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The technical report on crazing in polymeric and composite systems encompasses several phases of mesomechanics studies which lead into continuum and non-continuum microdamage mechanics investigations. Based upon the first principles of physics and mechanics and the sciences of the microstructure of materials, this new interdisciplinary research has been quite challenging and very fruitful. As a result new ideas have been introduced in developing new theories and breakthroughs have occurred on several fronts in time dependent deformation, strength theories and damage criteria for solids and composite systems.

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CRAZING IN POLYMERIC AND COMPOSITE SYSTEMS

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I. Introduction

The study of an important and challenging problem in science and engineering has been the understanding of the strength and fracture behavior of stressed solid systems. This is particularly true of failure behavior and its prediction in viscoelastic material systems. Both the structural and functional application of these materials demand a better understanding of their behavior and failure mechanisms. When sufficiently large tensile stresses are associated with these materials, various modes of damage develop. To elucidate these, one common mode of response, namely crazing under an applied simple stress, must first be understood. Major advances and breakthroughs in the crazing behavior in microscopic and macroscopic levels of understanding will yield tremendously useful information not only theoretically but also practically. Considerable technological and scientific significance is attached to this proposed endeavor. The initiation and propagation of crazing as quasifracture, the time dependent fracture strength of oriented polymers, the associated molecular orientation and ultimate strength in and around a craze, and the interaction of crazes in polymeric and composite systems are just some of the features to be understood. The determination of the time dependent fracture strength of polymers and composite systems, the displacement field and the stress distribution in the vicinity of craze-crack transition regions as well as the propagation behavior of craze and crack are important problems to be solved prior to the consideration of many other relevant topics. Currently a firm foundation has been established. It appears that continued research in the relevant outgrowth topics will result in a truly fruitful understanding of the subject matter and lead into future fundamental investigations in mesomechanics, the connection between microstructure and mechanics.

II. Background information and objectives, with references

Advanced reinforced plastics, consisting of a polymer matrix and fibres, continue to generate great interest in their application to high performance structural components. Fracture of these composite systems may result from flaws in fibres or matrix as well as the failure of the bonds. Thus the strength of any such composite is governed by the time dependent strength characteristics of the matrix, the fibres and the bonds. Because of the difference in the mechanical behavior of the three constituents of composites, up to now many strength criteria have been considered and developed by scientists and engineers all over the world as reflected by, for example, several recent references [1–3].

The studies of time-dependent failure of composites have been relatively scarce in spite of the strong dependence of the failure characteristics on time. The formulation of the models must now be based upon the microstructural peculiarities of deformation, the molecular orientation, temperature and time [4–6]. Aside from the phenomenological models, perhaps, statistical models [7–9] should also be considered concurrently so that they may reinforce each other's findings and development.

References

1. Handbook of Composites Series (*Strong Fibres, Structure and Design, Failure Mechanics of Composites and Fabrication of Composites*). Edited by A. Kelly and Y. N. Rabotnove, North Holland (1985).

2. *Proceedings of International Symposium on Composite Materials and Structures.* Edited by T. T. Loo and C. T. Sun, Beijing, China (June, 1985).

3. M. F. Kanninen and C. H. Popelar. *Advanced Fractures Mechanics.* Oxford University Press, New York; Clarendon Press, Oxford (1985).

4. A. S. Krausz and H. Eyring. *Deformation Kinetics.* Wiley-Interscience, New York, London, Sydney, Toronto (1975).

5. C. C. Hsiao and W. Chen, A Constitutive Representation of Inhomogeneous Polymeric Systems, in *Polymer Networks, Structural and Mechanical Properties.* Plenum Press, New York, London, 395 (1971).

6. C. C. Hsiao and S. R. Moghe, Characterization of Random Micro-structural Systems, in *Proceedings of the International Conference on Structure, Solid Mechanics and Engineering Design in Civil Engineering Materials,* Part II (Southampton, England). John Wiley, London, 1203 (1971).

7. W. Chen and C. C. Hsiao, Nonlinear Viscoelastic Constitutive Behavior as a Statistical Dynamic System, in *Advances in Polymer Science and Engineering*, Plenum Press, New York, London, 115 (1972).

8. D. R. Axelrad. *Micromechanics of Solids*. Elsevier Scientific Publishing Co., Amsterdam, Oxford, New York; PWN: Polish Scientific Publishers, Warszawa, 1978.

9. D. R. Axelrad. *Foundations of the Probabilistic Mechanics of Discrete Media*. Pergamon Press: Oxford, New York, Toronto, Sydney, Paris, Frankfurt, 1984.

III. Micromechanics of polymers and composites

The phenomenon of crazing and its relation to some fracture analyses are considered as follows:

The formation of a craze comes about from a physical transformation in the deformation processes of the microscopic material molecules under tensile stress. The transformation takes place from a homogeneous deformation to a craze configuration when a critical condition is reached. Subsequently, the craze boundary propagates as a function of applied stress, time, temperature, physical and chemical influences as well as the actual microstructural changes subjected to geometrical constraints. As a result, usually minute voids are generated among oriented molecules and the density of the medium in the crazed region is nonuniformly reduced whereas the bulk of the homogeneous material body deforms more uniformly. The interface boundary layer enveloping crazes of many solid materials is capable of being drawn and transformed into bundles of highly oriented molecular domain structure in the craze region. Further stressing will eventually initiate craze-crack transition. It appears necessary to take these physical variations into consideration in any mathematical modeling and formulation in analyzing the stresses from the time when crazes incept to the time when they propagate and transform into real fractures.

The science of crazing, a quasifracture state, and subsequent cracking, a fracture state, of solid material systems under tension has been making large strides in the recent past. The crazing mechanism has been associated with molecular orientation and fracture strength [1 to 5].

Subsequently various methods have been utilized to determine and confirm the molecular mechanism with respect to craze formation and fracture in thermoplastics [5, 6]. Essentially under tensile stresses certain solid materials deform from sites where high stress concentrations are created and crazes develop. Because of geometrical constraints and energy requirements, the material molecules orient themselves in the direction of stressing with voids among them. As stated earlier, the presence of oriented polymeric molecules in a craze region bounded by surprisingly smooth interface layers is visualized as an actual physical phase transformation in the deformation processes from one orientation state to another depending upon the magnitude and rate of applied tensile stress [8], material characteristics as well as, of course, temperature and physical and chemical environments, etc., surround the solid body. As a result, the mechanical behavior of the material is greatly affected by the macroscopic geometry and the distribution and interaction of the individual crazes as well as the microscopic molecular configuration and voids within each craze region and along its immediate boundaries enveloping the area. Macroscopically the development of crazes and their distribution can be detected statistically by laser diffraction techniques [9]. The geometry of an individual craze which can be studied by focused laser beams [10] is of primary importance in understanding the processes of its initiation and propagation as well as the deformation, quasifracture-fracture transition, and eventually the fracture behavior of the medium. Knowledge of craze initiation and geometry helps in determining the craze displacement field, the stress distribution and the craze-crack transition and propagation under load [11, 12]. An eventual understanding of the true mechanism of molecular strength and fracture behavior of a simple solid matrix and a complex composite system can be obtained if fundamental microscopic information is utilized in macroscopic analyses.

In a craze the highly strained molecular bundles act as boundary tractions with great strength; any governing mathematical formulation must include this feature for any adequate analysis. Crazes of different forms and properties have occurred in polymeric materials [13, 14] and other solid systems including even single crystals [15]. An analysis is highly desirable and may be useful for studying general solid systems.

Both long- and short-range programs may be considered. It appears fruitful that emphasis be placed on the study of micromechanics of individual craze-crack transition, the source of failure under various internal and external stresses for the matrix and the composite systems.

The nature of the stresses in and around a craze-crack transition region is the key to the understanding of the morphology and nucleation as well as the propagation of crazes and cracks. The first attempt in calculating the state of macroscopic tensile stress field in the direction of the applied load as a function of craze length has been based upon a model with an assumed craze boundary displacement as a crack opening in an infinite elastic sheet [16]. The stresses were calculated as though the craze were a continuum and the craze boundary developed no stress perpendicular to the direction of applied stress. The solution of the two-dimensional-homogeneous biharmonic equation for a semi-infinite elastic medium due to the application of an external pressure to the surface has been used [17, 18]. This implies that the craze behavior is independent of the craze medium [18, 19] under stress. The solutions were obtained using a Fourier transform technique [20] or a complex variable method of analysis [19, 21, 22]. With proper assumed boundary conditions the latter method of approach gives probable stress and displacement fields surrounding a craze. A model for craze growth has also been considered with the creep of craze material as the cause of craze propagation. The craze growth was found to be linear with respect to the log of time [19].

The aforementioned stress analyses have been made essentially on the basis of the classical elasticity theory for a homogeneous elastic medium with either an assumed stress distribution for certain portions of a crack without considering any time dependency.

The development of crazing is not only a function of stress but also a function of time [23, 24]. Using the current theory and by taking into consideration the isotropic and anisotropic material constants the mathematical model describing the crazing mechanism have been successful [25–29].

References

1. J. A. Sauer, J. Marin and C. C. Hsiao, *J. Appl. Phys.* **20**, 507 (1949).
2. C. C. Hsiao and J. A. Sauer, *J. Appl. Phys.* **21**, 1071 (1950).
3. C. C. Hsiao, *J. Appl. Phys.* **30** , 1492 (1959).
4. C. C. Hsiao, Section IV in *Fracture Processes in Polymeric Solids*, Interscience, John Wiley, 529 (1964).
5. S. R. Kao and C. C. Hsiao, *J. Appl. Phys.* **35**, 3127 (1964).
6. S. Rabinowitz and P. Beardmore, CRC Critical Reviews in *Macromolecular Science 1*, (1972).
7. R. P. Kambour, *J. Poly Sci-Macromolucular Reviews* 7, 1 (1973).
8. R. W. Truss and G. A. Chadwick, *J. Mat. Sci.* **11**, 1385 (1976).
9. C. C. Hsiao, *Appl. Phys.* Lett. **23**, 20 (1973).
10. C. C. Hsiao, *J. Appl. Phys.* **48** , 1168 (1977).
11. A. P. Wilczynski, C. H. Liu and C. C. Hsiao, *J. Appl. Phys.* **47**, 4301 (1976).
12. A. P. Wilczynski, C. H. Liu and C. C. Hsiao, *J. Appl. Phys.* **48**, 1149 (1977).
13. H. H. Kausch and M. Dettenmaier, *Polymer Bulletin* 3, 565 (1980).
14. M. Dettenmaier and H. H. Kausch, *Polymer Bulletin* 3, 571 (1980).
15. K. F. Ha and Z. Z. An, *J. Appl. Phys.* 55, 95 (1984).
16. A. C. Knight, *J. Polymer Sci.* 3A, 1845 (1965).
17. H. C. Krenz, Relationships Between Structure and Micromechanics of Solvent Crazes in Glassy Polymers, Ph.D. thesis, Cornell University, 115 (January, 1977).
18. N. Verheulpen-Heymans, *J. Polymer Sci. Phys.* **14**, 93 (1976).
19. N. Verheulpen-Heymans and J. C. Bauwens, *J. Mat. Sci.* **11**, 7 (1976).
20. B. D. Lauterwasser and E. J. Kramer, *Philo. Bull.* 3, 565 (1980).

21. N. I. Muskelishvili, *Some Basic Problems of the Mathematical Theory of Elasticity*, P. Noordhoff Groningen, 333 (1953).

22. T. Y. Fan, *Foundations of Fracture Mechanics* (in Chinese), Jiangsu Scientific and Technical Publisher, Jiangsu (December, 1978).

23. S. S. Chern and C. C. Hsiao, *J. Appl. Phys.* **52**, (10) 5994 (1981).

24. S. S. Chern and C. C. Hsiao, *J. Appl. Phys.* **53**, (10) 6541 (1982).

25. S. S. Chern, Z. D. Zhang and C. C. Hsiao, *J. Poly. Sci. Phys.* **23**, 2579 (1985).

26. C. C. Hsiao and S. R. Moghe, *Characterization of Random Microstructural Systems*, Proceedings, International Conference on Structure, Solid Mechanics and Engineering Design in Civil Engineering Materials, Southampton, England, 1969, John Wiley, London, Part I, 95 (1971).

27. V. S. Kuksenko and V. P. Tamuzs, *Fracture Micromechanics of Polymer Materials*, Martinus Nijhoff Publishers, 202 (1981).

28. S. S. Chern and C. C. Hsiao, *J. Appl. Phys.* **53**, 6541 (1982).

29. Z. D. Zhang, S. S. Chern and C. C. Hsiao, *J. Appl. Phys.* **54**, 5568 (1983).

IV. Progress during the first year—publication

A paper on "Noncontinuum Craze-Crack Transition" by C. C. Hsiao was presented at the 1988 Annual Meeting of ASME, Boston and published in *Damage Mechanics in Composites—AD—Vol. 12* (Eds. A. S. D. Wang and G. K. Haritos), (Book No. G00376).

V. Progress during the second year—publications

1. "Analysis of Crack-Induced-Craze in Polymers", by B. N. Sun, H. S. Hou and C. C. Hsiao, published in *Eng. Fracture Mechanics* **30**, 595 (1988).

The analysis of the crack-induced-craze in polymers is believed to be a fairly general phenomenon in fracture studies. This work will deal with the use of a viscoelastic boundary element method for analyzing a polymer quasi-fracture. A time dependent boundary stiffness will be considered and the viscoelastic solution in the time domain may be obtained by applying the collocation Laplace inversion technique. Using these methods, the quasifracture problem with time dependent stiffness tractions in a two-dimensional case may be analyzed. Both the craze opening displacement profile and the envelope stress distribution around a craze can be computed. This will pave the way in evaluating the propagation history of both the crack and the craze. Results thus obtained may be compared with those obtained by previous considerations such as the use of the Dugdale model and the concern on the stress concentration phenomenon.

