) at small stresses. If the molecular fracture process happens to be that of a main chain immediate reformation of the same primary bond seems to be unlikely in view of recent EPR-experiments (12)
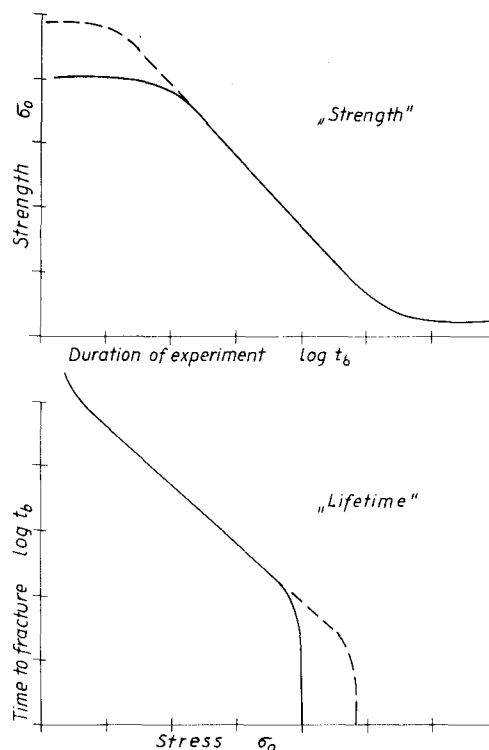

Fig. 1. Schematic representation of stress-lifetime curves with emphasis on strength (upper diagram) or lifetime (lower diagram). The dashed line indicates change, which would result from increase in "upper limit of strength" (22)

which indicate a rapid transfer of the free radicals formed and a negligible rate of recovery of a stressed specimen (Nylon 6).

The kinetic theory of *Knauss* (27) for time-dependent fracture of viscoelastic materials also is based on a dynamic equilibrium between broken and unbroken bonds. Crack initiation then is due to a stress induced change of the equilibrium state. Even though it is assumed that equilibrium in the unstressed state exists when one half of all bonds capable of rupture are broken it is

also stated that the point where equilibrium is established is not important but rather the way deviations from this reference state occur. If the rate functions K_b and K_r are functions of temperature and the amount of energy available to a bond the change of the equilibrium number of broken bonds in a "weak region" can be calculated. The number of newly broken bonds can be interpreted as a measure of the size of a defect. It is assumed that the size of the defect continues to grow following the same mathematical description until it reaches a critical value which is determined from energy considerations. In this case shape and size of the crack, therefore, do not influence the rate functions K_b and K_r.

The *shape* of a crack has not received special consideration in any of the above mentioned kinetic theories. The *size* enters the calculations only indirectly and only if the increase in load with decreasing number of elements (load sharing) is considered. There is no question that size and shape of a crack are of prime importance as far as the stability of a crack is concerned. And there is also no question that a stable crack some time prior to reaching the critical size influences its own rate of growth.

In a series of papers *Prevorsek* and *Lyons* (35–38) presented a theory of crack nucleation and growth where the interdependency of crack size and rate of growth was especially considered. They made use of the calculations of *Sack* (40) for the decrease in strain-free energy associated with the presence of a circular micro-crack in a continuum. The net energy to create a crack of radius r is composed of this term and the surface energy and it has a maximum at some radius r^*. The value of r^* is the critical radius because any crack with $r > r^*$ becomes unstable and propagates rapidly. The authors assume that a crack can grow by incorporating in its surface layer molecular segments from the "standard state phase". The rate of crack growth is formulated as a function of the radius, uniaxial stress, two activation energies and the concentrations of the crack nuclei and the molecular segments in their surrounding. The probability of fracture is then given by the slowest step, i. e. by the smallest rate, which is the rate of growth of a crack having radius r^*. Out of a great number of slowly and by no means monotonically growing cracks one will be able to reach the critical size and cause a failure.

Summing up this brief review we may say that three statistical concepts have been proposed, which involve a) a number of independent elements, b) a number of load sharing elements, or c) the probability of a single event (formation of an unstable crack). "Mechanical" concepts concern stress concentration, viscoelastic deformation of load carrying elements, energy required to form new surfaces, and elastically stored energy within a certain sample volume.

