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For a homogeneous oriented and stressed medium, a theory of strength behavior is formulated and analyzed on the basis of considering the kinetic breaking and forming processes present in the microscopic molecular structure. The theory developed in this manner is particularly applicable to polymeric systems. The solution to this formulation gives not only reasonable results comparable to available experimental findings, but also yields new information which may not be possible to be verified experimentally at present. In general, it is found that under either fairly large or moderate stresses, the fracture strength is almost linearly related with logarithm of time. For small stresses, the kinetic nature of molecular reformation is found to be quite influential and thus the time required for fracture becomes larger and larger and finally approaches to infinity. The analysis is also extended to a partially oriented molecular system under more general loading conditions.

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TIME DEPENDENT STRENGTH OF FULLY ORIENTED MEDIA

It is well known that the macroscopic mechanical strength of a solid is intimately tied in with the microscopic constituents and their configurations. For example, variations in molecular orientation as a result of deformation will certainly affect the macroscopic behavior. This is particularly true for solids such as some high polymers having pronounced time-dependent properties. Ultimate strength is one such property which can be considered on the basis of a kinetic concept in the fracturing processes. It is realized that the highly complex kinetic nature of molecular behavior precludes an exact, yet detailed analysis. However, a rough estimation seems possible and desirable even if an ideal model is considered. With this in mind, the mathematical model used for analysis is a matrix of oriented elements representing molecular forces, embedded in an arbitrary domain. For simplicity, consider that the system is composed of a large number of identical elements. For such a system, the state of stress in the vicinity of a point in the solid may be represented by determining the time dependent stress tensor $\sigma_{ij}(i,j = 1,2,3)$ at that point[1]

$$\sigma_{ij}(\varepsilon,t) = \int \rho(\theta,\phi,\varepsilon) f(\theta,\phi,t) \psi(\theta,\phi,t) s_i s_j d\omega \qquad (1)$$

where ρ is the density of probability distribution function of orientation, ψ is the longitudinal stress acting along each element, and is a function of orientation designated by the spherical coordinates (θ,ϕ)

and time t. Depending upon the nature of molecular behavior, two extreme cases of molecular orientation may be expressed. For a system with randomly oriented loose or unconnected elements[1],

$$\rho(\theta,\phi,\varepsilon) = \frac{(1+\varepsilon)^3}{[\cos^2\theta + (1+\varepsilon)^3\sin^2\theta]^{3/2}}\,\rho(0) \tag{2}$$

where ε represents a uniform strain which varies from -1 to ∞. For a system with randomly connected elements, ρ can be modified as follows[2],

$$\rho(\theta,\phi,\varepsilon) = \frac{\alpha}{[\cos^2\frac{\theta}{2} + \alpha\sin^2\frac{\theta}{2}]^2}\,\rho(0) \tag{3}$$

where

$$\varepsilon = \frac{2}{\alpha-1}\left[\alpha + 1 + \frac{4\alpha}{\alpha-1}\ln\frac{\alpha+1}{2\alpha}\right]$$

In addition, f is the fraction of unbroken elements and is also a function of orientation and time. s_i and s_j are unit vectors, and $d\omega$ is the infinitesimal solid angle within which the elements are considered to be parallel.

In general the time dependent nature can be formulated utilizing the statistical theory of the absolute reaction rate for a given orientation of the elements with respect to the direction of applied stress[1,3] such that the rate of change of f is given as follows:

$$\frac{df}{dt} = K_r(1 - f) - K_b f \tag{4}$$

where

$$K_r = \omega_r e^{-U/RT - \gamma\psi(t)} \tag{5}$$

is the rate of reformation of broken elements and

$$K_b = \omega_b e^{-U/RT} + \beta\psi(t) \tag{6}$$

the rate of rupturing of unbroken elements, ω_r and ω_b are respectively the frequencies of the jump motion of the elements with respect to forming and breaking processes. U is the activation energy, R is the universal gas constant and T is the absolute temperature. β and γ are positive quantities which modify the energy barrier because of the non-zero applied stress in the direction of each element.