2. "Analyzing Polymer Crazing as Quasifracture", by B. N. Sun and C. C. Hsiao, published in *J. Polymer Science,* Phys. **26**, 967 (1988)

Before any real fracture develops under stress in polymeric or composite systems, it seems that, in a fairly general picture common to most solid systems, crazing incepts first. Following the previously stated craze-crack transition and crack-induced-craze, the initiation of crazing is simply a special case. In the absence of crack the craze as quasifracture has been studied by many scientists. Since the boundary element method has become recently a powerful technique for solving boundary value problems including some nonlinear ones, it is especially important as a tool to be used in problems having viscoelastic deformations and fractures. Therefore, it may be fruitful in developing proper procedures for calculating the stress distributions around a craze envelope.

3. "Time Dependent Fracture Strength of Solid Bodies", by O. M. Ettorney and C. C. Hsiao, published in *J. Appl. Phys.* **64**, No. 10, Part 1, 4884 (1988)

Statistical theories in fracture kinetics constitute a very important role in investigating the fracture strength of solids and their utilization in modern engineering. In this short report, a review of some of the recent concepts and models is provided. The main concern is the effect of the breaking stress on the time-to-break. Based upon the consideration of the fraction of integrity of a medium, a number of models have been evaluated and compared. Two basic considerations used for evaluation and comparison are Zhurkov's empirical kinetic relationship and Hsiao's statistical absolute reaction rate model. Other considerations reducible from these two are also given for comparison. Using a well-known numerical analysis method, it appears that the nonlinear mathematical consideration is more realistic in describing the time-dependent fracture strength behavior of a medium over any linear ones. The computed results seem to fit reasonably well with the general observations.

4. "Temperature Variation During Polymer Failure", by C. C. Hsiao and Y. S. Cheng, published in Europhysics Conference Abstracts, 20th Europhysics Conference on Macromolecular Physics and 3rd Lausanne Polymer Meeting on Physical Mechanisms in Polymer Failure, (Lausanne, Switzerland) Vol **12J**, September (1988)

This paper attempts to discuss the temperature variation during polymer failure using a statistical absolute reaction rate theory. At fracture, the temperature may increase or decrease depending upon a quantity named fraction of integrity f and its rate $\dot{f}$ and accelerator $\ddot{f}$ as well as a stress modifier β.

For over a century, scientists and engineers have observed temperature variations during loading and testing of solids. Most work in this area focused on metallic systems: temperature changes during elastic and/or plastic deformations, as well as theoretical investigations based on mechanics and thermodynamics.

Using the statistical absolute reaction rate theory, the present work attempts to analyze the temperature variation during polymer failure.

5. "A New Generalized Damage Criterion for Polymers" by C. C. Hsiao, published in Europhysics Conference Abstracts, 20th Europhysics Conference on Macromolecular Physics and 3rd Lausanne Polymer Meeting on Physical Mechanisms in Polymer Failure, (Lausanne, Switzerland) Vol **12J**, September (1988)

Since the dawn of human culture, the problem of strength of solids has been experienced and utilized empirically. Probably not until the past 500 years has the problem of strength and deformation of solid bodies been investigated quantitatively. The phenomena of yielding and strength have been carefully considered during the past 100 years. It is only during the last twenty years that special attention has been given to the study of craze initiation criteria of polymers by Sternstein and Ongchin (1969), Gent (1970), Bowden and Oxborough (1973), and Argon et al.

volume variations among others. Using series expansion the damage resistance is given in terms of internal and external energies. As a result a new general anisotropic damage criterion is constructed.

2. "Kinetic Strength of Solids", C. C. Hsiao, Advances in Fracture Research, Proceedings of the Seventh International Conference on Fracture (ICF7), 2913 (1989)

The time dependent kinetic strength of solids has been studied for over half a century. In general, two levels of approach have been employed. One is submicroscopic atomic consideration and the other may be referred to as supermacroscopic continuum investigations. The latter is mostly phenomenological which results in numerous empirical relationships. One of the most extensive experimental investigations is that done by Zhurkov [1]. Under a state of constant stress creep condition more than 50 different kinds of solids including metallic and nonmetallic, amorphous and crystalline, oriented and unoriented systems were recorded the stress dependent of the time-to-break data. Even data on the temperature variations were tested and analyzed. It was found that the logarithm of time-to-break and the applied uniaxial tension were linearly related as

$$t_b = t_o \exp[(U - \gamma\sigma)/kT] \tag{1}$$

where

t_b is time-to-break,
t_o is a constant,
U is a constant which may be related to the activation energy of the solid,
γ is a positive definite constant,
σ is the applied constant stress,
k is the Boltzmann constant and
T is the absolute temperature.

However, in reality, there is deviation from this empirical linearity when either super high stresses or relatively low stresses beyond the meso-stress range is encountered.

This short report is to address this point using an equation derived from the Tobolsky-Eyring-Hsiao expression [2]. Essentially, the theory is based upon considerations at a submicroscopic atomic level. At this level, the statistical nature of any system behavior can be calculated according to the rates of forming and breaking of bonds. To make it easily accessible to engineering applications, the mathematical model used is a matrix of oriented submicroscopic bonds randomly distributed in an arbitrary domain. The fraction of intact bonds "f" measures the degree of integrity of the system. The integrity or strength of a solid body is identified by calculating $\dot{f}$, the rate of change of f, as follows:

$$\dot{f} = K_r(1-f) - K_b f \qquad (2)$$

where

K_r is the rate of reformation of broken bonds.
K_b is the rate of breaking of intact bonds.

These rates can further be expressed in terms of the following submicroscope quantities:

$$K_r = \omega_r \exp(-U/RT - \rho\psi)\,, \qquad (3)$$

$$K_b = \omega_b \exp(-U/RT + \beta\psi)\,. \qquad (4)$$

where

ω_r is the frequency of motion of the broken bonds,
U is the activation energy,
R is the universal gas constant,
T is again the absolute temperature,
ρ is a positive definite stress modifier,
ψ is the stress in the bonding direction,
ω_b is the frequency of motion of the intact bonds and
β is a positive definite stress modifier.

It would be interesting to compare the high kinetic strengths with experiment values. Up to now little or no data have been found yet. However, it is felt that expression (2) should predict the kinetic strength behavior adequately.

As stated, Zhurkov's model was and is an empirical relationship whereas the present model is based upon submicroscopic atomic as well as molecular considerations. It is also quite apart from Hoff's [3] or Kachanov's [4, 5] models. Using an atomistic approach, the current model should not be looked upon as a one-dimensional model as it is easily extended to a three-dimensional situation by introduction of a molecular orientation mechanism as a result of deformation [6]. This mesomechanics approach is considered to be very sound as it makes the connection between microstructure, micromechanics, and macromechanics. Therefore the kinetic strength is given in terms of the basic atomic and molecular quantities, so that the mechanical properties can be deduced for solids exhibiting creep, diffusion, or dislocation glide and so on as the time, temperature, molecular motion, and elementary bonding stresses, etc. have been incorporated into the model in the first place [7, 8, 9].

References

1. Zhurkov, S.N. (1965). Kinetic concept of the strength of solids. *Int. J. Frac. Mech.* **1**, 311.

2. Krausz, A.S. and H. Eyring. (1975). *Deformation Kinetics*. John Wiley, New York, p. 349.

3. Hoff, N.J. (1953). The necking and rupture of rods subjected to constant tensile loads. *J. Appl. Mech.* **20**, No. 1, 105.

4. Kachanov, L.M. (1974). *Principles of Fracture Mechanics*. Moscow. Nauka, Moscow.

5. Kachanov, L.M. (1958). On the time of fracture under creep conditions. *Izv. AN SSSR. Otd. teckn nauk.* **8**, 26.

6. Mun, M.S. and C.C. Hsiao. (1986). Time dependent fracture strength of oriented polymers. *J. Appl. Phys.* **60**, 2655.

7. Hsiao, C.C. (1964). Molecular orientation–dependent fracture strength. *Fracture processes in Polymeric Solids,* Chap IVC, p. 529.

8. Hsiao, C.C. and S.R. Moghe (1971). Characterization of random micro-structural systems. *Proc. Int. Conf. in Structure, Solid Mechanics, and Engineering Design in Civil Engineering Materials, Part I.* (Southampton, England). p. 95. John Wiley, London.

9. Ettorney, O.M. and C.C. Hsiao (1988). Time dependent fracture strength of solid bodies. *J. Appl. Phys.* 64, 4884 (1988).

3. "Analyses of Three-Dimensional Crazing in Polymers"—in preparation for publication

Polymers and polymeric composites usually fail by first developing crazing on the surface of the material system. Internal crazes can also be initiated when sufficient and necessary conditions exist. The time-dependent craze failure process, whether two-dimensional or three-dimensional, may be characterized by several stages: deformation, development of microporosity, craze initiation, craze-crack transition and propagation until complete failure occurs. The interrelationship among the applied stress, craze initiation, time and temperature has been established and a fairly general time-dependent theory on craze initiation in viscoelastic media has been formulated.

In 1982, C. C. Hsiao et al proposed and analyzed a two-dimensional craze growth on surface of polymeric materials. It gave information on the time-dependent nature of craze growth in viscoelastic media. In many actual cases of damage, however, the craze growth in a polymer is of 3-dimensional nature. But till now it does not seem that there is any work available in the literature describing time-dependent 3-dimensional crazing-cracking behavior in polymers.

To gain a better understanding for the craze behavior in polymers, here in this report an analysis for the time-dependent crazing in polymers is developed. The analytical work is divided into two parts. In the first part of this report, a "DISK" model of the 3-dimensional craze is proposed, and then a complete set of governing equations is given on the basis of viscoelastic principles, energy theorem and variational considerations. Basic time dependent unknown functions are the craze envelope stress (CZES), craze opening displacement (CZOD) and craze radius (CZR). Using the variational considerations, conditions for admissible envelope stresses (CZES) are given by singularity analysis of the stresses at the craze tip. In the second part, an important class of craze growth, i. e. "self-similar" solutions is proposed and considered. In this case, any unknown field, say ψ, is not considered to be directly related to the polar radius r and time t, but only with one variable, $r/c(t)$, here $c(t)$ is the craze radius at time t. Thus, mathematical simplifications could be obtained in the treatment of the quadrature of the basic equations with complexity and nonlinearity. The complicated basic equations are reduced to a single nonlinear ordinary differential equation for the craze growth. Analytic expressions are obtained for the craze opening displacements in terms of elliptical integrals of the first and second kinds.

Two types of simple viscoelastic media, i. e., the Maxwell and Voigt solids have been considered. Numerical quadrature is used to evaluate the integral expressions containing elliptic integrals. The nonlinear equations are solved by Runge-Kutta method numerically, to obtain the craze opening displacements (CZOD).

Computed 3-dimensional results of craze growth are also compared with those of two-dimensional cases.

Introduction

The study of craze initiation and growth has lasted around four decades since the first paper given by C. C. Hsiao and J. A. Sauer in 1950 [1]. Some questions and concerns related to the understanding of the crazing problem may be stated as follows:

a. For polymers under a set of given conditions will craze occur [2,3,4] ?

b. What are the temperature and time effects on craze initiation and growth [5–9,20] ?

c. How to model the real process of crazing behavior in polymers [9–14] ?

The knowledge obtained from crazing research is important in predicting the durability of plastics and polymeric engineering components. Besides the theoretical approach in modelling and analyzing the craze growth, certain other experimental work has also been reported [15–23]. In studying the craze growth processes, many different models have been considered and analyzed. Knight [11] has proposed a craze critical initiation stress in the local craze tip area. When the local tensile stress reaches this critical level, crazing is produced. This model gives rate insensitive craze initiation which contradicts to the experimental observations [15,16]. Heymans et al [12] presented a craze model, in which craze was divided into two zones with the polymer inside the craze as being deformed plastically and outside as elastic. The results show that the craze length increases as a logarithmic function of time, in agreement with their experimental data on polycarbonate. Chern and Hsiao [14] analyzed a two-dimensional craze in which the viscoelastic behavior of the bulk polymeric medium and the nature of molecular orientation within the craze region are taken into account. Based upon this time-dependent viscoelastic model, both craze opening displacements and craze length extensions have been computed. To obtain a better understanding on crazing in a polymeric medium, a time-dependent theory and analysis of craze growth in viscoelastic solids is given in the present report to elucidate the fundamental mechanism of a 3-dimensional crazing behavior in polymers.

In this report, the work is divided into two parts. The first part is concerned with a 3-dimensional DISK model of the time-dependent craze growth. A complete set of governing equations and solutions are developed on the basis of viscoelasticity theory [24], energy theorems and variational considerations. Basic unknown functions are the time-dependent craze envelope stress (CZES), craze opening displacement (CZOD) and craze radius (CZR). Using the variational methods, the admissible conditions for the craze envelope stress are given by singularity analysis of the stress at the craze tip. In the second part, the complex nature of the mathematical equations is discussed and the self-similar solutions have been proposed. Important mathematical simplifications are obtained in the treatment of the quadrature of the basic equations for the craze size. Analytic expressions in terms of elliptical integrals are also obtained for the craze opening displacements [25].

Two types of simple viscoelastic media: i. e., the Maxwell and Voigt solids are considered. Numerical quadrature is used to evaluate some integral expressions containing elliptic integrals in their integrand appearing as parameters in solving the nonlinear ordinary differential equation for crazing by Runge-Kutta method [26]. The craze opening displacements (CZOD) are then computed. Results are compared with those for the two-dimensional cases.