In the next section fracture of glassy polymers is discussed and it will be attempted to describe it within the framework of the above concepts.

Fracture of glassy polymers

In the previous section statistical and mechanical models of kinetic fracture processes have been discussed which were applied to a large variety of polymers and glasses and widely different modes of excitation. We would like to discuss in more detail the fracture of polymers in their glassy state.

A polymer network in its glassy state, i. e. below the glass transition temperature, T_g, is believed to be in a state of thermodynamical non-equilibrium, but it is nevertheless a quasi-stable state because configurational changes take place at infinitely slow rates. Whereas chemical crosslinks and physical crosslinks like entanglements determine the cohesion of a polymer in the rubbery region intermolecular attraction through *Van der Waals* forces contributes significantly to the cohesion of a glassy polymer. These forces are called secondary bonds or also physical crosslinks. It may be clearly pointed out, however, that these secondary "bonds" are not nearly as localized or well defined as primary bonds are. Due to the fact that the *Van der Waals* attraction involves whole segments rather than individual atoms the binding potential varies greatly. Strong dipol-dipol interaction and hydrogen-bonds are a certain exception. They tend to be more localized and more uniform in their binding potentials. In statistical considerations the concept of localized secondary bonds has been used successfully (34, 45). It is with this understanding that the term "secondary bonds" will be used. Secondary bonds at temperatures below T_g are remarkably stable as may be concluded from the absence of a time proportional flow component in creep of thermoplasts or

glasses under moderate stresses (31). It may also be deduced from the fact that failure usually does not occur in shear.

The energy of activation calculated from the temperature dependency of the fracture strength for various polymers was found to be comparable to the binding energy of primary bonds (47). It was thus suggested that the breakage of primary bonds in the chain molecules actually takes place. Furthermore, this phenomenon is considered to be the dominant cause of the eventual failure of these solids.

A conformation of this assumption was obtained by *Zhurkov* (49), *DeVries* (12), *Campbell* and *Peterlin* (5), *Becht* and *Fischer* (1a), and the author by studying the formation of free radicals during fracture of various polymers. Using electron paramagnetic resonance (EPR) free radicals formed by broken polymer backbone chains have been observed directly and also in a more stable form after being trapped by impurities. Constant loads up to about 60% of the fracture strength do not lead to any detectable EPR-signal.

These findings indicate that the strength of a polymer in its glassy state is that of a physically crosslinked network of main chains. Initially all primary bonds capable of rupture are unbroken. Under load small chain ends may be pulled loose, segments and side groups will slip past each other, closed loops can be opened and backbone chains are stressed until they break or slip past each other. In the temperature region of brittle fracture only the breakage of main chains provides a time-dependent accumulative damage, which will lead to fracture initiation. It can safely be assumed that a small amount of segment slippage does not decrease the load carrying capability of a certain volume element.

It seems to be an adequate approach, therefore, to discuss the fracture strength of a polymer in terms of the load carrying chains. It is assumed that part of the load is carried by extended chains which form a statistical network. Upon stressing of a sample chain scission will occur only within this network. And as stated above, the accumulation of this effect will eventually lead to failure of the stressed specimen. The two-network-model of *Stuart* and *Anderson* (43) describes this situation. We can modify it slightly and say that the *viscoelastic properties* of a polymer below its glass transition temperature may be represented by a

"network of one-dimensional elastic elements" embedded in a "viscoelastic continuum". The time-dependent fracture strength will be determined by the oriented elastic network the response of which is modified by the viscoelastic continuum.

It is attempted in the next section, therefore, to study the performance of a well defined, oriented elastic molecular network under constant load. It will then be necessary to adapt the results from these calculations to the conditions of a real polymer network and also to give the limitations of this theory in terms of stress, strain and strain rate, inhomogeneities, etc.

Time-dependent changes in an elastic network

The elastic properties and the fracture strength of oriented polymers have been studied extensively by *Hsiao* (19, 20, 33).

In the rubbery region a polymer shows increasing orientation with increasing elongation. In a stress-free state a rubber has no orientation. This is different with thermoplasts or organic glasses which can undergo large plastic deformations (drawing at elevated temperatures or cold-drawing at much higher stresses) and where the stress can be removed at temperatures below T_g to leave the material in a highly oriented quasi-stable state. Elastic and anelastic response as well as fracture strength depend upon the degree of orientation of the polymer. If one assumes that a uniaxial plastic deformation of a sample is an affine deformation the orientation distribution ϱ is described by the *Kratky*-formula (28):

$$\varrho\,(\theta) = \frac{1}{2\,\pi}\,\frac{\lambda^3}{[\cos^2\theta + \lambda)^3\sin^2\theta]^{3/2}}\,,\qquad [13]$$

where λ is the uniaxial draw ratio.

We may, therefore, characterize the uniaxial plastic deformation of a polymer by λ. In accordance with the considerations of the previous section we will neglect anelastic deformations of a sample as long as they are small compared with λ and as the rate of strain does not influence stresses measurably. The "elastic network" and the "viscoelastic continuum" are both made up of polymer chains and there is no way to tell whether a particular segment belongs to one or the other. It is reasonable, however, to assume that those sections of a polymer chain which form an almost straight line for a length of 10 to 20 or more monomer units

are subjected to larger axial forces than chains which change their orientation in space every few monomer units. We will, therefore, consider long straight sections of the polymer chains as part of the "elastic network" and represent them by linear elastic elements of uniform length l_0. The time-dependent fracture strength will then depend upon the performance of the oriented, elastic network. It was considered that such a network on a macroscopic scale is homogeneous so that continuum theory of elasticity may be applied to relate prescribed forces and deformations to the state of strain of a small subvolume. Within the subvolume the presence of the molecular elements and their orientation is taken into account. If the macroscopic body is subjected to forces the response of the material will lead to a deformation of the elements within the network. We assume that within the subvolume the strain is a continuous function[3]) of the spherical coordinates θ, Φ, so that the strain experienced by a certain element in the direction of its axis is given by[4])

$$\Delta l/l_0 = \varepsilon_{mn} s_m s_n \qquad m, n = 1, 2, 3 \qquad [14]$$

and the force, acting in the same direction by

$$F(\theta, \Phi, t) = \varkappa\, l_0\, \varepsilon_{mn} s_m s_n , \qquad [15]$$

where $\varkappa$ is the spring constant of the elastic elements, and s_m, s_n are components of the unit vector in the direction of orientation identified by θ and Φ ($s_1 = \sin\theta\,\cos\Phi$, $s_2 = \sin\theta\,\sin\Phi$, $s_3 = \cos\theta$).

If for convenience we replace forces by local stresses, we obtain:

$$\psi(\theta, \Phi, t) = E\, \varepsilon_{mn} s_m s_n \qquad [16]$$

where $E = \varkappa\, l_0{}^2\, n_i$, if n_i is the initial number of elements per unit volume.

It may be emphasized again that n_i will be much smaller than the number of chains between "secondary bonds". This general scheme is roughly represented in fig. 2 with various possible orientations of the molecular network in a material body under a prescribed load, P. For uniaxial stress, $\sigma_{33} = \sigma_0$, and transverse symmetry about the 33-axis eq. [16] becomes:

$$\psi(\theta, t) = E\, (\cos^2\theta - \nu \sin^2\theta)\, \varepsilon_{33} \qquad [17]$$

where ν is the strain ratio $\varepsilon_{11}/\varepsilon_{33}$.

[3]) A discussion of the consequences following from this and alternative assumptions is given in reference (23).
[4]) The summation convention for repeated indices is used.

If no stress concentration has to be considered ε_{33} is equal to σ_0/E_λ where E_λ is the longitudinal modulus of elasticity of the oriented *sample*. It has been shown by *Hsiao* (19) that the stress tensor acting on a small volume element of the elastic network can be calculated from eq. [17] once the orientation distribution function, ϱ, is known:

$$\sigma_{ij}{}' = \oint \varrho(\theta)\, f(\theta, t)\, s_i\, s_j\, \psi(\theta, t)\, d\Omega \qquad [18]$$