For a completely oriented system, if the strength of a medium under a simple constant tension, say in 33-direction, is considered then from (1):

$$\psi(t)f(t) = \sigma_{33} = \sigma \tag{7}$$

where σ = constant is the applied simple tension and f is independent of molecular orientation. In this case differentiating (7) and combining with (4), yields the functional relationship between ψ and t.

$$\frac{d\psi}{dt} = \psi[K_b - K_r(\psi/\sigma - 1)] \tag{8}$$

Integration results in the time-to-break

$$t_b = \int\{K_b\psi[1 + (K_r/K_b)(1 - \psi/\sigma)]\}^{-1}d\psi + t_o \tag{9}$$

where t_o is a constant of integration.

As shown in (4), (5) and (6), K_b and K_r are both functions of $\psi(t)$. The basic concept of the dependence

of K_b and K_r on ψ can be described according to the absolute reaction rate theory. In general the effect of stress on elastic deformation and viscous flow is capable of being related to a comprehensible activation process as a consequence of the movement of the whole or a segment of a molecule, from one equilibrium state to the next. If U is the original potential energy barrier to be crossed between two equilibrium states, the frequency with which such steps occur under the influence of the thermal agitation will be proportional to $e^{-U/RT}$. After a stress σ is applied to the oriented system, individual elements are subjected to a stress $\psi(t)$. The energy barrier associated with the breaking process becomes modified to $U/RT - \beta\psi(t)$ in the direction of the applied stress. Whereas in the opposite sense, the energy barrier is modified to $U/RT + \gamma\psi(t)$. As a result both the rates of modified kinetic processes become different exponential functions of stress. With this information, (9) can be modified to give the following integral for the time-to-break with $t_o = 0$:

$$t_b = e^{U/RT}\int \frac{d\psi}{\psi[\omega_b e^{\beta\psi} + \omega_r e^{-\gamma\psi}(1 - \psi/\sigma)]} \qquad (10)$$

where the integral is to be evaluated from $\psi = \psi_o$, an initial value of ψ, to $\psi = \psi_b$ for which the microscopic element ceases to carry any load. The initial value ψ_o can be expressed through the use of (7) in terms of the applied simple tension σ when the initial value f_o of f is known. Evaluation of the integral (10) will give the required solution.

It can be seen that integration of (10) explicitly in terms of the known functions may not be possible and numerical evaluation may become a necessity. However

(10) can be evaluated explicitly if we restrict to stress ranges within which σ is relatively large. Since f has a bounded variation between 0 and 1, $\psi(t)$ will also be relatively large. Then (10) may be approximated to give

$$t_b = e^{U/RT} \int_{\psi_o}^{\psi_b} \frac{d\psi}{\omega_b \psi e^{\beta\psi}} \tag{11}$$

Evaluating we get

$$t_b = \omega_b^{-1} e^{U/RT} [Ei(-\beta\psi_b) - Ei(-\beta\psi_o)] \tag{12}$$

where Ei(-x) is the exponential integral defined by

$$-Ei(-x) = \int_x^{\infty} \frac{dy}{ye^y} \tag{13}$$

Substituting $\psi_o = \sigma/f_o$ we obtain

$$t_b = \omega_b^{-1} e^{U/RT} [Ei(-\beta\psi_b) - Ei(-\beta\sigma/f_o)] \tag{14}$$

A variation of t_b against σ is shown on logarithmic scale in Fig. 1 by the solid curve. The maximum limit of the applied stress is indicated by σ_b which in terms of ψ_b becomes $\sigma_b = f_o\psi_b$. The corresponding strength behavior is that it is likely to be linearly related with the logarithm of time. Below this section of the curve there is a considerable region where the curve is again nearly linear between the applied stress and logarithm of time-to-break. The lower portion of the curve shown as dotted curve, evaluated without considering the reformation processes, does not characterize the true behavior because the contributions resulted in from

the reformation processes are not negligible. In this region, the applied stress is relatively small. There exists a minimum value σ_m for which t_b goes to infinity asymptotically. This value is given by the condition that

$$\int_{\psi_m}^{\psi_b} \{[\omega_b e^{\beta\psi} + \omega_r e^{-\gamma\psi}(1 - \psi/\sigma_m)]\psi\}^{-1} d\psi \Rightarrow \infty \qquad (15)$$

where $\psi_m f_o = \sigma_m$.

If we let σ_r represent approximately the stress at which reformation processes become **influential, then the** true curve can be expressed by two integrals:

$$t_b = e^{U/RT}\left[\int_{\sigma_r}^{\psi_b} \frac{d\psi}{\omega_b \psi e^{\beta\psi}} + \int_{\sigma}^{\sigma_r} \frac{d\psi}{\psi[\omega_b e^{\beta\psi} + \omega_r e^{-\gamma\psi}(1 - \psi/\sigma)]}\right] \qquad (16)$$

If $\sigma_r - \sigma$ is small then the integrand in (16) can be approximated as

$$t_b = \frac{e^{U/RT}}{\omega_b}\left[Ei(-\beta\psi_b) - Ei(-\beta\sigma_r) + \int_o^{\sigma_r - \sigma} \frac{d\phi}{(\sigma + \phi)P_n(\phi)}\right] \qquad (17)$$

$$(o \leq \psi - \sigma = \phi \leq \sigma_r - \sigma)$$

where $P_n(\phi)$ is a polynomial of n^{th} degree in ϕ. The evaluation of (17) is simple and accuracy can be improved by increasing the number n. Comparison of this analytical result with experimental data has been made. Good agreements have been obtained. Detailed information has been reported elsewhere[4].

It might be of interest to mention that the initial horizontal portion of the curve in Fig. 1 represents the strength behavior of a medium for an extremely short duration of testing ($<10^{-2}$ microsecond). Under our

present available testing capabilities, the experimental strength data lie mostly below this portion in the almost straignt line region except for small applied simple stresses shown as the lower section of the curve.

In addition, on the basis of this model it is found qualitatively from (12), for a moderately high constant applied tension, the logarithm of time-to-break, for a certain region, is almost inversely proportional to the absolute temperature at which the medium is fractured. This is shown in Fig. 2. In the determination of this theoretical curve, β has been assumed as directly proportional to the reciprocal of the absolute temperature. This is justified because both β and γ are likely to be functions of $1/T$ since $\beta\psi(t)$ or $\gamma\psi(t)$ modify the energy barrier in the molecular processes as shown in (5) and (6). In case β is independent of temperature, the inverse proportionality as in Fig. 2 still holds. With this information and some assumed values for constants involved in (12) a qualitative representation of the temperature and time-dependent behavior for fracturing a medium is obtained. Similar qualitative behavior can be evaluated if an exact dependence of β on temperature is known.

TIME DEPENDENT STRENGTH OF PARTIALLY ORIENTED MEDIA

In the previous section we have explored the strength behavior of a fully oriented solid under constant simple tension. We can also formulate a similar problem for a partially oriented anisotropic solid under more general type of stresses. Results pertaining to an applied state of intense stresses, when reformation processes are negligible, have already been reported[5]. Following a somewhat similar concept, we can formulate the time-to-break and strength behavior under a general constant loading condition when stresses are not large enough to warrant the neglect of the molecular reformation processes in the media. Here we are looking for a relation between t_b and stresses σ_{ij}, which constitute a solution of (1) and (4) subjected to given stresses $\sigma_{ij}(t)$.

Restricting to the condition that σ_{ij} = constant with respect to time, differentiation of (1) with respect to time t gives

$$0 = \int \rho (\psi \frac{\partial f}{\partial t} + f \frac{\partial \psi}{\partial t}) s_i s_j d\omega \tag{18}$$

which may be reduced to

$$\psi \frac{\partial f}{\partial t} + f \frac{\partial \psi}{\partial t} = 0 \tag{19}$$

Integration of (19) yields

$$\psi f = \psi_o \tag{20}$$

where ψ_o is a parameter independent of time but depends upon the orientation direction defined by (θ,ϕ). The relation shown in (20) may also be anticipated from (1) since all the time dependent functions in the integrand together must be equivalent to a time independent function in the case that σ_{ij} is considered constant. The complete significance of ψ_o will become apparent later on. Equations (19) and (20) hold for every representative element in any direction (θ,ϕ). Eliminating f from (4), (19) and (20), we obtain, for the representative element directed along (θ,ϕ), an equation

$$\frac{\partial\psi}{\partial t} = \psi[K_b - K_r(\frac{\psi}{\psi_o} - 1)] \tag{21}$$

which, when solved, yields

$$t + t_o = \int \frac{d\psi}{\psi[K_b - K_r(\frac{\psi}{\psi_o} - 1)]} \tag{22}$$

where t_o is a constant of integration. Since it has been assumed that all the elements are identical except for their orientation we can establish an adequate criterion for the fracture of any element and ultimately of the entire solid. We will assume as in previous section that elements will break when $\psi(\theta,\phi,t) \rightarrow \psi_b$ independent of θ,ϕ and t. Also if initially at t = 0, f = 1, then the time-to-break for any element becomes

$$t_b(\theta,\phi) = \int_{\psi_o}^{\psi_b} \frac{d\psi}{\psi[K_b - K_r(\frac{\psi}{\psi_o} - 1)]} \tag{23}$$

where

$$\psi(t = 0) = \psi_o$$

From the definition, $\psi_o(\theta,\phi) = Ee_{mn}s_m s_n$ where e_{mn} is a strain tensor and E is the elastic constant for each element. Substituting into (1), we obtain

$$\sigma_{ij} = EC_{ijmn}e_{mn} \tag{24}$$

where

$$C_{ijmn} = \int \rho(\theta,\phi,\varepsilon)s_i s_j s_m s_n d\omega \tag{25}$$

If we define B_{ijmn} as the inverse of C_{ijmn} such that

$$\|B_{ijmn}\| = \|C_{ijmn}\|^{-1} \tag{26}$$

then

$$Ee_{mn} = B_{ijmn}\sigma_{ij} \tag{27}$$

Here both C_{ijmn} and B_{ijmn} are functions of orientation[6] and strain ε. Then ψ_o can be expressed as

$$\psi_o = B_{ijmn}\sigma_{ij}s_m s_n \tag{28}$$

Substituting for ψ_o in (23) results in a required time-to break t_b for an arbitrary element. The relation expressed in (23) will be identical to (10) if we replace σ in (10) by ψ_o. Therefore all conclusions from (10)

based on σ will hold in this case for ψ_o. This gives rise to another interesting interpretation that (28) can be considered as defining a generalized surface in six coordinates σ_{ij}. It can be shown that there exists a critical surface for a representative element in some arbitrary direction (θ,ϕ) defined by that value of $\psi_o = \psi_o^{min}$ which corresponds to infinite time-to-break. If the loading condition is represented by a point on or below this surface, i.e. if σ_{ij} are such that $\psi_o \leq \psi_o^{min}$, then the element will never break. However, this value ψ_o^{min} is independent of the position of the element which is apparent from inspection of (23). This limitation will in a way restrict relative magnitudes of σ_{ij} if the fracture of the solid is to occur in finite time.

It is also clear from (23) and (28) that elements oriented in different directions initially will break at different times, and the choice of the time-to-break for the entire solid becomes somewhat arbitrary. However, a statistical mean with respect to the distribution function $\rho(\theta,\phi,\varepsilon)$ can hopefully be expected to give a more representative value to t_b. For a continuous distribution of elements, as in the present case, the statistical mean of the time-to-break t_b is defined[5] by

$$\bar{t}_b = \int t_b(\theta,\phi,\varepsilon)\rho(\theta,\phi,\varepsilon)d\omega \;/\; \int \rho(\theta,\phi,\varepsilon)d\omega \qquad (29)$$

which can be evaluated easily. Here we have assumed that the integral exists under the given loading conditions. Using $\rho(\theta,\phi,\varepsilon)$ as defined in (2), we obtain

$$\int \rho(\theta,\phi,\varepsilon)d\omega = 1$$

Therefore

$$\bar{t}_b = \int \rho(\theta,\phi,\varepsilon) t_b(\theta,\phi,\varepsilon) d\omega \tag{30}$$

To obtain some idea about the results represented by (30), let us consider a triaxial state of stress $\sigma_{11} = \sigma_{22} = \sigma_{33} = \sigma$ (say) for an isotropic medium, then it can be shown that $B_{ijmn}\sigma_{ij}s_m s_n = 3\sigma$. Substituting into (29) we obtain

$$\bar{t}_b = \int_{3\sigma}^{\psi_b} \frac{d\psi}{\psi[K_b - K_r(\frac{\psi}{3\sigma} - 1)]} \tag{31}$$

Equation (31) enforces a limitation on the maximum value σ_{max} of σ since $\bar{t}_b$ cannot be negative. This condition requires that $\sigma_{max} = \psi_b/3$. Also there is a minimum value of σ, say σ_{min}, for which $\bar{t}_b = \infty$. The expression (31) can be easily evaluated for all stresses $\sigma_{min} \leq \sigma \leq \psi_b/3$. A qualitative curve is shown in Figure 3. The shape of the curve is similar to that in Fig. 1 as may be expected.

REFERENCES

1. C. C. Hsiao, J. Appl. Phys. 30, 1492 (1959)

2. O. Kratky, Kolloid-Z. 84, 149 (1938)

3. C. C. Hsiao, Physics Today 19, No. 3, 49 (1966)

4. H. H. Kausch von Schmeling, S. R. Moghe, and C. C. Hsiao, J. Appl. Phys. 38, 201 (1967)

5. S. R. Moghe and C. C. Hsiao, J. Appl. Phys. 37, 3965 (1966)

6. S. R. Kao and C. C. Hsiao, J. Appl. Phys. 35, 3127 (1964)

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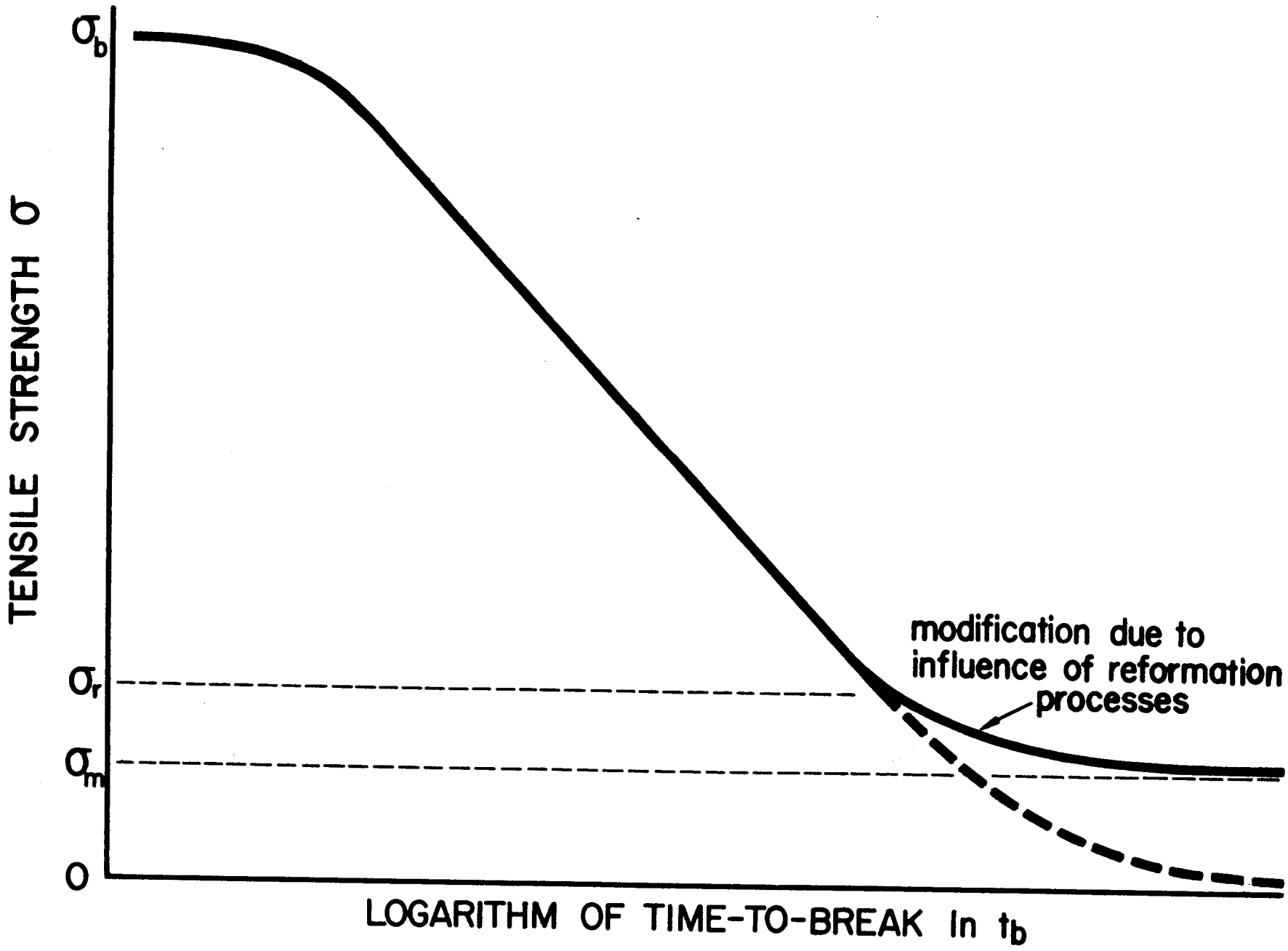

Fig. 1 Time-Dependent Mechanical Strength of Oriented Media

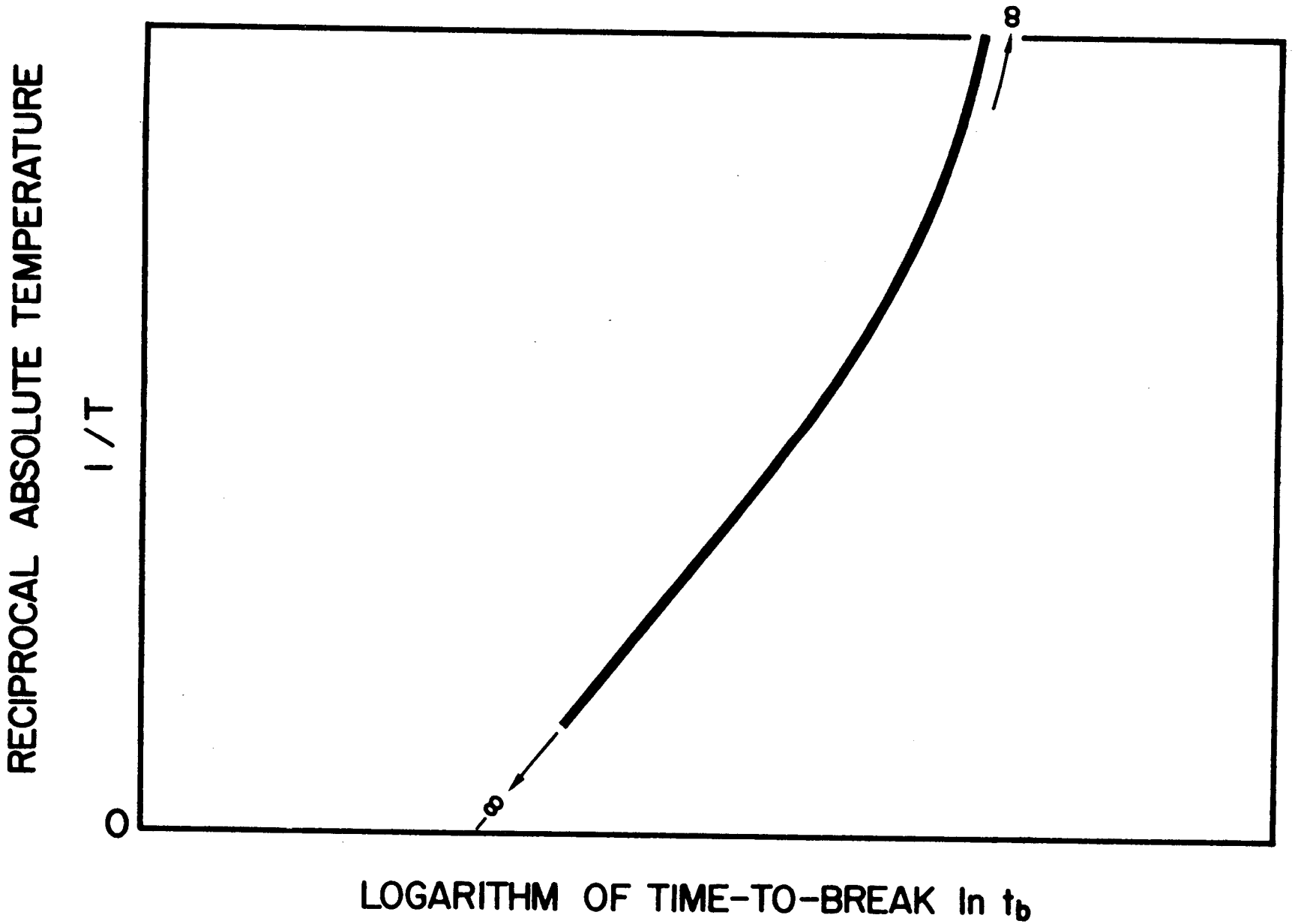

Fig. 2 Temperature and Time Dependent Mechanical Strength of Oriented Solids

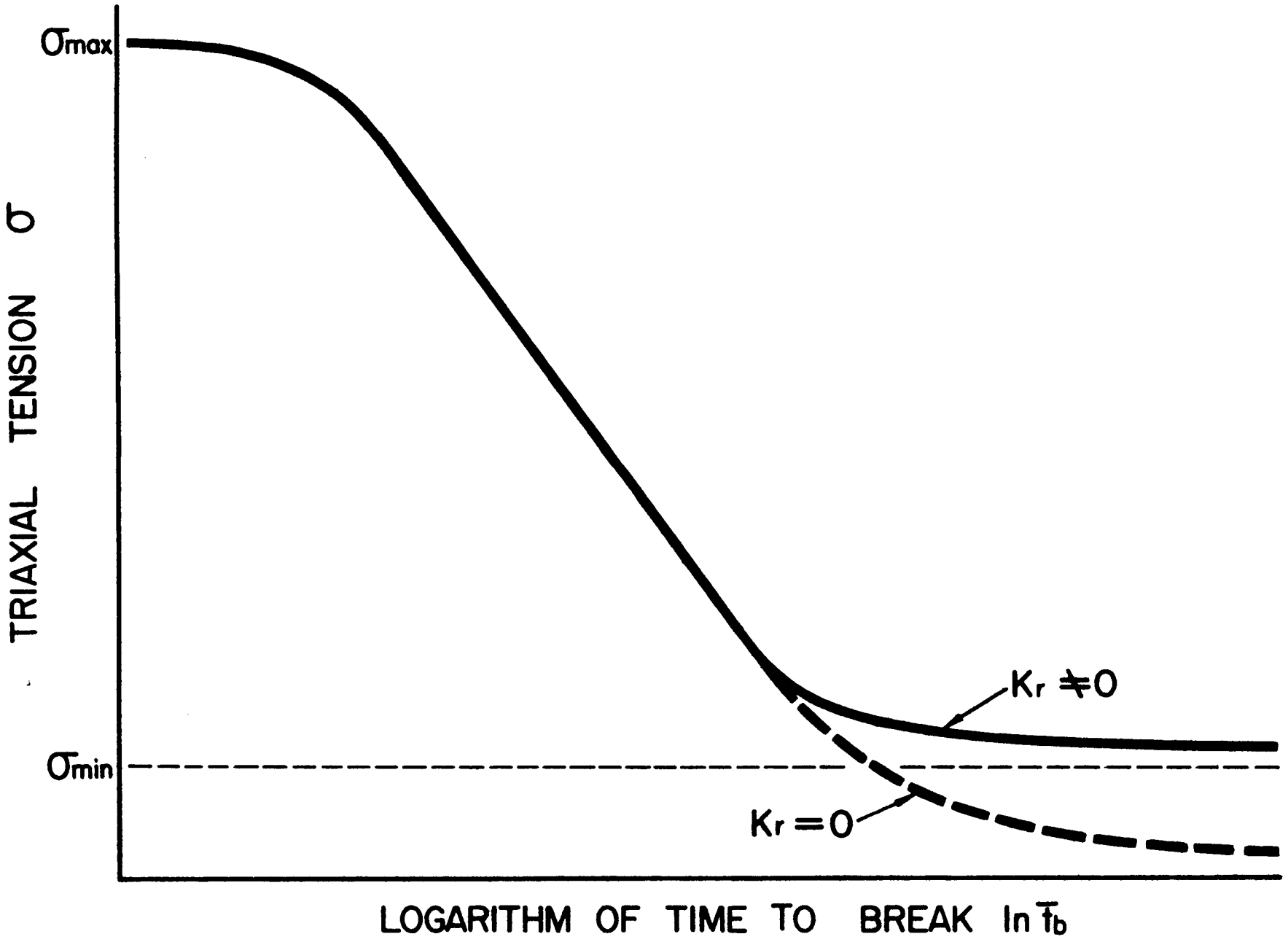

Fig. 3 Time Dependent Strength of Isotropic Medium under Triaxial Tension