A 3-dimensional DISK model of craze

To deal with the analysis of a 3-dimensional craze growth problem, it is desirable to consider the following DISK model as shown in Fig. 1 and Fig. 2:

In the above figures and below, the following notations are used:

$c(t)$:	Radius of the craze at time t
$w(r,t)$:	Craze opening displacement at r and time t
$d(r,t)$:	Diameter of fibril bundle domain at r,t in a craze
$\sigma_c(r,t)$:	Craze envelope stress at r,t
$\sigma_f(r,t)$:	Stress of fibril domain at r,t
$V_f(r,t)$:	Volume fraction of fibrils in a craze at r,t
$\sigma_o(t)$:	Remote applied stress at t
$N(r,t)$:	Number of load bearing fibrils per unit craze area
$w_m(r,t)$:	Thickness of primordial layer from which fibril domain is drawn out
$w_o(r,t)$:	Equals to $w(r,t)-w_m(r,t)$

Figs.1 and 2 describe a 3-D symmetrical craze in a simple stress field σ_o. In the craze region, oriented molecular fibrous bundles and voids are formed. Surrounding the craze region there is the viscoelastic bulk polymer. The fibril connections are load bearing which can take stress $\sigma_f(r,t)$. The craze envelope stress $\sigma_c(r,t)$ is an average engineering stress which may be calculated by dividing the applied force with the volume containing both the fibrils and the voids. Based upon experimental observations, an idealized craze structure is composed of cylindrical fibrils domains of diameter $d(r,t)$, which may vary from position to position. During crazing process, the diameter

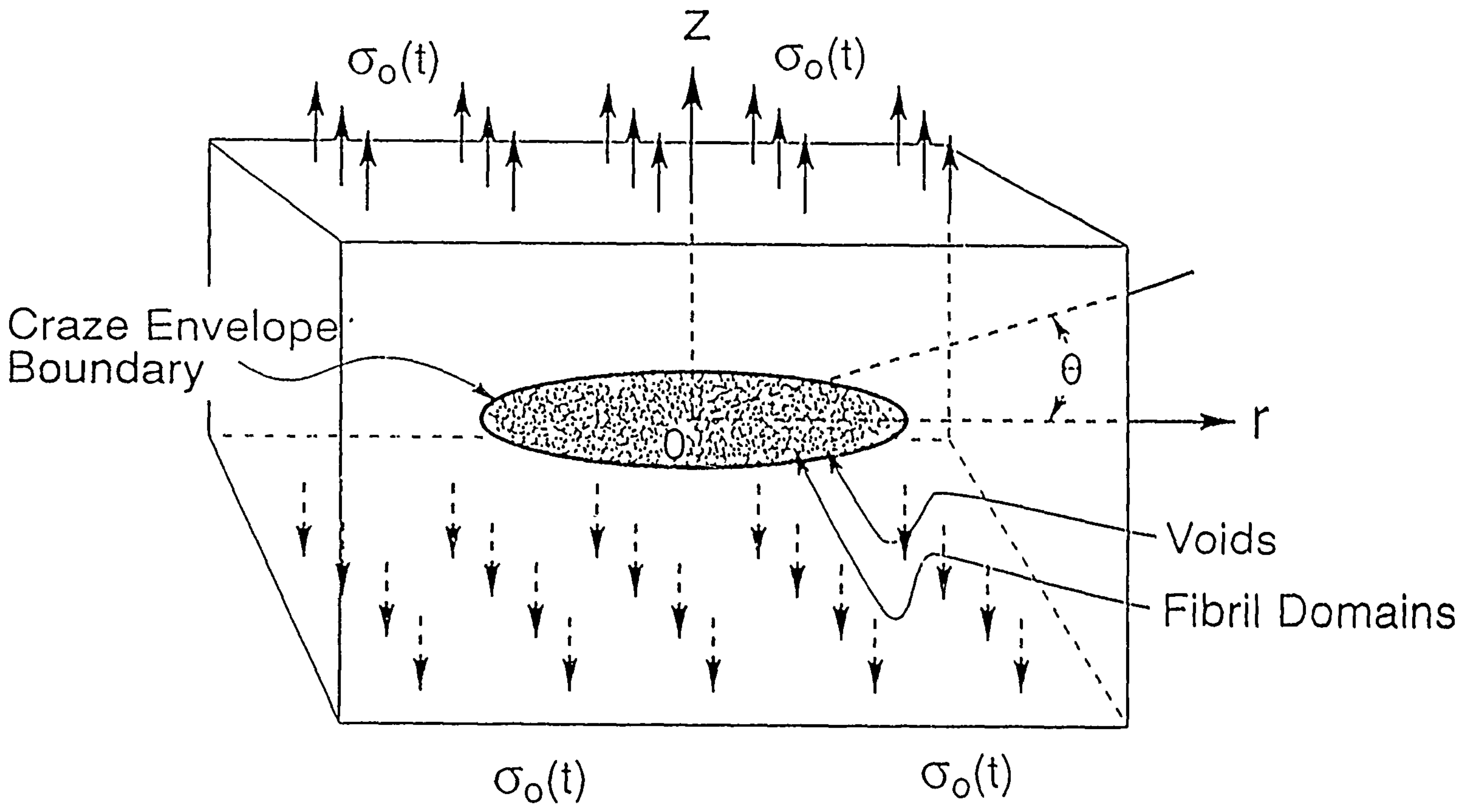

Fig. 1. A Circular 'Disk' Model of Craze in Polymers Viewed at an Angle.

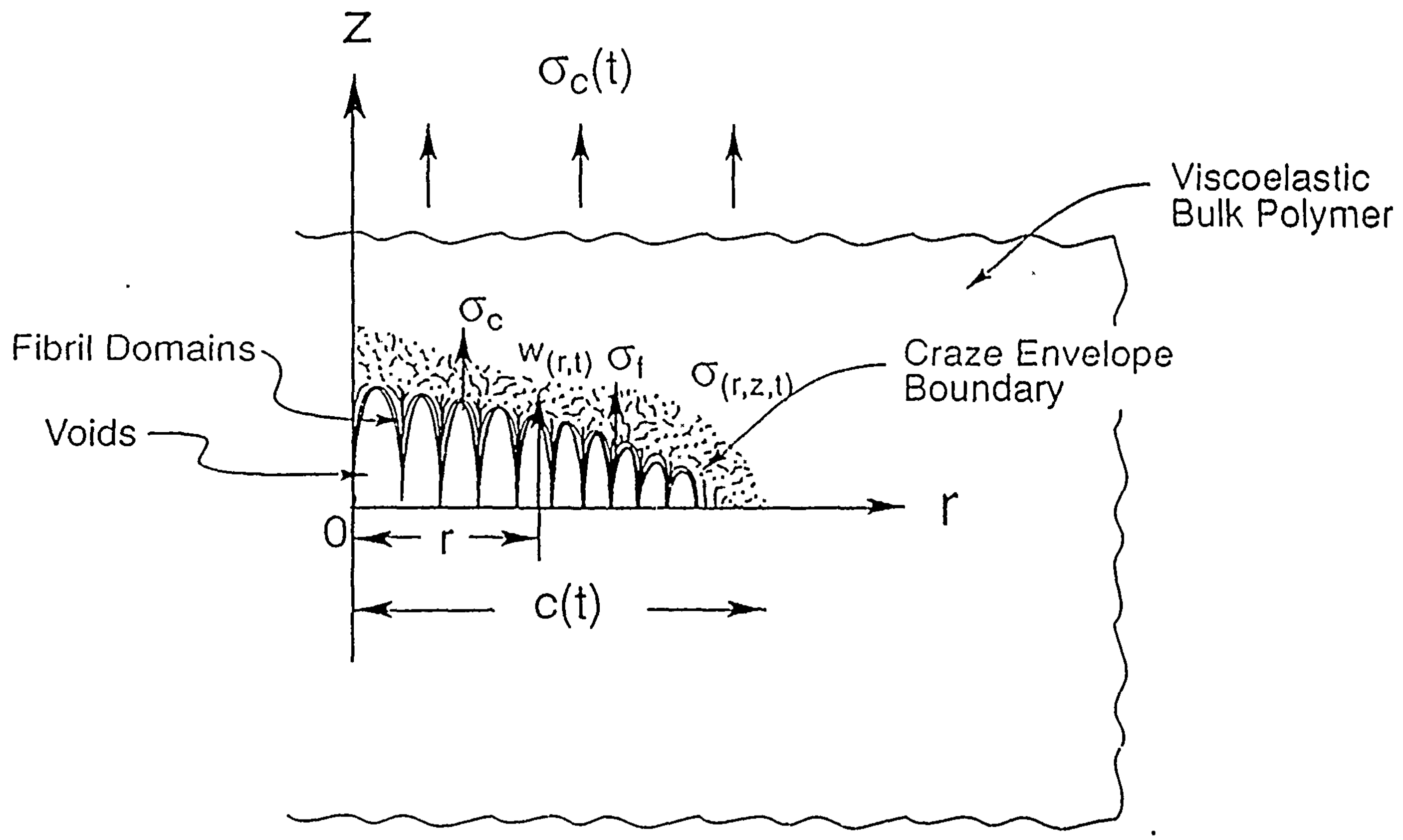

Fig. 2. Radial Cross-section of a 'Disk' Craze.

of each fibril domain changes with time as its length changes. The craze fibrils are formed by continuous drawing from the unoriented bulk polymer. This drawing process causes mass to flow from parent phase (unoriented bulk polymer) into new phase (highly oriented fibrils). The general state of stress in the bulk polymer is expressed by $\sigma(r,z,t)$ as shown in Fig.2. It is easily seen that the volume fraction of fibrils in a craze $V_f(r,t)$ can be expressed by $\sigma_c(r,t)/\sigma_f(r,t)$. In Fig. 1, the fibril density distribution $N(r,t)$ is defined as the number of load bearing fibrils passing through a unit craze area at r,t. Permitting some possible fibrils breakdown under high loading conditions from time to time, the function $N(r,t)$ is considered time dependent.

Governing equations for the craze opening displacement

Using cylindrical polar coordinates, the equations for the viscoelastic boundary value problem governing the 3-dimensional DISK craze growth problem are given as follows:

Equilibrium Equations

$$\sigma_{ij;j}(r,\theta,z,t) = o \qquad (i,j = r,\theta,z) \qquad (1)$$

Geometrical Equations

$$\varepsilon_{ij}(r,\theta,z,t) = \frac{1}{2}\left(u_{i;j} + u_{j;i}\right) \qquad (i,j = r,\theta,z) \qquad (2)$$

Constitutive Equations

$$S_{ij}(r,\theta,z,t) = \int_{-\infty}^{t} G_1(t-\tau)\, de_{ij}(\tau) \qquad (3)$$

$$\sigma_{ii}(r,\theta,z,t) = \int_{-\infty}^{t} G_2(t-\tau)\, d\varepsilon_{ii}(\tau) \qquad (4)$$

$$S_{ij} = \sigma_{ij} - \frac{1}{3}\delta_{ij}\sigma_{kk} \qquad (i,j = r,\theta,z) \qquad (5)$$

$$e_{ij} = \varepsilon_{ij} - \frac{1}{3}\delta_{ij}\varepsilon_{kk} \qquad (6)$$

where (r,θ,z) are the cylindrical polar coordinates and t is time.The symbol ";" means co-variant differentiation. σ_{ij}, ε_{ij} are stress and strain tensors respectively, and u_i are displacements. S_{ij}, e_{ij} are deviatoric stress and strain tensors, δ_{ij} is the delta symbol and $G_1(t)$, $G_2(t)$ $(t > o)$ are respectively the deviatoric and dilatational moduli of the bulk polymeric media.

To complete the boundary value problem, the following boundary and initial conditions are introduced:

Boundary Conditions ($t \geq o$) :

$$\sigma_{zr}(r,\theta,o,t) = \sigma_{z\theta}(r,\theta,o,t) = o \qquad (r < c(t)) \qquad (7)$$

$$\sigma_{zz}(r,\theta,o,t) = \sigma_c(r,\theta,t) = \sigma_c(r,t) \qquad (r < c(t)) \qquad (8)$$

$$\sigma_{zz}(r,\theta,z,t) = \sigma_o(t) \qquad (r^2 + z^2 \to +\infty) \qquad (9)$$

$$\sigma_{r\theta} = \sigma_{rr} = \sigma_{zr} = \sigma_{z\theta} = \sigma_{\theta\theta} = o \qquad (r^2 + z^2 \to +\infty) \qquad (10)$$

Here $\sigma_o(t)$ is the applied stress given for $t \geq t_o$

Initial condition:

$$c(t) = c_o, \ (t = t_o) \qquad (11)$$

In general, for the DISK craze model, in standard cylindrical coordinates it allows an axisymmetrical solution. The individual equations can be expressed in the following form where all the stresses, strains and displacements are functions of time:

$$\frac{\partial\sigma_{rr}}{\partial r}+\frac{1}{r}\frac{\partial\sigma_{r\theta}}{\partial\theta}+\frac{\sigma_{rr}-\sigma_{\theta\theta}}{r}+\frac{\partial\sigma_{rz}}{\partial z}=0 \qquad (12)$$

$$\frac{1}{r}\frac{\partial\sigma_{\theta\theta}}{\partial\theta}+\frac{\partial\sigma_{r\theta}}{\partial r}+2\frac{\sigma_{r\theta}}{r}+\frac{\partial\sigma_{r\theta}}{\partial z}=0 \qquad (13)$$

$$\frac{\partial\sigma_{zz}}{\partial z}+\frac{1}{r}\frac{\partial\sigma_{z\theta}}{\partial\theta}+\frac{\partial\sigma_{rz}}{\partial r}+\frac{\sigma_{rz}}{r}=0 \qquad (14)$$

$$\varepsilon_{rr}=\frac{\partial u_r}{\delta r} \qquad (15)$$

$$\varepsilon_{\theta\theta}=\frac{u_r}{r}+\frac{1}{r}\frac{\partial u_\theta}{\partial\theta} \qquad (16)$$

$$\varepsilon_{r\theta}=\frac{1}{2}\left(\frac{1}{r}\frac{\partial u_r}{\partial\theta}+\frac{\partial u_\theta}{\partial r}-\frac{u_r}{r}\right) \qquad (17)$$

$$\varepsilon_{zr}=\frac{1}{2}\left(\frac{\partial u_r}{\partial z}+\frac{\partial u_z}{\partial r}\right) \qquad (18)$$

$$\varepsilon_{z\theta}=\frac{1}{2}\left(\frac{1}{r}\frac{\partial u_z}{\partial\theta}+\frac{\partial u_\theta}{\partial z}\right) \qquad (19)$$

$$\varepsilon_{zz}=\frac{\partial u_z}{\partial z} \qquad (20)$$

The time dependence of these equations can be eliminated by taking the Laplace transformations in the following manner:

$$\bar{f}(r,\theta,z,s) = \int_{o}^{\infty} e^{-st} f(r,\theta,z,\tau)\, d\tau , \ (\mathrm{Re}(s) \geq s_0 > o) \tag{21}$$

where $\bar{f}(s)$ is the Laplace transform of f(t) with s as the Laplace parameter and then the above basic governing equations in the s-domain become time independent:

$$\bar{\sigma}_{ij|j}(s) = o \qquad (i,j = r,\theta,z) \tag{22}$$

$$s) = \frac{1}{2} (\bar{u}_{i|j}(s)+\bar{u}_{j|i}(s)) \qquad (i,j = r,\theta,z) \tag{23}$$

$$\bar{S}_{ij} = s\, \bar{G}_2(s)\, \bar{e}_{ij}(s) \qquad (i,j = r,\theta,z) \tag{24}$$

$$\bar{\sigma}_{ii} = s\, \bar{G}_1(s)\bar{\varepsilon}_{ii}(s) \qquad (i,j = r,\theta,z) \tag{25}$$

Here, $\bar{\sigma}_{ij}$, $\bar{\varepsilon}_{ij}$, $\bar{u}_i$, $\bar{G}_1$, $\bar{G}_2$, $\bar{S}_{ij}$, $\bar{e}_{ij}$ are the corresponding Laplace transforms of σ_{ij}, ε_{ij}, u_i, G_1, G_2, S_{ij} and e_{ij} respectively.

In order to avoid the varying boundary conditions, we let σ_0, σ_c and c remain constant as piecewise step functions in each of the infinite intervals and finally sum up all the contributions.

Therefore the boundary conditions become:

$$\bar{\sigma}_{zr}(s) = \bar{\sigma}_{z\theta}(s) = o \qquad (r< c ,) \tag{26}$$

$$\bar{\sigma}_{zz}(s) = \bar{\sigma}_c(s) = \sigma_c / s \qquad (r< c ,) \tag{27}$$

$$\bar{\sigma}_{zz}(s) = \sigma_0 / s \qquad (r^2 +z^2 \rightarrow + \infty) \tag{28}$$

$$\bar{\sigma}_{r\theta} = \bar{\sigma}_{rr} = \bar{\sigma}_{zr} = \bar{\sigma}_{z\theta} = \bar{\sigma}_{\theta\theta} = o \qquad (r^2 + z^2 \rightarrow + \infty) \qquad (29)$$

Using the linear elastic and viscoelastic correspondence principle the corresponding viscoelastic and elastic parameters and variable functions are as follows:

$$\begin{array}{ccccccc} s\bar{G}_1 & s\bar{G}_2 & \sigma_o/s & \sigma_c/s & \bar{S}_{ij} & \bar{e}_{ij} & \bar{u}_i \\ | & | & | & | & | & | & | \\ G_1 & G_2 & \sigma_o & \sigma_c & S_{ij} & e_{ij} & u_i \end{array} \qquad (30)$$

Then from the governing equations of the time dependent viscoelastic boundary value problem (12)–(28), a corresponding elastic problem may be expressed in the following form:

$$\sigma_{ij;j} = o \qquad (31)$$

$$\varepsilon_{ij} = \frac{1}{2} (u_{i|j} + u_{j|i}) \qquad (32)$$

$$s_{ij} = G_1 \, e_{ij} \qquad (33)$$

$$\sigma_{ii} = G_2 \, \varepsilon_{ii} \qquad (34)$$

$$\sigma_{zr} = \sigma_{z\theta} = o \qquad (r < c) \qquad (35)$$

$$\sigma_{zz} = \sigma_c/s \qquad (r < c) \qquad (36)$$

$$\sigma_{zz} = \sigma_o/s \qquad (r^2 + z^2 \rightarrow +\infty) \qquad (37)$$

$$\sigma_{r\theta} = \sigma_{rr} = \sigma_{zr} = \sigma_{z\theta} = \sigma_{\theta\theta} = o \qquad (r^2 + z^2 \rightarrow +\infty) \qquad (38)$$

Using this approach, the elasticity solution in the s-domain may be obtained. Inversion of the solution will give the time dependent results.

Now consider the case of an axisymmetrical problem with respect to θ:

$$u_\theta = \sigma_{r\theta} = \sigma_{z\theta} = \varepsilon_{z\theta} = \varepsilon_{r\theta} = 0 \tag{39}$$

$$\frac{\partial}{\partial\theta}(\,) = 0$$

where ( ) may be any given function.

The governing equations become:

$$\frac{\partial\sigma_{zz}}{\partial z} + \frac{\sigma_{rr}-\sigma_{\theta\theta}}{r} + \frac{\partial\sigma_{rz}}{\partial z} = 0 \tag{40}$$

$$\frac{\partial\sigma_{zz}}{\partial z} + \frac{\partial\sigma_{rz}}{\partial r} + \frac{\sigma_{rz}}{r} = 0 \tag{41}$$

$$\varepsilon_{rr} = \frac{\partial u_r}{\partial r} \tag{42}$$

$$\varepsilon_{\theta\theta} = \frac{u_r}{r} \tag{43}$$

$$\varepsilon_{zr} = \frac{1}{2}\left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}\right) \tag{44}$$

$$\varepsilon_{zz} = \frac{\partial u_z}{\partial z} \tag{45}$$

$$S_{ij} = G_1\, e_{ij} \tag{46}$$

$$\sigma_{ii} = G_2\, \varepsilon_{ii} \tag{47}$$

Similarly the boundary conditions can also be reduced:

when z = o :

$$\sigma_{rz}(r,o) = o, \qquad (r \geq o) \tag{48}$$

$$\sigma_{zz}(r,o) = -p(r), \qquad (r < c) \tag{49}$$

$$u_z(r,o) = o, \qquad (r > c) \tag{50}$$

when $|z| \rightarrow \infty$:

$$u_i = \sigma_{ij} = o \tag{51}$$

Here

$$p(r) = \sigma_o - \sigma_c(r) \tag{52}$$

This set of equations (40)-(52) correspond to a crack problem shown in the following figure: Fig.3.

In solving this problem, Hankel transform and Mellin transform methods have been employed [27, 28]. Using minimum potential energy considerations and the variational principle, the craze envelope stress has been calculated as a function of time as it is not only dependent upon position but also on time as shown in Fig. 4.

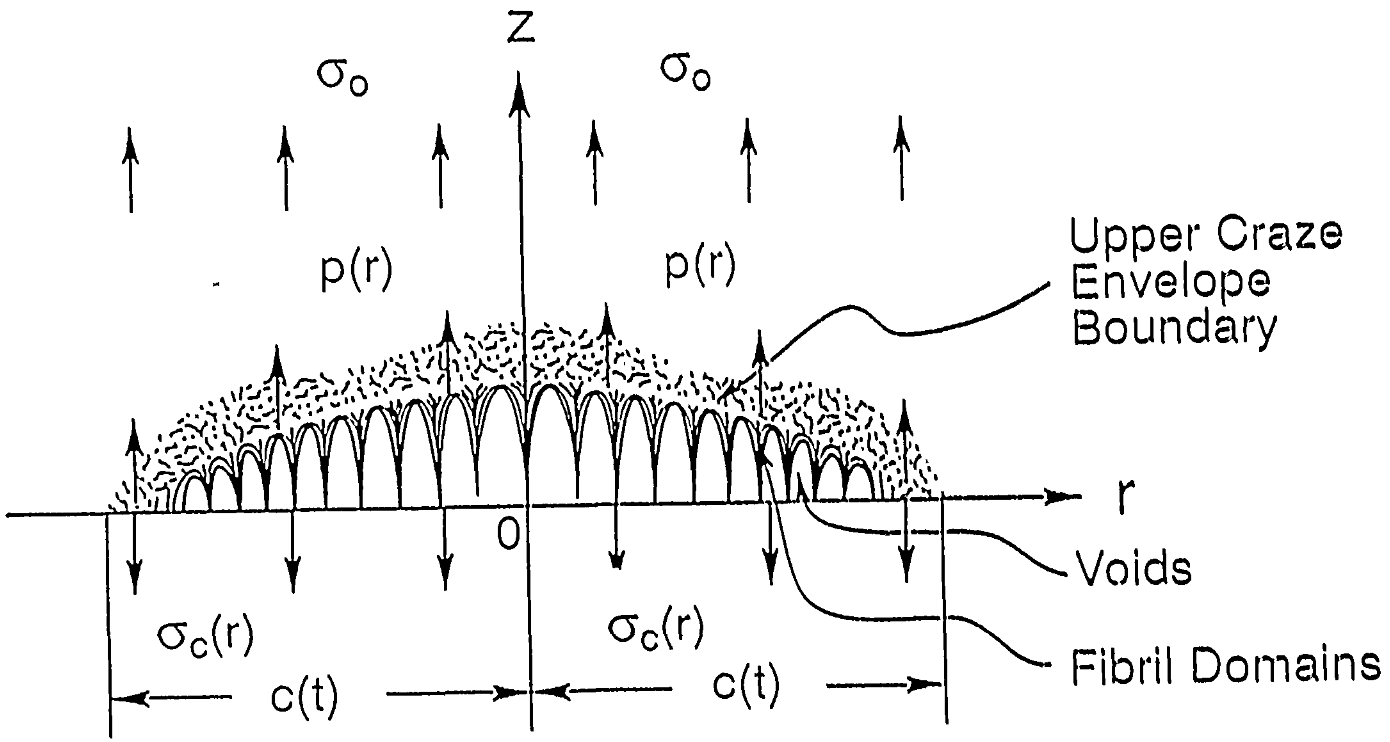

Fig. 3. Radial Cross-sectional View of the Upper Half Craze Envelope.

The craze envelope surface is opened by pressure $p(r) = \sigma_o - \sigma_c(r)$.

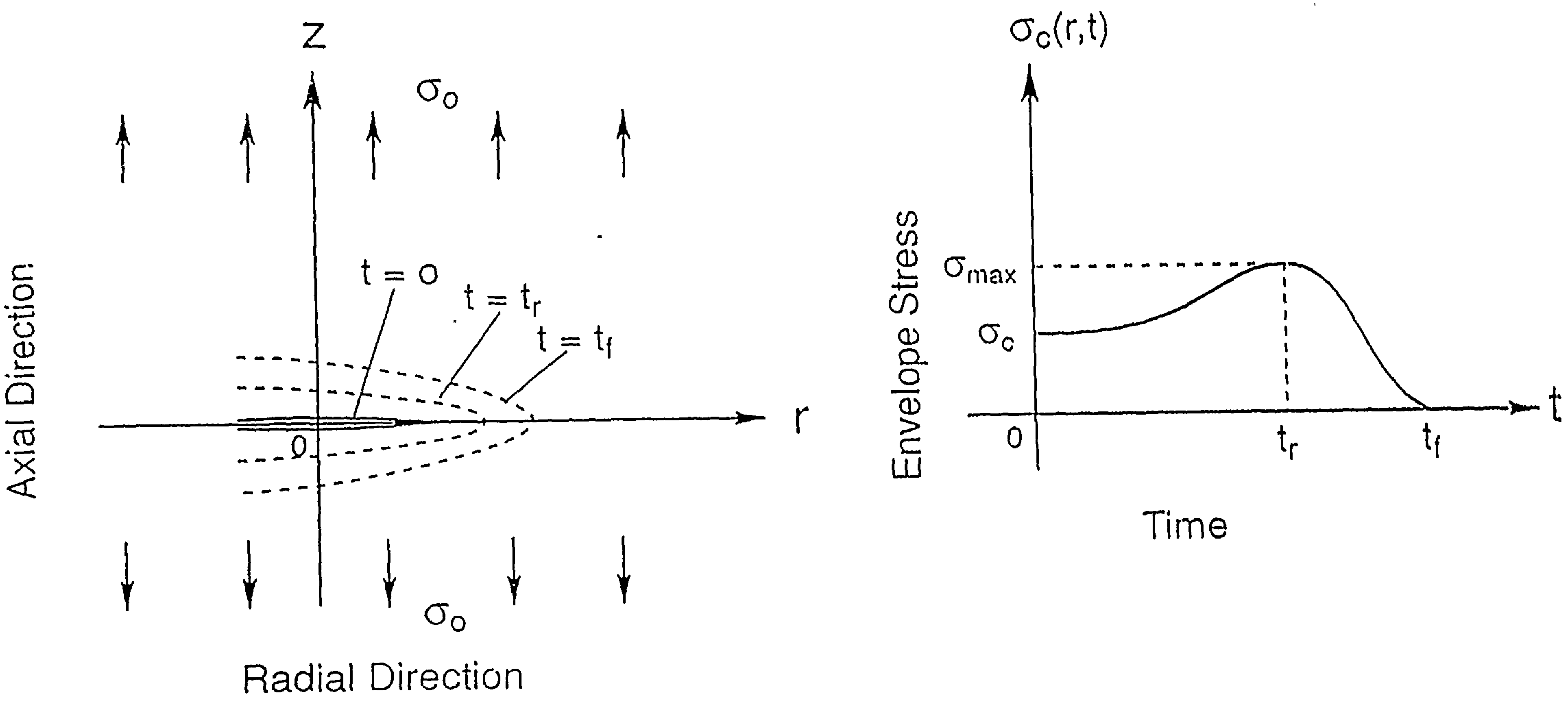

Fig. 4. Time Dependent Circular Craze Growth.

$t = o$: Craze ends at c_o, so $\sigma_c(r,t = o) \approx \sigma_o$

$t = t_r$: Craze border arrives at r, so $\sigma_c(r,t_r)$ reaches a maximum value

$t = t_f$: All fibrils within the circle of radius r breakdown and $\sigma_c(r,t_f) = o$

In order to effect a solution, a self-similar type of envelope stress has been considered as illustrated in Fig. 5. After a lengthy analysis, the final form of a nonlinear equation governing craze growth has been obtained. Preliminary results have been computed [29–31] and compared with those of the two-dimensional cases for both Maxwell and Voigt media as shown in Figs. 6 and 7. It is hoped that this work will be continued and the mathematical details will be presented in a report.

References

1. C. C. Hsiao and J. A. Sauer, J. Appl. Phys. 21, 1071 (1950)
2. S. Robinowite et al, Crit. Rev. Macromol. Sci. 1, 1 (1972)
3. R. P. Kambour, J. Polymer Sci. D7, 1 (1973)
4. S. S. Chern and C. C. Hsiao, J. Appl. Phys. 57, 1823 (1985)
5. W. B. Klemperer, in the Theodore Von Karman Anniversary Volume, Appl. Mech., 328 (1941)
6. J. A. Sauer and C. C. Hsiao, ASME Trans. 75, 895 (1953)
7. O. S. Bruller, Polymer, Polym. Eng. Sci. 18, 42 (1978)
8. R. P. Kambour, Appl. Appl. Symp. 7, 215 (1968)
9. H. H. Kausch et al, Polym. Bull. 3, 565, (1980)
10. M. Dettenmair et al, Polym. Bull. 3, 571 (1980)
11. A. C. Knight, J. Polym. Sci. A3, 1845 (1965)
12. N. V. Heymans et al, J. Mater. Sci. 11, 7 (1976)
13. A. S. Argon et al, Phil. Mag. 36, 1195 (1977)
14. S. S. Chern and C. C. Hsiao, J. Appl. Phys. 53 (10), 6541 (1982)
15. A. Robinson et al, J. Appl. Phys., 31, 1602 (1960)
16. C. C. Hsiao, J. Polym. Sci. 44, 71 (1960)
17. M. I. Bessonov et al, Sov. phys. Solid state, 3, 950 (1961)
18. G. Biglione, Proc. Int. Conf. Fract. 2, 503 (1969)

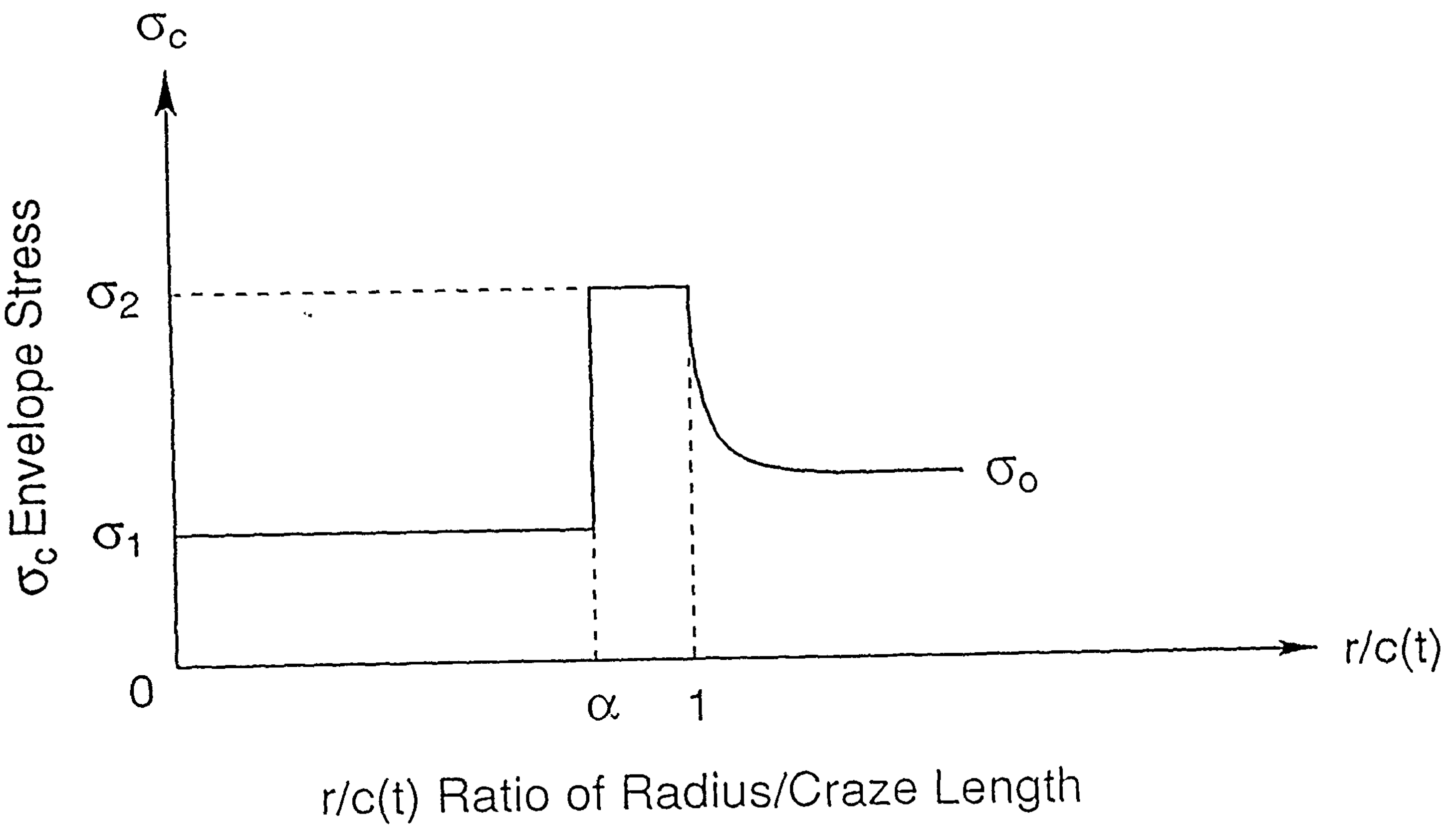

Fig. 5. 'Self-Similar' Type of Envelope Stress Across a Circular Craze.

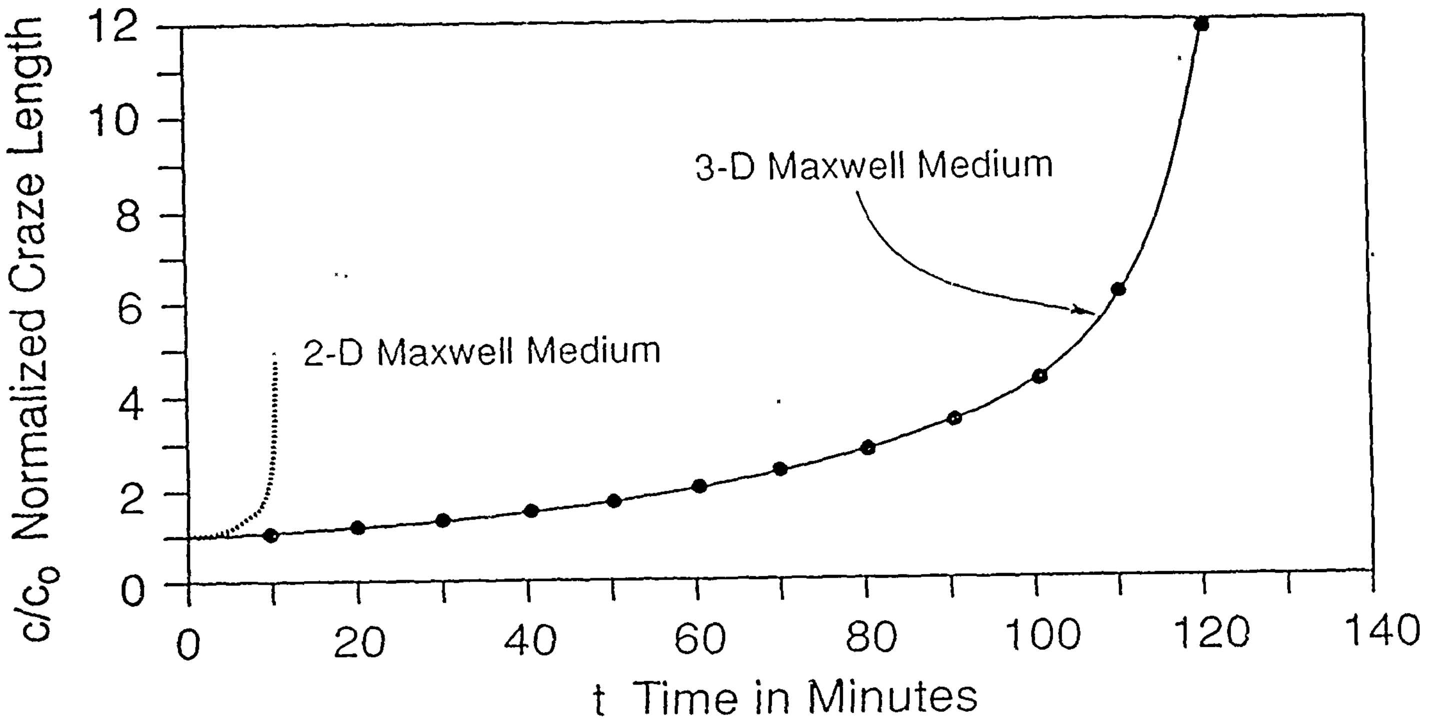

Fig. 6. Craze Growth in Maxwell Medium for 2-D and 3-D Cases.

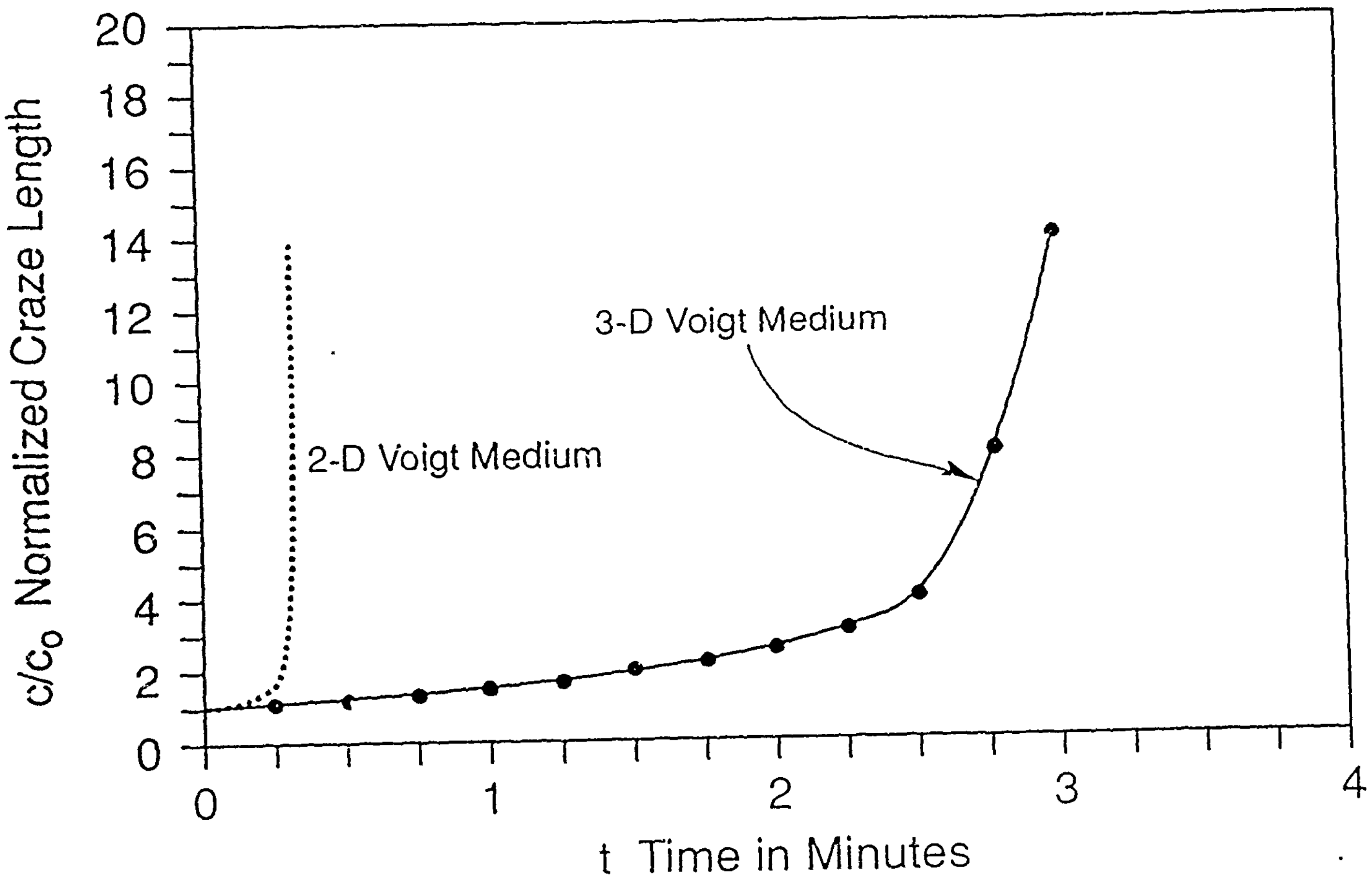

Fig. 7. Craze Growth in Voigt Medium for 2-D and 3-D Cases.

attempt is made here to observe and characterize the behavior of polymers under simultaneous irradiation and stress conditions. The results obtained from this approach can be combined with those from chemical and other relevant experiments to formulate a better and broader explanation and description of the physical process undergone by polymers when exposed to stress and irradiation. In order to achieve a model description of the phenomenon under these conditions the physical process of crazing, which has been known about for more than thirty years [11–13], will be emphasized in the light of earlier work on craze initiation [14], propagation [15], and energy absorption of crazing [16].

Exposure of polymers to irradiation results in a number of physical and chemical changes, either temporary or permanent. Polymers can undergo one or more of the following processes: cross-link, depolymerization, evolution of gases, change in color and/or change in crystallinity. Among these, degradation and cross-linking are fundamentally important, because these processes strongly affect the mechanical properties of the polymer, The behavior of a polymer depends directly upon its molecular weight and chain entanglement. The variation of the aforementioned processes can take place simultaneously. However, the ratio between the changing rates depends on the structural configuration of the polymer, the nature of the substance present in the system and the type of irradiation energy.

Both the degradative and cross-link processes originate from an initial bond breaking reaction which occurs as a result of the absorption of the influential wavelength of electromagnetic radiation. In the case of degradation, the initial reaction may represent the total extent of damage or it may be the prelude to a series of secondary bonding reactions leading to further scission, recombination or substitution of bonds. However, in the case of cross-linking, the process leads to the formation of three-dimensional network structures.

As for the role of mechanical action at the atomic level, electron spin resonance spectroscopy has graphically demonstrated that stretching, grinding, milling or any type of polymer shearing process can also produce free radicals as a result of the fracture of the main chain of the polymer [17, 18].

This article devotes special attention to the study of the craze density development and craze propagation in samples subjected to simultaneous irradiation and mechanical action. Results are them compared with those found earlier in samples subjected to mechanical action only.

By piecing together the results and observations obtained thus far, a paper is being prepared for possible publication in the future.

References

1. B. Ranby and J. F. Rabek, Photodegradation, Photo-oxidation and Photostabilization of Polymers: Principles and Applications, Wiley-Interscience, New York (1975).
2. Ultraviolet Light-Induced Reactions in Polymers, Am. Chem. Soc., Symp. Ser. 25 (1976).
3. D. L. Allara and W. L. Hawkins, eds., Stabilization and Degradation of Polymers, Adv. Chem. Ser. 169 (1978).
4. Longterm Properties of Polymers and Polymeric Materials, Appl. Polym. Symp., 35 (1979)
5. A. Davis and D. Sims, Weathering of Polymers, Applied Science Publishers Ltd., London (1983).
6. N. S. Allen, ed., Developments in Polymer Photochemistry, vol.2, Applied Science Publishers Ltd., London (1982).
7. F. A. Makhlis, Radiation Physics and Chemistry of Polymers, John Wiley & Sons, New York (1975).
8. A. D. Jenkins, Polymer Science, vol. 2, North-Holland Publishing Co. (1972)
9. T. Fukushima, Durability Build. Mater., 1(4), 327–343 (1983).
10. K. Sh. Bocharov, Y. S. Stroilov, V. F. Udovenko and M. V. Zinov'ev, Probl. Prochn., (11), 108–10 (1976)
11. C. C. Hsiao and J. A. Sauer, J. Appl. Phys. 21, 1071 (1950)
12. S. Rabinowitz and P. Beardmore, Crit. Rev. Macromol. Sci. 1, 1 (1972)
13. R. P. Kambour, J. Polym. Sci. D.7, 1 (1973)

14. S. S. Chern and C. C. Hsiao, J. Appl. Phys. 57(6) (1985)
15. Z. D. Zhang, S. S. Chern and C. C. Hsiao, J. Appl. Phys. 54(10) (1983)
16. S. S. Pang, Z. D. Zhang, S. S. Chern and C. C. Hsiao, J. Polym. Sci. 23, 683–693 (1985)
17. J. Shoma, Dev. Polym. Deg. 2, 99 (1979)
18. G. Scott, Adv. Chem. Ser. 169, 30 (1978)
19. S. S. Chern, Z. D. Zhang, and C. C. Hsiao, J. Polym. Sci. 23, 2579–2597 (1985)

5. "Propagation of Crack-Induced-Crazing in Unidirectional Composites"

This paper is in preparation for publication.

The paper deals with the propagation of a crack-induced craze which bisects a unidirectional lamina of composites into two regions with orthotropic viscoelastic properties. This complex crack-induced crazing problem has been separated into two modes: normal mode and shear mode. Using the superposition principle and the Fourier transform technique, the associated elasticity solution has been obtained for the determination of the time-dependent crack and craze propagation velocities $\dot{a}(t)$ and $\dot{c}(t)$, employing the elastic-viscoelastic and Laplace inversion technique numerically. It is interesting to find that the crack propagation will be arrested if the initial crack length a_o is less that a critical length a_c. The viscoelastic properties of the composite matrix is considered. The crack-induced crazing displacement at any point on the envelope surface and the propagation history have been calculated numerically for two viscoelasticity model matrices: Maxwell linear model matrix and generalized Kelvin model matrix.

It is well-known that the strength of a lamina composite is much greater than that of a single matrix material of the same geometry. But the strength of individual lamina in a laminate varies over a wide range. In many cases the composite structure will contain a number of weak sheets. These weak laminae will fail first due to craze-crack transition and subsequent crack-induced crazing. As a result, the load-bearing capability of the composite may be greatly reduced

Therefore, it is significant to investigate the crack-induced crazing in a single lamina which contains an initial crack after craze initiation and craze-crack transition. Because of the development of minute voids and the orientation of the polymer molecules in front of the crack tip, craze is induced; thus it is referred to as crack-induced craze. On the other hand, the matrix material of the composites, such as epoxy resin, is a typical time-dependent viscoelastic medium, and so is the lamina. In this case both the stresses and the displacements are time-dependent, as the are functions of the viscoelastic properties. Obviously it is important to study the time-dependent crack-induced craze propagation.

However, in the past twenty years, most analyses of crack-induced craze growth considered only the time-independent behavior of the stresses and strains. G. C. Sih [1] considered the unidirectional composites as homogeneous anisotropic or nonhomogeneous isotropic elastic media, and applied his criterion of minimum energy density for studying the crack propagation. This is linear elastic fracture estimation only; the rate of crack-induced craze propagation cannot be predicted. Some other scientists did consider the time-dependent crack-induced craze propagation: for example, McCartney [2, 3] applied the linear isotropic viscoelastic model to study the crack propagation and Schapery [4] developed the study of crack growth in nonhomogeneous viscoelastic media for normal crack mode. However, these results still could not be applied to the composite materials because the lamina of composites usually consist of anisotropic viscoelastic media and each cracking lamina should be represented by a complex fracture mode composed of a combination of normal and shear modes.

Experimental results revealed that the rate of crack propagation can be modified significantly by controlling resin properties [5] in composite materials. Therefore the fracture characteristics of the matrix are controlling parameters in crack-induced craze for aligned composite materials. Some scientists thought that the crack propagation might be dependent upon the polymer yield strength beyond the crack tip [6]. In that case, the Dugdale model of fracture was borrowed to consider the propagation of crack in polymers [7]. However, it appears that the

Dugdale model is unlikely to be suited for studying the quasifracture problem of polymers because new phases are created as a result of molecular orientation and many bundles of fibril domains are usually found beyond the crack tip in the matrix of the composite. Such Fibril structure of the craze beyond the crack is the feature that distinguishes it from other localized fracture in metals. The small fibril domains, which can range from 5 to 50 nm in diameter, are loadbearing members of the craze. Embedded in voids, the fibril domains can break down to form larger voids causing crack propagation until fast fracture ensures [8–11]. The stress distribution along the envelope of a craze has been successfully considered as simple step functions [12–14]. Using this crack-induced crazing model together with energy criteria the propagation rate of cracking and crazing along the fiber direction of a composite is studied in the present work.

For most composites there exists an angle between the fiber and the load direct. The crack-induced crazing is a complex quasi-fracture. Some experimental work [15, 16] has shown that the crack-induced craze propagation in a lamina is located in the matrix between the fiber domains originated from initial defects such as voids or other flaws. Based upon these experimentally observed failure models, this paper is directed toward the analysis of the lamina composite consisting of a crack-induced craze formation in a sheet having orthotropic viscoelastic properties. The crack-induced crazing of finite length is situated in the matrix and parallel to the fiber domains. That means the unidirectional composite contains an initial crack-induced craze surrounded by orthotropic viscoelastic materials. The analysis is separated into two parts: one dealing with the normal mode and the other, the shear mode. An integral transform technique is used to reduce the problem to the solution of dual integral equations. Then applying the superposition principle and Laplace inversion technique, the associated elasticity solution in the Laplace domain has been obtained and correspondingly the stress distribution, the crack and craze opening displacement have been inverted into the real time domain. According to the universal energy rate balance, the crack and craze growth rates $\dot{a}(t)$ and $\dot{c}(t)$ in the unidirectional composite material have been derived and calculated numerically.

References

1. G. C. Sih, Fracture of composite materials, Proceedings of the First USA-USSR Symposium on Fracture of Composite Materials. Sizthoff and Noordhoff 111 (1979)

2. L. N. McCartney, *Int. J. of Fracture* **13**, 641 (1977)

3 L. N. McCartney, *Int. J. of Fracture* **14**, 547 (1978)

4. L. N. McCartney, *Int. J. of Fracture* **14**, 293 (1978)

5. P. J. Hogg and D. B. P. F. Hull, 13th Reinforced Plastics Congress, Brighton 29 (1982)

6. S. Yamini and R. J. Young, *J. Mat. Sci.* **14**, 1609 (1979)

7. W.-C. V. Wang and E. J. Kramer, *J. Mat. Sci.* **17**, 2013 (1982)

8. C. C. Hsiao, *J. Appl. Phys.* **23**, 1189 (1952)

9. C. C. Hsiao, *Nature.* **186**, 535 (1960)

10. C. C. Hsiao and S. R. Moghe, Characterization of Random Micro-structural Systems, in *Proceedings of the International Conference on Structure, Solid Mechanics and Engineering Design in Civil Engineering Materials,* Part I (Southampton, England). John Wiley, London, 95 (1971).

11. E. J. Kramer, *Polym. Eng. Sci.* **24**, 76 (1984)

12. S. S. Chern and C. C. Hsiao, *J. Appl. Phys.* **53**, 6541 (1982)

13. Z. D. Zhang, S. S. Chern and C. C. Hsiao, *J. Appl. Phys.* **54**, 5568 (1983)

14. E. H. Andrews, Development in Polymer Fracture—1, Applied Science Publishers Ltd., London (1979)

15. M. A. Biot, Proceedings of the Fourth Midwestern Conference on Solid Mechanics 94 (1955)

16. Zvi, Hashin, *AIAA Journal* 4 No. 8 1411 (1966)

VII. Current research development and possible future impact

As a natural outgrowth several important phases of research have been considered and preliminary breakthrough investigations have been made. It appears that very fruitful results are forthcoming.

1. "A New General Unified Strength Theory and Damage Criterion for Anisotropic Solids and Composite Systems"

Preliminaries

Using an energy approach, the concept of a new general unified strength theory and damage criterion is put forward. The total critical energy, including distortional and dilatational energies, must be overcome for damage initiation in any solid or composite systems. Using variational principles, the extremum critical energy is obtained with respect to the specific mean free volume of the microstructural material system. An application of the calculus of variations yields a differential equation identifying the specific mean free volume variation of a material system as a function of time-dependent microstructural parameters. Solutions of the differential equation will yield the energy required for damage initiation in anisotropic solids and composite systems.

However, if the total energy representing the intrinsic damage resistance function is given simply in terms of a series, a general time-dependent expression can be easily established. Eigenvalues of specific mean free volume and eigenfunctions of extremum energy quantities are obtainable. Damages by yielding, crazing and/or subsequent fracturing are associated with these energy quantities. The new general theory can be reduced to most existing individual prominent strength theories and damage criteria for time-independent material systems.

The damage mechanism of material systems under stress may be associated closely with shear deformation, molecular orientation, and microcavitation. From the microstructural viewpoint, stressing may be visualized as a source of energy which develops an instable process, causing the field of homogeneous deformation to develop into localized flow and cavitation characteristics. Thus, the creation of microcavities and the formation of micromolecular slippage and orientation occur in regions as crazes. This bifurcation creates variations of the vacant spaces or the free volume, in contrast to the volume occupied by atoms and molecules, and sharp flow which is provided by the existence of loading and the available work done to the material system.

As a result, the compatibility condition for a continuum analysis breaks down. This non-continuum behavior creates singularities. The transition from a homogeneous to non-homogeneous state must be taken into consideration in the analysis if the strength and damage behavior of the solid systems is to be better understood.

It is the purpose of this paper, based upon mesomechanics and energy considerations for material systems, to develop new concepts and new governing equations in terms of eigenvalues—eigenfunctions appropriate to different given conditions. Since the emphasis is placed on time-dependent solid and composite systems, a few words on polymeric glass transition, the thermodynamic aspect of the glassy state, and the equation of state of the material may be relevant.

In this study dimensional changes of polymeric matter are important. There are many factors which can cause the dimensional change of matter. Among the most important ones are temperature, mechanical stresses, materials structure, and the effects of time. Then physical phenomena such as the formation of voids and crazes during mechanical deformation, fracture initiation and propagation, and shape changes are second order transitions. Most of these changes are related to the variation of volume. In certain situations, when a medium is in an equilibrium state, its volume can be expressed by an equation of state which describes the dependence of the volume on several other state variables. However, in the solid state the properties of a material, including the volume, may depend on external stresses and temperature. Their path and time dependency is intimately tied to specifying the degree of precision of the specific free volume used in analyses. Nevertheless, the behavior of the specific free volume has served well in describing the equilibrium and quasi-equilibrium transitions for amorphous polymeric systems.

While the concept of specific free volume is still qualitative, it has been useful in explaining many properties and phenomena for polymers in their glassy state. Based upon the consideration of the effect of time, the specific volume of a material may be written as:

$$\text{Specific Volume} \equiv \frac{\text{current volume} - \text{original volume}}{\text{original volume}}$$

where the current volume is the volume measured at time t and the original volume is that determined at original time t_0. The current volume at time t equals the vacant space or the free volume plus the actual volume occupied by atoms and molecules at time t. Thus the specific volume may be written as:

$$\frac{\text{actual volume} + \text{free volume} - \text{original volume}}{\text{original volume}}$$

where the actual volume is not considered to vary greatly with respect to stress, temperature, and time. This is particularly true when a polymer is below its glass transition temperature. This means that the actual volume is essentially a constant. Then the variation of the specific vacant space or free volume can be approximated by the variation of the specific volume. That is, in dealing with the volume change, the specific free volume can be used approximately in place of the specific volume. Therefore the specific free volume is considered in the analysis. The term specific free volume is preferred because it characterizes and dominates the internal microscopic damage behavior of a material system whether it be simultaneously due to microstructural distortion or dilation or both as an internal state variable. In dealing with time-dependent mesomechanics it may be convenient to employ the term specific mean free volume in a mesodomain in any kinetic analyses where various degrees of free volume variation can occur, and it may be satisfactory to consider their average information.

General Approach on Strength Theory and Damage Criterion

Using the stress tensor components σ_{ij}, the magnitude of the total energy is expressible for an anisotropic state of stressing in terms of an anisotropic tensor B_{ij}:

$$\mathcal{E}=B_{ij}\sigma_{ij}\,. \tag{1}$$

At any locale in a medium, when the magnitude of this energy is greater than or equal to a critical value $\mathcal{E}_c$ (i.e. $\mathcal{E} \geq \mathcal{E}_c$), damage will develop. Here $\mathcal{E}_c$ is seen as an intrinsic damage resistance associated with the non-uniform and non-gradual behavior of yielding, crazing and/or subsequent fracturing, representing, among many others, distortional and/or dilatational changes.

The intrinsic damage resistance is dependent upon the intermolecular forces and in turn the intermolecular and interatomic spacings. The average intermolecular distance may be related closely to the specific mean free volume, characterizing this distance. Hence it may be useful to consider the critical energy as an intrinsic damage resistance function of the specific mean free volume.

$$\mathcal{E}_c = \Phi(\bar{v}), \tag{2}$$

where $\bar{v}$ is the specific mean free volume, a dimensionless quantity identifying the variation of the specific mean free volume in a small domain in a given medium. Assuming this is accurate enough, then to a first approximation, it may be adequate to establish a fairly general theory of strength and damage initiation criterion for material systems in the following form when a critical energy is overcome.

$$\mathcal{E} \geq \mathcal{E}_c = \Phi(\bar{v}), \tag{3}$$

where the function Φ is to be determined for initial yielding, crazing and/or subsequent fracturing.

The material system is considered as an ensemble of microstructures in mechanical equilibrium but not necessarily in thermodynamic equilibrium. The cohesive energy, the internal energy, and the entropy of the system are intimately associated with the stress and strain tensors through derivatives. Based upon thermodynamics and statistical mechanics considerations, the macroscopic mechanical properties may be deduced from the microstructure by neglecting the entropy contribution [1]. And the total potential energy becomes a dominating quantity in determining the constitutional internal stress and the anisotropic relaxation moduli as a function of the straining. This deformational strain gives rise to the total energy variation as a function of the specific mean free volume in a mesodomain of the microstructural system. The critical energies are the minima and maxima of the specific mean free volume vs. energy curve. The minima correspond to the natural conformation and configuration of a system of microstructures in their most stable free energy states through natural molecular arrangements which give the stable equilibrium states, while the maxima identify the unstable nonequilibrium behavior of crazing and fracturing. Between any adjacent minimum energy and maximum energy states there exists a transition region at which the damage due to "yielding" may occur. Usually "yielding" is interpreted as the inception of plastic flow without considering any other possible damage microscopically or macroscopically. It does not seem accurate enough to describe the true behavior of a medium under load when both its shape and its volume change simultaneously. It may be adequate to state that "yielding" describes the energy transition region of a material system under straining when the energy rate changes. In other words, yielding should describe the inflection of the energy rate between a stable minimum energy state and an unstable maximum energy state. Further explanation on this point will be given later.

Complex Material Systems with Time-Dependent Microstructural Characteristics

First let us look at this theory as an extremum problem. Whether it involves the extremization of a definite integral or just a function, the general concept is to determine the stationary value at a function. The necessary and sufficient condition that a function Φ of n variables shall have a stationary value at a certain point is that the n partial derivatives of Φ with respect to all the n variables shall vanish at that point. However, in analyzing the thermodynamic aspects of materials in their glassy state, a certain nonequilibrium state of the microstructure exists. Aside from temperature and pressure, a set of structural parameters $[z_1, z_2, \ldots, z_n]$ should be used to characterize the nonequilibrium thermodynamic state. At the glassy state, some of the structural parameters are locked in and would not attain their equilibrium value and thus the variation of the free energy with respect to each of the structural parameters which deviates from its equilibrium value would not vanish. Therefore the attention is fixed on the multiple integral in the application of the variational principle in a definite region of multiple space.

Utilizing the method of calculus of variations, the critical strength and damage resistance function of any material system Φ may be obtained through the application of the extremization process. Collectively consider that the specific mean free volume representing the straining characteristics of the material system under load as a function of time and temperature as well as other parameters associated with the material system $z_j (j=1, 2, \ldots, n)$ where these variables can be pictured as coordinates of a point in a space of n dimensions. In motion, this extremum problem involves a definite integral in such a way that the total energy $\mathcal{E}$ of the system is to be made an extremum by suitably determining $\bar{v}$ as a function f of z_j corresponding to points in the boundary of the surface $z_1 z_2 z_3 \ldots z_n$ in the n+1 dimensional space. Mathematically the energy is represented as a surface by the following multiple integral containing an integrand function $\mathcal{F}$:

$$\mathcal{E} = \int \int \ldots \int \mathcal{F}(z_1, z_2, \ldots, z_n, \bar{v}, q_1, q_2, \ldots, q_n)\, dz_1 dz_2 dz_3 \ldots dz_n \,. \qquad (4)$$

where

$$q_1 \equiv \frac{\partial \bar{v}}{\partial z_1}\,,\ q_2 \equiv \frac{\partial \bar{v}}{\partial z_2}\,,\ \ldots,\ q_n \equiv \frac{\partial \bar{v}}{\partial z_n}\,.$$

The integration is over a given surface area in the $z_1 z_2 \ldots z_n$ plane, $\bar{v}$ being given for all values of z_j ($j=0, 1, 2, \ldots, n$) corresponding to points in the boundary of the surface area.

Here the variation of the specific mean free volume $\bar{v}$ is the increment produced in $\bar{v}$ by altering the form of the function f, z_j's being held fast, and is a function of z_j ($j=1, 2, \ldots, n$).

If $\delta q_1 = \frac{\partial}{\partial z_1}\delta\bar{v}, \ldots, \delta q_n = \frac{\partial}{\partial z_n}\delta\bar{v}$, then $\delta q_1, \ldots, \delta q_n$ are the increments produced in $q_1, \ldots, q_n$ respectively. Now let ϵ be a small quantity and

$$\bar{v} = f(z_1, z_2, \ldots, z_n) + \epsilon\,\delta\bar{v}\,. \tag{5}$$

is one of a family of surfaces which is slightly different from the original one:

$$\bar{v} = f(z_1, z_2, \ldots, z_n)\,. \tag{6}$$

Then

$$\mathcal{E}(\epsilon) = \int\int\ldots\int \mathcal{F}(z_1, z_2, \ldots, z_n, \bar{v}+\delta\bar{v}, q_1+\epsilon\,\delta q_1, q_2+\epsilon\,\delta q_2, \ldots, q_n+\epsilon\,\delta q_n) \cdot dz_1 dz_2 \ldots dz_n \tag{7}$$

$$\mathcal{E}'(0) = \int\int\ldots\int \left(\frac{\partial\mathcal{F}}{\partial\bar{v}}\delta\bar{v} + \frac{\partial\mathcal{F}}{\partial q_1}\delta q_1 + \frac{\partial\mathcal{F}}{\partial q_2}\delta q_2 + \ldots + \frac{\partial\mathcal{F}}{\partial q_n}\delta q_n\right) \cdot dz_1 dz_2 \ldots dz_n \tag{8}$$

or

$$\mathcal{E}'(0) = \delta\int\int\ldots\int \mathcal{F}\,dz_1 dz_2 \ldots dz_n = \delta\mathcal{E}\,. \tag{9}$$

The necessary condition is that $\mathcal{E}$ shall be an extremum when $\delta\mathcal{E}=0$.

Now in order to find the form of the surface or the differential equation which renders the integral an extremum,

$$\mathcal{E} = \int\int \cdots \int (1+\sum q_j^2)^{1/2}\, dz_1 dz_2 \ldots dz_n \tag{10}$$

must be taken over the area bounded by the projection of the given curve in the $z_1z_2\ldots z_n$ plane. Then the variation

$$\begin{aligned}\delta\mathcal{E} &= \int\int \cdots \int \frac{\sum q_j \delta q_j}{(1+\sum q_j^2)^{1/2}}\, dz_1 dz_2 \ldots dz_n \\ &= \int\int \cdots \int \frac{\sum q_j \frac{\partial}{\partial z_j} \delta\bar{v}}{(1+\sum q_j^2)^{1/2}}\, dz_1 dz_2 \ldots dz_n\end{aligned} \tag{11}$$

Integration by parts for any z_k ($k=1, 2, \ldots, n$) results in

$$\int \frac{q_k \frac{\partial}{\partial z_k} \delta\bar{v}}{(1+\sum q_j^2)^{1/2}}\, dz_k = \frac{q_k \delta\bar{v}}{(1+\sum q_j^2)^{1/2}} - \int \frac{\partial}{\partial z_k} \frac{q_k}{(1+\sum q_j^2)^{1/2}}\, \delta\bar{v} dz_k \tag{12}$$

In each of the z_k integrations, other z_k's ($k=1, 2, \ldots, n$) are held fast. The limits are the abscissas of the points on the projection of the given boundary which correspond to the value of the z_k in question, and for these points $\delta\bar{v}=0$. Thus the term outside the integral sign vanishes and

$$\int \frac{q_k \frac{\partial}{\partial z_k} \delta\bar{v}}{(1+\sum q_j^2)^{1/2}}\, dz_k = -\int \frac{\partial}{\partial z_k} \frac{q_k}{(1+\sum q_j^2)^{1/2}}\, \delta\bar{v} dz_k\,, \quad (k=1, 2, \ldots, n) \tag{13}$$

Hence

$$\begin{aligned}\delta\mathcal{E} &= -\int\int \cdots \int \sum_{k=1}^{n} \frac{\partial}{\partial z_k} \frac{q_k}{(1+\sum q_j^2)^{1/2}}\, \delta\bar{v}\, dz_1 dz_2 \ldots dz_n \\ &= -\int\int \cdots \int \sum_{k=1}^{n} \frac{(1+\sum q_j^2)\frac{\partial q_k}{\partial z_k} - q_k(\sum q_j \frac{\partial}{\partial z_k} q_j)}{(1+\sum q_j^2)^{3/2}}\, \delta\bar{v}\, dz_1 dz_2 \ldots dz_n\end{aligned} \tag{14}$$

$\delta\mathcal{E}=0$ when and only when

$$\sum_{k=1}^{n} \left[(1+\sum q_j^2)\frac{\partial q_k}{\partial z_k} - q_k\sum q_j \frac{\partial}{\partial z_k} q_j\right] = 0 . \tag{15}$$

This is the differential equation of the required extremum energy which can be put into the following form:

$$\sum_{k=1}^{n} \left[\left(1+\sum\left(\frac{\partial \bar{v}}{\partial z_j}\right)^2\right)\frac{\partial^2 \bar{v}}{\partial z_k^2} - \frac{\partial \bar{v}}{\partial z_k}\sum\frac{\partial \bar{v}}{\partial z_j}\,\frac{\partial^2 \bar{v}}{\partial z_k \partial z_j}\right] = 0 . \tag{16}$$

After this differential equation is solved, the specific mean free volume variation as a function of material parameters $z_j(t)$ will determine the stability, transitional and ultimate damage behavior, i.e.

$$\bar{v}(t) = f(z_j) . \quad (j=1, 2, \ldots, n) \tag{17}$$

Equation (16) may have many solutions. The individual possible solutions when they are minima will indicate the stable situation of the material system, while the maxima will correspond to the unstable damage condition such as crazing or fracturing when their corresponding energy values are overcome. That is, for any time-dependent material system in motion, the new unified strength and damage criterion at any spatial position x may be specified and expressed as follows:

$$\mathcal{E}\ (x, \bar{v}, z_1, \ldots, z_n) \geq \mathcal{E}_c\ (x, \bar{v}_d, z_1, \ldots, z_n) \tag{18}$$

where $\mathcal{E}_c$ is the critical energy for stability or damage initiation corresponding to specific mean free volume $\bar{v}_d$ which makes the energy integral an extremum.

This work is being extended. A paper will be prepared in the future.

2. "Significance of Critical Energy Theory for Damage of Anisotropic Solids and Composite Systems"

Using an energy approach, a general unified strength theory and damage criterion is developed in terms of a microscopic specific mean free volume concept. The general time and temperature dependent formulation is reducible to most individual existing specific strength theories and damage criteria for linear elastic material systems as special cases. Damages including the initiation of yielding, crazing, fracture and fatigue as well as propagation of cracks are a result of overcoming complex energy quantities in terms of a measure of the specific mean free volume. Associated with an eigenvalue of the specific mean free volume there exists an eigenfunction of energy which governs the stability, transition and instability of the material system. In this paper the significance of the strength and damage is interpreted and analyzed. The various possibilities of utilizing the fundamental concept and formulations are discussed.

Based upon mesomechanics considerations [1–16] the damage mechanisms of solid systems under stress may be associated primarily with both shear deformation and volume variation, as a result of molecular slippage and orientation, microcavitation and microfracture. From the microstructural viewpoint, stressing may be visualized as a source of energy input into a system which develops localized unstable processes. As a result, the compatibility conditions for a continuum analysis breaks down. Transitions from homogeneous equilibrium to non-equilibrium states involve nonlinear, kinetic deformational analyses.

References

1. C.C. Hsiao, A new general unified strength theory and damage criterion for anisotropic solids and composite systems, to be published.
2. S.S. Chern and C.C. Hsiao, A generalized time-dependent theory on craze initiation in viscoelastic media, *J. Appl. Phys.* 57, 1823 (1985).
3. C.C. Hsiao, Kinetic strength of solids Advances in Fracture Research, Proc. 7th Int'nat'l Conf. on Fracture (ICF7), Houston, Texas, March 20–24, 1989, pg. 2913.

4. O.M. Ettorney and C.C. Hsiao, Time-dependent fracture strength of solid bodies, *J. Appl. Phys.* **64**, 4884 (1988).

5. A.S. Krausz and H. Eyring, *Deformation Kinetics*, Wiley-Interscience, New York (1975).

6. V.S. Kuksenko and V.P. Tamuzs, *Fracture Micromechanics of Polymer Materials*, Martinus Nijhoff Publishers, The Hague (1981).

7. C.C. Hsiao, Theory of mechanical breakdown and molecular orientation of a model linear high-polymer solid, *J. Appl. Phys.* **30**, 1492 (1959).

8. C.C. Hsiao, Time-dependent tensile strength of solids, *Nature* **186**, 535 (1960).

9. C.C. Hsiao, Fracture, *Physics Today* **19**, 49 (1966).

10. M.S. Mun and C.C. Hsiao, Time-dependent fracture strength of oriented polymers, *J. Appl. Phys.* **60**, 2655 (1986).

11. C.B. Henderson, P.H. Graham and C.N. Robinson, A comparison of reaction rate models for the fracture of solids, *Int. J. Fracture Mech.* **6**, 33 (1970).

12. C.C. Hsiao, Non-continuum craze-crack transition in *Damage Mechanics in Composites—AD*—Vol. 12 (ed. A.S.D. Wang and G.K. Haritos) (Book No. G00376) Am. Soc. of Mech. Engs. **25** (1987).

13. S.N. Zhurkov, Kinetic concept of the strength of solids, *Int. J. Frac. Mech.* **1**, 311 (1965).

14. C.C. Hsiao, Flow orientation and fracture strength of a model linear hard polymer solid, *J. Polymer Sci.* **XLIV**, 71 (1960).

15. C.C. Hsiao and T.S. Wu, Orientation and strength of branched polymer systems, *J. Polymer Sci. A.* **1**, 1789 (1963).

16. A.S. Krausz, The theory of non-steady state fracture propagation rate, *Int. J. of Fracture* **12**, 239 (1976).

3. "Mechanical Strength and Damage of Polymers and Composites"

Introduction

The macroscopic properties of polymers and their composites are determined to a large extent by the molecular structure of the constituent chains. Up to now, however, the explorations of material properties are mainly qualitatively descriptive rather than quantitatively predictive.

The statistical mechanical theory of amorphous molecular system in bulk polymer provides methods to deal with the random molecular system. With the advent of modern computers, it is possible to apply the principles of statistical mechanics to real life systems. Computer simulation has provided some needed insight on the properties of polypropylene.

Preliminary work has been started and continued which attempts the step from chemical structure to the damage and mechanical strength of amorphous polymeric glasses and their composites.

Briefly, the objectives of this project are:

1. To develop a quantitative computer model of molecular structure for an amorphous polystyrene below its glass transition temperature. It provides detailed information on the conformation and relative arrangement of chains in the bulk.
2. To simulate a mechanical deformation of the model mentioned above. Damage point will be predicted by studying the breakage of molecular chains.
3. To develop a quantitative computer model of molecular structure in a unidirectional fiber-reinforced amorphous polymer composite.
4. To determine some elastic constants of the composite material by simulating a small-strain mechanical deformation which is perpendicular to the fiber direction on the model for the composite system.

Background information

From the microscopic viewpoint, amorphous polymers and their composites are inhomogeneous materials. Although bonding lengths and bonded angles in the molecular structure can be consider to be rather rigid, the molecular configurations are random because of the rotational possibilities around the bonds.

Flory has introduced a statistic theory to consider the amorphous polymer system. The basic idea is to replace the random system by a crystalline system so that once a model molecule is available, the whole molecular system can be set up. To reasonably represent the actual molecular system, the model molecule having the average information of an amorphous system must be considered.

The basic approximation of Flory's molecular configuration theory is [1, 2]: each molecule, or bond, is treated as appearing in one or another of discrete rotational states. These states ordinarily are chosen to coincide with potential minima. Fluctuations about the minima are ignored. This is the so-called rotational isomeric state (RIS) approximation.

The probability of each discrete rotational state is determined by the potential energy of that state. by considering the atomic interactions in a molecular structure, one can calculate the values of the potential minima. Then the statistical weight of the minima can be obtained. Using the Monte Carlo method, the configuration of model molecular structure can be generated. The sequence of states of the model chain is an equivalent Markov chain. If the model chain is sufficiently long, it can represent the average information of the amorphous system.

Using Flory's theory and Suter and Flory's work on potential energy analysis of polypropylene, Theodorou and Suter [3, 4] have constructed a model for a polypropylene molecule. By introducing a small deformation to the model system, the change of the molecular structure and corresponding bonding force across a specific surface may be calculated. Subsequently the elastic coefficients can be accurately determined.

Research already developed

We consider atactic polystyrene and atactic epoxy composites at room temperature (21° C). Atacticity of the polymers makes their molecular structure completely amorphous. At room temperature polystyrene and epoxy are glassy polymers.

Our molecular model rests on the following assumptions: a) the model does not incorporate thermal motion, i.e. it is static; b) bond lengths and bond angles are kept fixed. Molecular rearrangement can occur exclusively through relation around skeletal bonds; c) we concentrate on the purely elastic response to deformation.

It is verified that these assumptions are reasonable.

For the atactic polystyrene molecular system, Rotational Isomeric State Theory can be directly used in generating molecular conformation. A two-state RIS model, developed by Yoon, Sundararajan and Flory [5], will be used for this new program.

For the atactic epoxy, a program, CHEM-X, which is designed to calculate minimum potential energy states for small molecules, is ready to calculate the isomeric rotational states for the molecular system [6].

For the fiber-reinforced epoxy composite, it is more difficult to use RIS theory because interaction between fibers and polymer matrix is introduced in the system. The molecular model has to cover this kind of interaction. Probabilities of the minimum potential energy states for molecular conformation must be obtained. The quasi-Newton matrix-updating algorithm of Broyden, Fletcher, Goldfarb and Shanno [7] will also be used for relaxing the molecular system.

To date the program of determining the elastic coefficients for polystyrene has already been half done. A program dealing with composites is being prepared.

References

1. P. J. Flory, Statistical Mechanics of Chain Molecules, Interscience, New York (1969)
2. P. J. Flory, Foundations of rotational isomeric state theory and general methods for generating configurational averages, *Macromolecules* 7, 381 (1974)
3. D. N. Theodorou and U. W. Suter, Detailed molecular structure of a vinyl polymer glass, *Macromolecules* 18, 1467 (1985)
4. D. N. Theodorou and U. W. Suter, Atomistic modeling of mechanical properties of polymeric glasses, *Macromolecules* 19, 139 (1986)
5. D. Y. Yoon, P. R. Sundararajan and P. J. Flory, Conformational characteristics of polystyrene, *Macromolecules* 8, 6 (1975)
6. S. S. Pang, Z. D. Zhang, S. S. Chern and C. C. Hsiao, Energy absorption in polymer crazing, *J. Polym. Sci.* 23, 683 (1985)
7. J. E. Dennis, Jr. and J. J. More, Quasi-Newton method, motivation and theory, *SIAM Review* 19 (1977)

4. "Computer Model for Amorphous Polystyrene"

Introduction

In polymer science, physical properties of materials and their relationship with spatioconfigurations and conformations have been subjects of intensive study.

Flory established a statistical treatment for macromolecules [1, 2]. By using Flory's rotational isomeric state (RIS) theory, detailed computer simulations for linear polymer chains (e.g. vinyl polymers) are possible due to the simplicity of its simple spatial configurations.

Theodorou [3] utilized RIS theory and generated a computer model which successfully predicted the properties of polypropylene under small elastic deformations ($|\varepsilon|<<1\%$), where ε is the simple strain.

It is possible to study more complicated behavior (such as defects inside the materials, crazing, microcrack initiation, etc.) by detailed computer simulations on the atomic level.

Theoretical considerations

Polystyrene is an ideal material for computer simulations because of its brittle behavior at room temperature and the readiness of crazing under relatively small deformations.

From thermodynamic and statistical mechanics analyses, under the temperatures below glass transition temperature (T<Tg-20C°), the entropic contributions and vibrational contributions to the internal energy can be neglected. Thus the molecular potential energy will be the dominant factor which characterizes the internal energy of polymer chains.

Computer generation of model polystyrene

Molecular dynamics (MD) and Monte Carlo (MC) methods are two effective means of computer simulations. Two methods have their own advantages and disadvantages [4, 5].

Molecular Dynamic simulation can only cover for an exceedingly short time span due to the limited calculating capacity of computers. In contrast, the Monte Carlo method can be used in a step by step manner with well relaxation procedures in each step. MC method showed its successful usage in the study of plastic deformation in a model amorphous metal.

Statistical weight matrices of amorphous polystyrene

The two rotational stages are assigned [8] to be at $\phi_t=10°$ and $\phi_g=110°$.

The principal conformations can be represented by two statistical weight matrices of 2×2 order.

The statistical weight matrices for the pair of bonds may be expressed as

$$U''_m = \begin{pmatrix} \omega'' & 1/\eta \\ 1/\eta & \omega/\eta^2 \end{pmatrix} \qquad \text{(for meso dyad)}$$

The complementary matrix U' for the pair of bonds flanking the substituent carbon C^{α} may be represented by

$$U' = \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}$$

The expectation of meso-dyads for conventional atactic polystyrene is given by

$$0.3 \le \omega_m \le 0.5$$

A priori probability and conditional probability

In Flory's RIS theory, each molecule, or bond, is treated as occuring in one another of several discrete rotational states [2].

The *a priori* probability for bond i in states is

$$p_{\eta;i} = Z^{-1} J \left[\prod_{h=2}^{i-1} U_h \right] U'_{\eta;i} \left[\prod_{j=i+1}^{n-1} U_j \right] J^{*T}$$

where Z is the rotational partition function of the chains and defined as

$$\begin{aligned} Z &= \int \exp\left[-\beta U^{pot}(\phi)\right] d\phi \\ &\approx J U_1 \left(\prod_{k=2}^{x-2} U_k \right) U_{x-1} J^{*T} \end{aligned}$$

and

$$J = [1\ 0],$$

$$J^* = [1\ 1]\,.$$

The statistical matrix U_k is defined as

$$U_k = U'U''_k \qquad (2 \leq k \leq x-2)$$

with

$$U''_k = U''_m \qquad \text{(if dyad is meso)}$$

$$U''_k = U''_r \qquad \text{(if dyad is racemic)}$$

and

$$U_1 = U'\mathrm{diag}(1,\eta)U''$$

$$U_{x-1} = U'U''\mathrm{diag}(1,\eta)$$

where U'' is either U''_m or U''_r, because

$$U'\mathrm{diag}(1,\eta)U''_m = U'\mathrm{diag}(1,\eta)U''_r$$

and

$$U'U''_m\mathrm{diag}(1,\eta) = U'U''_r\mathrm{diag}(1,\eta)\,.$$

The *a priori* probability for bond 2 to be in state ξ is

$$p_{\xi:2} = Z^{-1}JU_0U'_\xi\mathrm{diag}(1,\eta)U''_1\left[\prod_{k=2}^{x-2} U_k\right]U_{x-1}\,J^{*T}$$

where U'_ξ symbolizes the matrix obtained from U' by replacing all of its elements by 0, except those of column ξ.

The *a priori* probabilities $P_{\xi\xi;t}$ that bond i-1 will be in state ζ and bond i in state ξ are given as follows:

For bond 3,

$$p_{\zeta\xi 3} = Z^{-1}U'\mathrm{diag}(1,\eta)U''_{\xi\xi:1}\left[\prod_{k=2}^{x-2} U_k\right]U_{x-1}\, J^{*T}$$

For bond i ($4 \leq i \leq 2x-1$)

$$p_{\xi\xi;2h} = Z^{-1}JU_1\left[\prod_{k=2}^{h-1} U_k\right]U'_{\zeta\xi}\, U''_h\left[\prod_{k=h+1}^{x-2} U_k\right]U_{x-1}J^{*T}$$

$$p_{\zeta\xi;2h+1} = Z^{-1}JU_1\left[\prod_{k=2}^{h-1} U_k\right]U'\, U''_{\zeta\xi;h}\left[\prod_{k=h+1}^{x-2} U_k\right]U_{x-1}J^{*T}$$

$$p_{\zeta\xi;2x-2} = Z^{-1}JU_1\left[\prod_{k=2}^{x-1} U_k\right]U'U''_{\zeta\xi;x-1}\,\mathrm{diag}(1,\eta)J^{*T}$$

$$p_{\zeta\xi;2x-1} = