TIME DEPENDENT QUASIFRACTURE IN POLYMERS

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ABSTRACT

The quasifracture behavior of solids has been intensively investigated by scientists and engineers in many countries. A considerable amount of information has been published in the open literature. The interest in the understanding of the subject matter has greatly increased as additional phenomena associated with fracture are to be elucidated. The time dependent quasifracture in polymers becomes one of the first to be studied. It is hoped that this paper will lead naturally into the consideration of initiation and propagation of the time dependent fracture of viscoelastic solids.

KEYWORDS

Quasifracture, craze, crazing, fracture, cracking, surface crack, time dependent fracture behavior, viscoelastic fracture initiation.

INTRODUCTION

The phenomenon of quasifracture of solids especially polymers has long been observed and utilized. Despite its practical importance the development of a time dependent quasifracture theory on the basis of fundamental principles of science has been surprisingly slow. The fact that much work has been done on highly idealized elastic solids has greatly retarded the progress of quasifracture studies. Recently emphasis has begun to shift from time independent fracture investigations to those of time dependent quasi-fracture initiation and propagation.

Now the understanding of quasifracture of a solid is recognized to be not a simple straight forward process. It takes time as well as requires the going through of several stages before real fracture. Roughly the stressing of a solid causes the development of a plastic region, the formation of microporosity, the initiation and propagation of quasifracture, its transition into real fracture and finally the propagation of fracture in the solid. All these features are time dependent. Analyses based soley upon theory of elasticity

or plasticity cannot bring out the characteristic dependency on time. A pertinent first step is to employ at least the linear theory of viscoelasticity in continuum mechanics for the development of a time dependent theory on quasifracture phenomenon in a viscoelastic solid.

Evidences of the time dependent nature of the strength and quasifracture of solids have long been reported [1,2,3]. The development of microporosities and their coalescence is considered to be responsible for the nucleation of crazing or initiation of quasifractures which eventually dominates the strength of the solids.

ON INITIATION OF QUASIFRACTURE

Quasifracture is not a true fracture. The word crazing or craze has been used to describe this quasifracture for several decades. It is well known that a craze or quasifracture is associated with a localized sharp flow as a bifurcation from a homogeneous deformation into a new phase of oriented fibril domains and voids as shown in Fig. 1. The basic requirement to achieve this

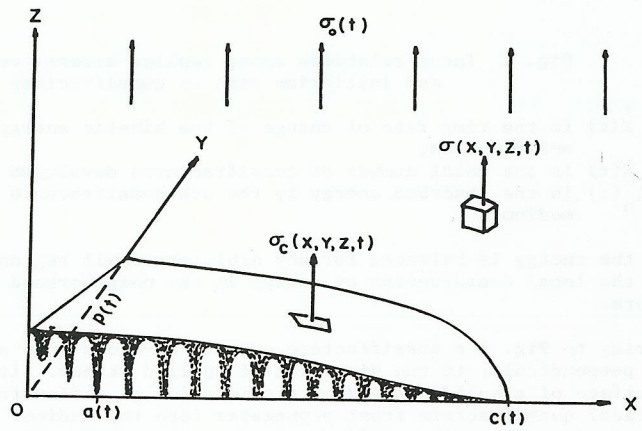

Fig. 1 Three-Dimensional Quasifracture Propagation in Solids

process is through the slippage of the micro-molecules in the solid. To guarantee the occurrence of this mechanism the magnitude S of the deviatoric component of the stress tensor $\underset{\sim}{S}$ must overcome the intrinsic flow resistance S_o, that is:

$$S(x,t) \geq S_o \tag{1}$$

where x stands for the triplet of coordinates (x,y,z) and t is time. The scalar S is defined as follows:

$$S = |\underset{\sim}{S}| = (\tfrac{1}{2}\underset{\sim}{S}:\underset{\sim}{S}^T)^{\frac{1}{2}} = (\tfrac{1}{2}\sum_{ij}\sum S_{ij}^2)^{\frac{1}{2}}, \tag{2}$$

$$(i,j = x,y \text{ or } z).$$

The intrinsic flow resistance S_o may be expressed as :

$$S_o = g(\Delta v, W, d) \tag{3}$$

where g is a scalar function of the specific free volume Δv, the structural parameters, such as the molecular weight W, and the average density d of the interactive forces in the material system (for example: the molecular entanglement or crosslinking in polymers, the molecular orientation or atomic dislocation in metal systems).

With respect to Δv, the function g may be expanded using Laurent's series as:

$$g(\Delta v, W, d) = \sum_{n=-\infty}^{\infty} \beta_n (\Delta v)^n, \tag{4}$$

where the coefficients β_n's are function of the structural parameters W and d only.

Furthermore, the specific free volume is a function of the magnitude of the isotropic stress tensor σ_{ii}, the temperature, T, the concentration of the chemical environment C and time t as follows:

$$\Delta v(t) = \mathbf{F}(\sigma_{ii}, T, C, t), \tag{5}$$

where $\mathbf{F}$ is a functional.

To a first approximation, for small deformations $\Delta v(x,t)$ is the sum of the three principal strains $\varepsilon_{ii}(x,t)$, which can be expressed as function of dilatational stresses $\sigma_{ii}(x,t)$, the temperature T, and creep compliance J(t) in linear viscoelasticity:

$$\Delta v(x,t) = \varepsilon_{ii}(x,t) = \int_{-\infty}^{t} J(\xi-\eta)\frac{\partial}{\partial\tau}\sigma_{ii}(x,\tau)d\tau + 3\alpha_o\theta(T) \tag{6}$$

where

$$\theta(T) \equiv \frac{1}{\alpha_o}\int_{T_o}^{T} \alpha(\nu)d\nu, \tag{7}$$

is the pseudo-temperature and $\alpha(T)$ is the temperature dependent coefficient of thermal expansion and α_o corresponds to the reference temperature T_o. $\xi=t\phi(T)$ and $\eta=\tau\phi(T)$ are the reduced times respectively for thermorheologically simple materials with a temperature shift factor $\phi(T)$ which is positive, monotonically increasing function of T with $\phi(T_o)=1$.

With the aid of the above relations, the initiation of quasifracture can be rewritten in the following form:

$$S(x,t) \geq \sum_{n=-\infty}^{\infty} \beta_n \left[\int_{-\infty}^{t} J(\xi-\eta)\frac{\partial}{\partial\tau}\sigma_{ii}(x,\tau)d\tau + \alpha_o\theta(T) \right]^n \tag{8}$$

This equation reduces to a simpler form when only a constant uniaxial tensile stress σ_o is applied to a two dimensional quasifracture:

$$\sigma_o/\sqrt{3} \geq \sum_{n=-\infty}^{\infty} \beta_n \left\{ \sigma_o J[t\phi(T)] + 3\alpha_o\theta(T) \right\}^n \tag{9}$$

The dilatational compliance J(t) can be obtained from creep data by curve fitting technique [See Appendix B of Reference 4]. To a first approximation the function $\Theta(T) = T-T_o$ and the time-temperature shift factor $\phi(T)=e^{k(T-T_o)}$ [5,6] where k is a material constant and $T_o = 20°$ C.

On this basis the initiation time t_c of quasifracture for polystyrene can be obtained with the following additional data:

$\alpha_o = 1.0 \times 10^{-5}$ $°C^{-1}$

$k = 0.01$

$\beta_n = 0$ ($n \neq 0$ or -1)

$\beta_o = -30$ MN/m^2

$\beta_{-1} = 0.3$ MN/m^2

Thus the inter-relationship among the applied tensile stress σ_o in MPa the temperature T in °C and the initiation time in hours for quasifracture to develop is shown in Fig. 2. The stress-time relationship is in good agreement with that measured by Klemperer [7]. In addition, the linear relationship between the applied stress and the temperature for the initiation of quasifracture or crazing is also in good agreement with that observed [8].

ON PROPAGATION OF QUASIFRACTURE

The development of quasifracture under tensile stress depends both upon the magnitude of stress and time. The phenomenon of quasifracture has been recognized as a prior deformational behavior in solids. In dealing with quasifracture, continuum models are usually utilized. Each individual quasifracture must obey the regular field and constitutive equations during its development. A fundamental principle of the global conservation of energy is:

$$\dot{W}(t) + \dot{Q}(t) = \dot{E}(t) + \dot{D}(t) + \dot{K}(t) + \dot{\overline{\sum_n \zeta_n}}^{N(t)}(t) \qquad (n=1,2,3,\ldots,N) \tag{10}$$

where $\dot{W}(t)$ is the rate of mechanical work done by external forces,
$\dot{Q}(t)$ is the heat supplied per unit time to the system,
$\dot{E}(t)$ is the stored strain energy rate of the original solid medium,
$\dot{D}(t)$ is the energy dissipation rate of the original solid medium,

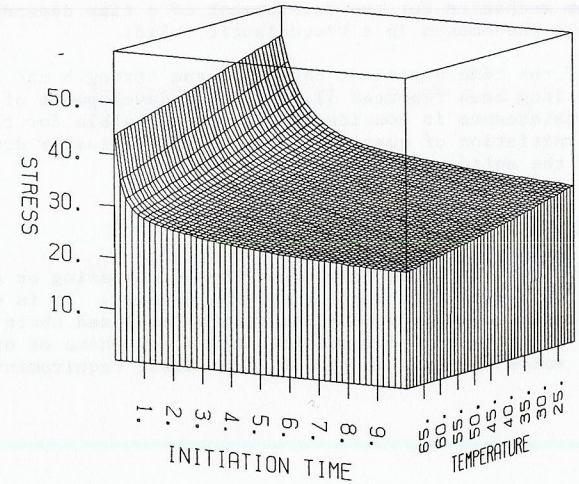

Fig. 2 Inter-relations among applied stress, temperature and initiation time on quasifracture

$\dot{K}(t)$ is the time rate of change of the kinetic energy of the original solid medium,
$N(t)$ is the total number of quasifractures developed at time t,
and $\zeta_n(t)$ is the absorbed energy by the nth quasifracture developed in the medium .

Since the energy is balanced for any arbitrary small regions, one may consider the local conservation of energy in the neighborhood of a single quasifracture.

Referring to Fig. 1 a quasifracture usually develops into a planar configuration perpendicular to the direction of applied stress. It occurs easily on the surface of a solid instead of its interior at a flaw from where an elliptical quasifracture front propagates into the medium. An idealized symmetrical quadrantal quasifracture section is shown in a rectangular coordinate system (o-xyz). Oriented molecular domains containing bundles of polymer fibers or crystalline aggregates for metals and voids or dislocations are initiated and formed. If xz plane is the surface of the solid then the major axis of the quasifracture region is represented by c(t) as a function of time t while the minor axis is p(t) at time t showing the central maximum penetration of the quasifracture front into the material body. The oriented domains are load bearing in spite of voids or dislocations. Each domain is assumed to be round which may change as a function of time. The distance between the xy-plane and the top quasifracture surface is the opening displacement designated by w(x,y,o,t) which reduces to w(x,o,o,t) on the surface of the solid at time t. On the envelope surface of the quasifracture, the stress component in the z-direction is shown as $\sigma_c(x,y,z,t)$. The general

state of stress, strain and displacement fields are respectively $\sigma_{ij}(x,y,z,t)$, $\varepsilon_{ij}(x,y,z,t)$ and $u_i(x,y,z,t)$ with i and j as tensor subscripts in the rectangular coordinate system(x,y,z).

Each oriented domain sustains a stress $\sigma_d(x,y,z,t)$ which may be different from the quasifracture envelope surface stress $\sigma_c(x,y,z,t)$. The former represents the true domain stress while the latter is an average engineering stress taking domains and voids altogether into consideration for polymers. Thus the ratio $V_f(x,y,z,t) = \sigma_c(x,y,z,t)/\sigma_d(x,y,z,t)$ is the volume fraction of domains within a quasifracture. The actual domain distribution density function $\rho(x,y,z,t)$ is defined as the number of load bearing domains passing through a unit area in the quasifracture plane at time t.

In general the initiation of quasifracture requires the increase of the internal energy including stored and dissipative energies to a critical level, beyond which the original structural configuration of the medium is no longer stable and a new phase must take place. As a result highly oriented molecular domains and voids as well as new surfaces are created. Referring to Fig. 3 in the reference frame $(0\text{-}X_1X_2X_3)$ an undeformed or unoriented

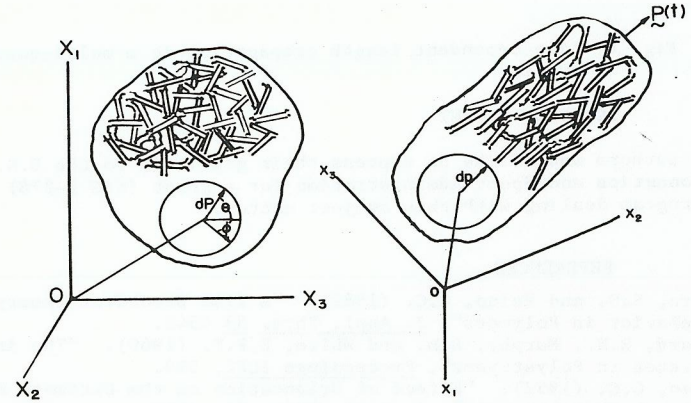

Fig. 3 Molecular Deformation and Orientation of Microstructures

material system is considered. Under a load P(t) the current frame of reference $(o\text{-}x_1x_2x_3)$ may be used to calculate the strength and the degree of molecular orientation of the microstructural system. Using random variables (θ,ϕ), any microelement dP will orient to its new direction as indicated in the current reference frame as dP [9,10]. Depending upon the nature of the

medium the variation of the modulus may be determined as a function of orientation strain ε as shown in Fig. 4. The modulus of elasticity E_{ZZ} in

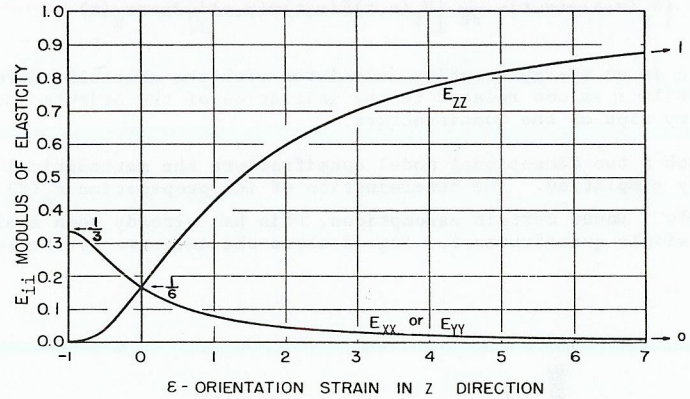

Fig. 4 Variation of modulus of elasticity vs. orientation strain

the direction of orientation increases for some linear polymeric model solids, while in the transverse direction the moduli E_{XX} and E_{YY} decrease. The oriented molecular domains may be amorphous or crystalline or both with high load carrying capabilities. Only when they cease to bear load, fracture commences. In time the microfractures may eventually develop into a macrofracture.

SIMPLIFICATIONS AND RESULTS

Returning back to the model with multi-quasifractures, mathematically $\dot{\zeta}_n(t)$ can be calculated in the following manner for any nth surface elliptical quasifracture:

$$\dot{\zeta}_n(t) = 4 \int_0^{c_n(t)} \int_0^{b_n(x,t)} \sigma_c(x,y,z,t)\, w(x,y,z,t)\, dydx \tag{11}$$

where $b_n(x,t) = p_n(t) \quad [1 - x^2/c_n^{\,2}(t)]^{\frac{1}{2}}$, (12)

$c_n(t)$ is the half craze length of the nth craze,

and $z = w(x,y,o,t)$. (13)

This absorbed energy rate governs the development of the quasifracture. Applying the energy balance again for the nth quasifracture only and after suitable mathematical manipulation and simplifications, an implicit nonlinear differential equation for the two dimensional quasifracture is obtained by omitting both y and z coordinates in the expression:

$$\int_0^{c_n} \left\{ \sigma_c(x,t)w(x,t) - \frac{\partial}{\partial t}\left[V_f(x,t)\xi(x,t)\dot{w}(x,t) \right] \right\} dx = \eta \dot{c}_n(t) \qquad (14)$$

where ε is an energy quantity associated with the molecular deformation process while η is one related to the initiation of the oriented domains near the very tips of the quasifracture.

For such a two dimensional model quasifracture the mathematical problem is greatly simplified. The determination of its propagation $c_n(t)$ becomes feasible. Under certain assumptions, this has already been analyzed [11], for a single quasifracture. Fig. 5 shows the increase of the length of a

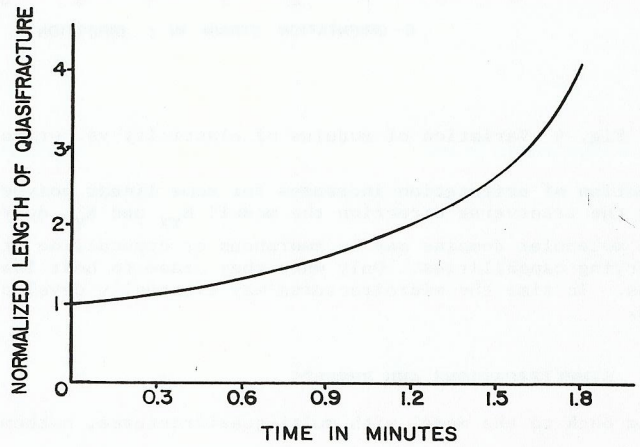

Fig. 5 Quasifracture length increase as a function of time

single quasifracture as a function of time. However, when a multi-quasifracture system is considered the nature of the length increase per each quasifracture behaves quite differently.

Based upon the measured value of the number of quasifractures on the surface of viscoelastic solid samples and the geometry of the individual quasifractures, Equation (14) has been solved through computer aided numerical methods. The calculated result of the quasifracture length propagation has been found to agree fairly well with the experimental measurements for polystyrene as

shown in Fig. 6. [4]

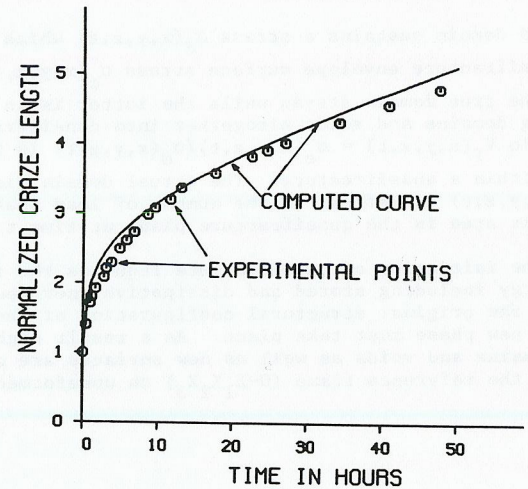

Fig. 6 Time dependent length propagation in a multi-quasifracture system

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