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Kinetic Considerations of the Strength of Oriented Solids

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The mechanical strength of an oriented and stressed solid is considered on the basis of using the statistical absolute reaction rate theory. It is shown that for large applied stresses the fracture strength is almost linearly related with logarithm of time. For small stresses the time-to-break required approaches to infinity.

Author

The macroscopic mechanical strength of a solid is intimately affected by microscopic structural changes. This is particularly true for solids 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 process. The mathematical model which can be used for analysis, is a matrix of oriented elements embedded in an arbitrary domain.[1] Assume that the fraction of unbroken elements per unit solid angle is represented by f. In general f is a function of time and orientation. The time-dependent function can be evaluated from the statistical theory of the absolute reaction rate[2] for a given orientation of the elements with respect to the direction of applied stress

$$\frac{df}{dt} = K_r\left(\frac{1}{4\pi} - f\right) - K_b f \qquad (1)$$

where $K_r = \omega_r e^{-[U/RT + \gamma\psi(t)]}$ is the rate of reformation

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1. One of the authors (CCH) is indebted to Professor S. Prager for the opportunities of obtaining his suggestions on the model and discussing the subject matter
2. C. C. Hsiao, J. Appl. Phys. 30, 1492 (1959)

of broken elements and $K_b = \omega_b e^{-[U/RT - \beta\psi(t)]}$, the rate of rupturing of unbroken elements. ω_r and ω_b are respectively the frequencies of motion with respect to reformation and rupture processes. U is activation energy, R is a universal constant, T is absolute temperature. β and γ are positive quantities which modify the energy barrier for the applied stress $\psi(t)$. Once the functional form of f is determined, the time-dependent fracture strength of a completely oriented solid can be studied by solving (1), from which f is found as follows:

$$f = \frac{1}{4\pi} e^{-\int_o^t (K_b + K_r)d\tau} \left[\int_o^t K_r e^{\int_o^\tau (K_b + K_r)dt} d\tau + f_o \right] \qquad (2)$$

where f_o is a quantity which can vary from 0 to 1 dependent upon the initial state of the system. When $\psi(t) = 0$ it is reasonable to believe that K_r and K_b are almost equal. Under these circumstances a state of equilibrium will be reached if

$$f_o = \frac{K_r}{K_r + K_b} = \frac{1}{2}$$

It is, however, very unlikely that this state of equilibrium will be reached by most polymeric systems until very long periods of time have elapsed. Referring to the measurements of Zhurkov[3] (e.g. for PMMA at +50°C) the constant $\omega_b e^{-U/RT}$ is of the order of $30 \cdot 10^{-20}$ year^{-1}. This means that the unstressed polymeric system will not reach its equilibrium state within a reasonable period of time.

According to the absolute reaction rate theory, 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 molecular 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 $e^{-U/RT}$.

3. S. N. Zhurkov, "Kinetic Concept on the Strength of Solids," presented at the International Conference on Fracture, Sendai, Japan, Sept. 12-17, 1965, will appear in the Proceedings

After a stress $\sigma(t)$ is applied to the oriented system, individual elements are subjected to a stress $\psi(t)$. The energy barrier becomes modified to $U/RT - \beta\psi(t)$ in the direction of the applied stress, to $U/RT + \gamma\psi(t)$ in the opposite sense where, as stated earlier β and γ are constants depending upon the modification of the energy barrier. As a result both the rates of modified kinetic process become different exponential functions of stress as given before. For large values of stress $\psi(t)$, K_r will be very much smaller compared with K_b. To a first approximation (2) may be reduced to

$$f = \frac{f_o}{4\pi} e^{-\int_o^t \omega_b e^{-[U/RT - \beta\psi(\tau)]} d\tau} \tag{3}$$

Then the stress function $\psi(t)$ in each element will be given as:

$$\psi(t) = \frac{\sigma(t)}{f(t)} = \frac{4\pi\sigma}{f_o} e^{\omega_b e^{-U/RT} \int_o^t e^{\beta\psi(\tau)} d\tau} \tag{4}$$

Furthermore, U is a material constant and $\psi(t)$ may be considered as a continuous and multi-differentiable function of time. We may write using the last equations:

$$\psi(t_m) = \frac{4\pi\sigma}{f_o} e^{\omega_b e^{-U/RT} \int_o^{t_m} e^{\beta[\psi(0) + \psi'(0)\tau + \frac{1}{2}\psi''(0)\tau^2 + \cdots]} d\tau} \tag{5}$$

where t_m is time to fracture for a constant applied stress σ.

It seems quite reasonable, at this stage, to assume that the fracture strength is associated with a limiting value ψ_m beyond which every element oriented in the direction of applied stress will break. Then

$$\ln \frac{4\pi\sigma}{f_o \psi_m} + \omega_b e^{-U/RT} \int_o^{t_m} e^{\beta[\psi(0) + \psi'(0)\tau + \frac{1}{2}\psi''(0)\tau^2 + \cdots]} d\tau = 0 \tag{6}$$

Again for simplicity by dropping higher order terms the first two terms are taken in evaluating the integral, we obtain

$$\ell n \frac{4\pi\sigma}{f_o \psi_m} + \omega_b e^{-U/RT} \left[\frac{e^{\beta\psi(0)}}{\beta\psi'(0)} \left(e^{\beta\psi'(0)t_m} - 1\right)\right] \tag{7}$$

From (5) it is easily seen that $\psi(0) = \frac{4\pi\sigma}{f_o}$. Substituting in (7) and approximating the last terms, we obtain

$$\ell n \frac{4\pi\sigma}{f_o \psi_m} + \omega_b e^{-U/RT} e^{\frac{4\pi\beta\sigma}{f_o}} e^{\ell n t_m} = 0 \tag{8}$$

For extremely high values of σ, if $4\pi\sigma/f_o$ is very near to the limiting stress ψ_m, the first term in (8) will be close to zero. Then (8) can be approximated by the following form

$$t_m \cong \frac{1}{\omega_b} \left(1 - \frac{4\pi\sigma}{f_o \psi_m}\right) e^{U/RT - \beta\psi_m} \qquad \left(\sigma \sim \frac{f_o \psi_m}{4\pi}\right) \tag{9}$$

It is evident that t_m is proportional to the negative values of the applied tensile stress.

For relatively large values of σ, it is seen from (8) that the logarithm of time will be essentially dependent on σ in the exponential term giving a linear relationship between σ and $\ell n \omega_b t_m$. Such linear relationships have been reported in various publications.[3,4,5,6,7] On the basis of the present analysis, we can easily write

$$\ell n \omega_b t_m \cong \frac{U}{RT} - \frac{4\pi\beta\sigma}{f_o} \qquad \left(\frac{f_o}{2\pi\beta} < \sigma < \frac{f_o \psi_m}{4\pi}\right) \tag{10}$$

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4. F. Bueche, J. Appl. Phys. 26, 1133 (1955); 28, 784 (1957); 29, 1231 (1958)
5. B. D. Coleman, J. Appl. Phys. 27, 862 (1956); 28, 1058 (1957); 29, 968 (1958); Trans. Soc. Rheol. 1, 153 (1957)
6. C. C. Hsiao, Nature 186, 535 (1960)
7. S. N. Zhurkov, Z. Phys. Chem. 213, 183 (1960)

where the limits for σ are selected on the basis of a careful analysis which will be published in the future.

If, on the other hand, σ is small, (8) is not valid for obtaining useful information. One should refer to (2) for proper consideration. Briefly, one can see that for very small applied stresses $\psi(t)$ will also be very small for a rather long period of time. In this case K_b and K_r are comparable. The modifiers β and γ may be regarded as equal and the frequencies ω_b and ω_r, the same. To a first order of approximation, integration of (2) will lead to the following result:

$$t_m > -\frac{e^{U/RT}}{2\omega_b} \ln\beta\sigma \qquad \left(\sigma < \frac{f_o}{20\pi\beta}\right) \tag{11}$$

where the limit of σ is again obtained from a more detailed analysis which will be reported elsewhere. It is seen that as σ approaches zero, t_m will approach infinity.

To illustrate the general trend, Fig. 1 shows schematically the variation of the fracture strength as a function of logarithm of time as approximated by (9), (10) and (11). This theoretical curve appears to cover a complete range of stress-time relations and fits very well with various reported findings.[8,9] In addition, it can also be used to explain the deviations from linear stress-lifetime relationships for different kinds of solids found experimentally by Zhurkov[3] for relatively high temperatures or low stresses.

According to a detailed consideration of (2) and the given approximations (9), (10) and (11), there exists a gap between the limits of the applied stress σ shown in (10)

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8. G. M. Bartenev and U. C. Zuev, Strength and Fracture of Viscoelastic Materials (in Russian), "Chemistry" Publisher, Moscow (1964)

9. C. C. Hsiao, Proc. Symposium on Structural Dynamics under High Impulse Loading, Tech. Docu. Report No. ASD TDR 63-140, 325 (1963)

and (11) and illustrated as dotted line in Fig. 1. This happens to be one of the most important sections of the curve from both theoretical and practical view points. At present calculations are being carried out with the hope of determining the precise time dependent nature of the fracture strength of a solid.

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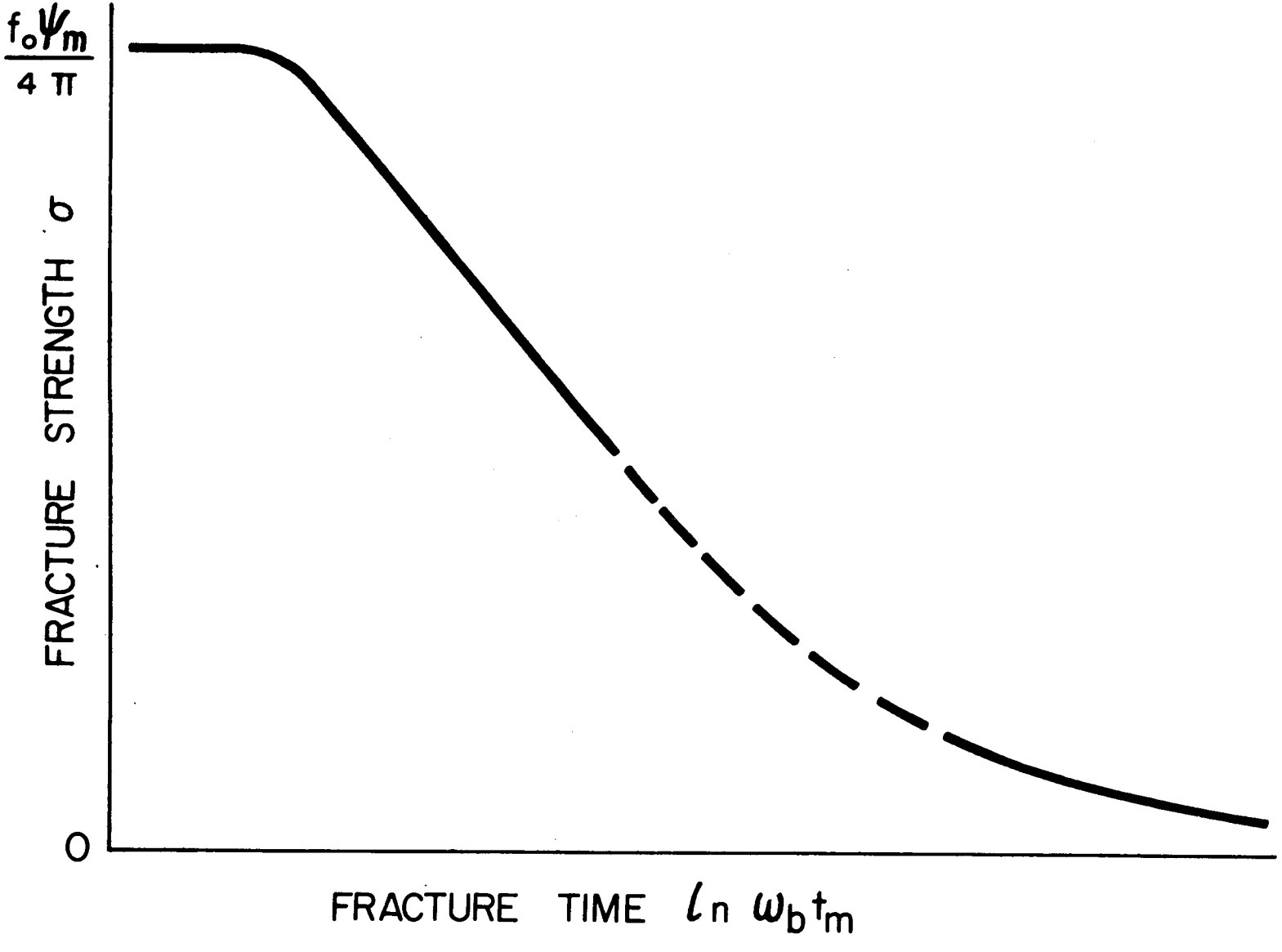

Fig. 1 Schematic representation of strength as function of time-to-break