where $d\Omega$ is the infinitesimal solid angle and $f(\theta, t) = N(\theta, t)/N(\theta, 0)$, the fraction of unbroken elements.
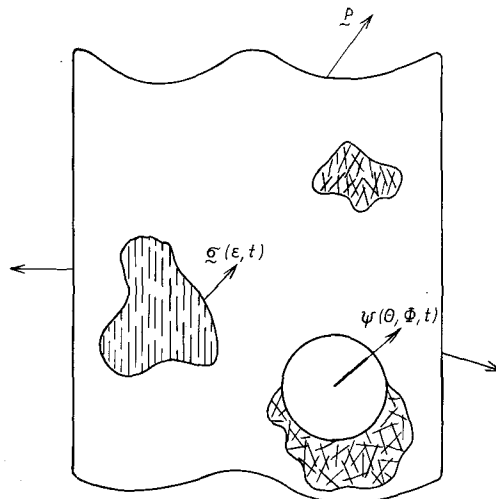

Fig. 2. Schematic representation of oriented solid showing areas of complete, partial and random orientation of molecular elements. P: forces acting on macroscopic body, $\sigma(\varepsilon, t)$: state of stress of subvolume, $\psi(\theta, \Phi, t)$: local stress, acting on molecular element

The tensor $\sigma_{ij}{}'$ acting on the elastic network will differ from the stress σ_{ij} acting on the subvolume because any forces transmitted by the viscoelastic continuum are omitted in the determination of $\sigma_{ij}{}'$ by eq. [18]. Also the strain ratio ν will differ for the linear elastic network ($\nu = 0.25$ for random orientation) and the actual polymer sample (0.35–0.50).

As outlined, however, in the previous section only the action of $\sigma_{ij}{}'$ is thought to be responsible for time-dependent damage to the elastic network. If ψ from [17] is introduced into [18] one obtains:

$$\sigma_{11}{}' = \sigma_{22}{}' = 0 = \int_0^{\pi/2} E\, \varrho(\theta)\, f(\theta, t)\, [\varepsilon_{11} \sin^2\theta + \varepsilon_{33} \cos^2\theta]\, \sin^3\theta\, d\theta \qquad [19]$$

$$\sigma_{33}{}' = 2\pi \int_0^{\pi/2} E\, \varrho(\theta)\, f(\theta, t)\, [\varepsilon_{11} \sin^2\theta + \varepsilon_{33} \cos^2\theta]\, \cos^2\theta \sin\theta\, d\theta . \qquad [20]$$

For all elements with "orientation θ" the rate of rupturing of the unbroken elements is given by the rate eq. [1] and with reference to eq. [9] by an exponential rate function K:

$$dN/dt = - N \, \omega_b \exp [- U/RT + \beta \, \psi \, (\theta, t)] \quad [21]$$

where ω_b and β are constants, R is the gas constant, T absolute temperature and U the activation energy.

The system of eqs. [19–21] cannot be solved analytically. An approximation method has been proposed, however, and carried out for randomly oriented elastic networks (25). Without repeating details of the method[5]) it may be said that the changes of N for a time interval Δt as calculated from eq. [21] are being fed back into eqs. [19, 20] giving the corresponding changes of $\varepsilon_{11} \, (t)$ and $\varepsilon_{33} \, (t)$, which in turn determine the changes of $\psi \, (t)$. The iterative integration of eqs. [19–21] can be carried out numerically. The result of this integration for an un-oriented specimen ($\lambda = 1$),

$$\langle \bar{\omega}_b \, t_b \rangle = \int\limits_0^{f_0=1} \frac{df \, (\theta, t)}{f \exp [\beta \, \psi \, (\theta, t)]} \quad [22]$$

is shown in fig. 3. The quantity $\bar{\omega}_b$ is the stress-independent part of the rate function:

$$\bar{\omega}_b = \omega_b \exp (- U/RT) . \quad [23]$$

Also shown in fig. 3 is the stress-lifetime curve for completely oriented specimens ($\lambda \to \infty$), which can be calculated according to eq. [11]. The curve for $\lambda = 3$ is obtained by interpolating the other two curves in a manner to be discussed shortly.
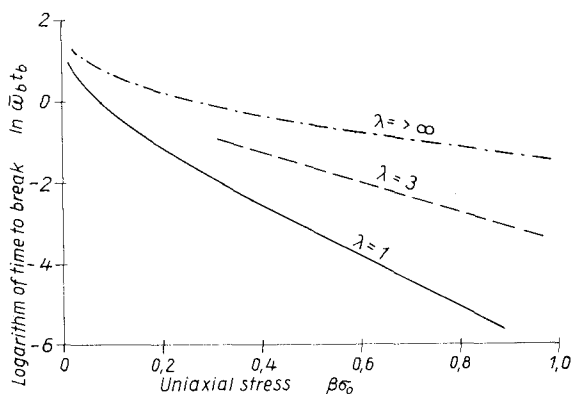

Fig. 3. Time-to-break for uniaxially stressed specimen (calculated from eq. [22])

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[5]) Details of the method may be obtained from reference (24) which is available upon request.

Discussion of the results

Eq. [22] describes the time to failure of a homogeneous elastic molecular network under constant load. It is obvious that a real polymer sample is not a homogeneous network, since it contains frozen-in tensions and statistically distributed deviations from all functions which characterize the average state of the material (ϱ, ε_{mn}, n_i). A variation of local stress $\psi \, (0,0)$ throughout the volume of the sample has to be expected. If this is so then the subvolume under maximum stress will fail first. A different interpretation of the same situation would be to say that the stress concentration factor s shows a variation throughout the sample volume. Since s is incorporated in β this leads to a variation of β. The response of the sample as a whole after failure of a load carrying subvolume depends upon the size of the subvolume and material properties. Previous investigations (25) have shown that an elastic network just prior to failure under-goes large deformations. These deformations are shared by the "viscoelastic continuum". Failure of the subvolume, therefore, will mean the creation of a void smaller than the subvolume, which is surrounded by a "torus" of highly oriented, plastically de-formed material.

If the subvolume is fairly large so that its failure gives rise to an unstable crack (rapid crack propagation) then the lifetime of the subvolume becomes almost identical to the lifetime of the sample.

If the subvolume is smaller so that the crack resulting from its failure is not un-stable then a period of slow crack growth will add to the lifetime of the sample. The theoretical and experimental investigations of *Sternstein* et al. (42) and *Cessna* and *Sternstein* (6) have shown that in Poly-(methylmethacrylate) and Poly(styrene) the critical diameter of the plastically deformed ring is of the order of 2000 Å. Their results, however, still fit into the general scheme shown in fig. 1, only that β now contains a stress concentration factor which depends upon the stress history of the sample.

If the subvolume is very small and encloses but a few elastic elements the failure of these will have no immediate consequences. This was also indicated by *Prevorsek* and *Lyons* (36).

Within the indicated restrictions the curves in fig. 3 are indeed stress-lifetime curves of real polymer samples. We observe

the large linear portion of these curves which is in accordance with the experimental evidence cited on page 55. The slope of the linear portions is proportional to (25):

$$d \ln \bar{\omega}_b\, t_b/d\beta\, \sigma_0 = - E/E_\lambda . \qquad [24]$$

This relationship has been used to draw the linear portion of the curve for partially oriented networks ($\lambda = 3$).

Whereas many experiments have been carried out to study the influence of orientation on the lifetime of samples subjected to constant *strain rates* few data are available for samples under constant *stress*. The data of *Regel* and *Leksovsky* (39) for oriented poly-(acrylonitrile) seem to affirm the present calculations. Direct comparison of their data with theoretical stress-lifetime curves
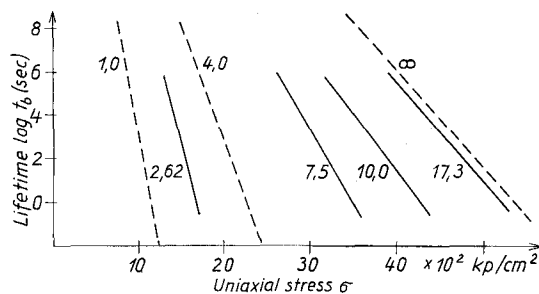

Fig. 4. Comparison of theoretical curves (dashed lines) and experimentally determined curves of lifetimes [solid lines, data of *Regel* and *Leksovsky* (39)]. Parameter is draw-ratio λ

is attempted in fig. 4. In order to transform the abscissa $\beta\, \sigma_0$ into σ_0 the value of β must be calculated from the slope of the experimental curves using eq. [24]. It was assumed that E/E_λ for $\lambda = 17.3$ is close to unity, 0.94 was arbitrarily adopted. This leads to a value of β of 0.01 cm²/kp. Similarly the value for $\bar{\omega}_b$ had to be determined to transform the ordinate of $ln\, \bar{\omega}_b\, t_b$ into log t_b. By shifting the experimental curve for $\lambda = 17.3$ close to the theoretical curve for $\lambda \to \infty$ a value for log $[\bar{\omega}_b$ (sec)] of $- 25.0$ was obtained. The agreement between theoretical and experimental curves is excellent.

The appearance of the theoretical curves in fig. 3 in connection with eq. [24] indicates that the lifetime of a partly-oriented specimen is predominantly determined by the term $- E\, i\, (- E\, \beta\, \sigma_0/E_\lambda)$. It will be of interest, therefore, to formulate the lifetime in terms of that expression and a correction function C_λ which measures how much the

predicted lifetime will actually deviate from the exponential integral:

$$\langle \bar{\omega}_b\, t_b\rangle = - E\, i\, (- E\, \beta\, \sigma_0/E_\lambda)\, C_\lambda\, (\beta\, \sigma_0,\, E/E_\lambda) . \qquad [25]$$

The correction function C_λ can be calculated for two cases, namely for unoriented specimens, $\lambda = 1$, from the numerical solution of eq. [22] and the tabulated values of the exponential integral and for completely oriented specimens ($\lambda \to \infty$). The correction function is a slowly varying function of $E\, \beta\, \sigma_0/E_\lambda$ with values close to unity for small arguments. For large arguments the curve for unoriented specimens may be approximated by:

$$C_1\, (\beta\, \sigma_0,\, E/E_\lambda) = 1.3 + 0.63\, E\, \beta\, \sigma_0/E_\lambda . \qquad [26]$$

If it is assumed that for an unoriented network of linear elements E/E_λ is equal to 6 an interpolation between C_1 and C_∞ can be achieved through:

$$C_\lambda = 1 + 1.2\, [0.3 + 0.63\, E\, \beta\, \sigma_0/E_\lambda]\, (E - E_\lambda)/E . \qquad [27]$$

In deriving eq. [27] it was assumed that C_λ transforms from C_1 into C_∞ proportional to $(E - E_\lambda)/E$ with $E_1 = E/6$ and $E_\infty = E$. E_λ as a function of λ may be taken from reference (23).

Extensibility of the presented kinetic theory

One of the restrictions imposed on the use of eq. [17] is that the elastic deformation ε_{33} is so small that no change in the orientation distribution ϱ has to be considered. It is sufficient, however, to require that the change through creep of the initial, elastic deformation during the lifetime of the sample is small compared with λ. The theory may be applied, therefore, to *rubbers* under constant load, if they show little creep, or to rubbers stressed at a rate small enough so that eq. [17] holds, but also large enough that essentially all "elements" break within a small time interval.

The latter case is also an example for extension of this theory to time-dependent loads. In cyclic loading, an equivalent stress, $\bar{\sigma}$, has to be used instead of σ_0. The most common application is a sinusoidal variation of stress:

$$\sigma\, (t) = \sigma_0 + \sigma_1 \sin\, (\omega\, t) . \qquad [28]$$

The stress $\bar{\sigma}$ is determined so that the rate according to eq. [10] integrated over one cycle is the same for $\sigma\, (t)$ and $\bar{\sigma}$. If the rate

of fracture of molecular elements is correctly described by eq. [10] this theory predicts the lifetime of samples under cyclic loading also. An indication for the adequacy of $\bar{\sigma}$ as a substitute for $\sigma(t)$ was found by several investigators (36, 39).

If the number of cycles or of repeated loading periods independently influences the time to fracture of a sample, as frequently found in metals and recently also in rubbers (17), the present theory cannot be used.

Eq. [16] forms the basis for an application to states of *multiaxial stress*. The local stress, $\psi(\theta)$, may be changed by either the state of stress or the orientation distribution function. In triaxial tension, $\sigma_{11} = \sigma_{22} = \sigma_{33} = \sigma_0$, $\psi(\theta)$ is constant and equal to $3\sigma_0$ if $\lambda = 1$. This situation is comparable to that within a completely oriented sample where all elements carry identical loads. In the first quadrant of stress space (σ_{11}, σ_{22}, σ_{33}) only two points have been investigated: $(0, 0, \sigma_0)$ and $(\sigma_0, \sigma_0, \sigma_0)$. Even though many experiments with specimen under multiaxial stress have been carried out (21, 31), their results cannot be related to the present investigation, since the orientation distribution of the specimens used (pipes) is not known. Further work on this subject is in progress.

From the consideration that the lifetime of a partly oriented specimen subjected to multiaxial stress is determined predominantly by the rate of failure of those elements which are oriented in the direction of maximum strain, we would like to propose as a failure criterion a "kinetic version of *St. Venant*'s criterion of maximum elastic strain". The criterion can only be formulated as an implicit function of stress. Until further work is completed it may be restricted to states of stress where the largest normal component, σ_0, has the direction of the axis of orientation. In this case a stress σ will not lead to fracture of a sample within t_b if:

$$- E\,i\,(- E\,\beta\,\sigma_0/E_\lambda) \cdot C_\lambda\,(\beta\,\sigma,\,E/E_\lambda) < \langle \bar{\omega}_b\,t_b \rangle. \quad [29]$$

C_λ is known exactly for one- and triaxial tensions and can be interpolated for intermediate cases.

Zusammenfassung

In der vorliegenden Arbeit werden die statistischen und mechanischen Modelle untersucht, die der kinetischen Theorie des Bruches von Gläsern, Thermoplasten und Gummi zu Grunde liegen. Dabei werden die für Hochpolymere im glasartigen Zustand zutreffenden Voraussetzungen angegeben. Die Ergebnisse jüngster ESR-Versuche und die elastische, anelastische und plastische Verformung des Polymeren werden besonders in Betracht gezogen. Ein mathematisches Modell des Festkörpers wird formuliert, das in Übereinstimmung mit den beobachteten Eigenschaften des Materials ist, und das aus einem elastischen Netzwerk besteht, eingebettet in eine viskoelastische Umgebung. Auf der Grundlage der angegebenen Bedingungen werden für einachsig belastete Proben Bruchzeiten als Funktion der Last und des Orientierungsgrades des polymeren Netzwerkes berechnet. Diese Bruchzeiten werden mit experimentell bestimmten Werten verglichen.

Die Erweiterung des vorgelegten Modells auf den Bruch von Elastomeren und auf mehrachsige oder zeitabhängige Spannungszustände wird untersucht. Ein Bruchkriterium wird vorgeschlagen, das die „Kinetische Version von *St. Venant*'s Kriterium der größten elastischen Verformung" genannt werden könnte. Darin wird die Bruchgefährlichkeit eines Spannungszustandes durch die größte Komponente der Normalspannung und das Verhältnis zweier elastischer Moduln bestimmt, nämlich das Verhältnis des Moduls eines Netzwerkfadens und des longitudinalen Moduls (in Orientierungsrichtung) der Probe insgesamt.

Summary

The statistical and mechanical models underlying the kinetic theories of fracture of glasses, thermoplasts and rubbers are analyzed and specified for polymers in their glassy state. Special attention is given to results from recent electron resonance experiments, and to the elastic, anelastic and permanent deformation of a polymer before and during the experiment leading to failure. A model is constructed which is in accordance with the observed material behavior, and which consists of an elastic molecular network embedded in a viscoelastic continuum. On the basis of the specified conditions times-to-break are calculated as a function of applied load and degree of orientation of the polymer network. The calculated times-to-break are compared with experimental data.

The extensibility of the theory to fracture of rubbers and to failure under multiaxial or time-dependent stress is discussed. A fracture criterion is proposed which may be called the „kinetic version of *St. Venant*'s criterion of maximum elastic strain", in which the criticality of a state of stress is essentially determined by the components of normal stress and the ratio of two longitudinal elastic moduli, namely that of the molecular network and that of the sample as a whole.

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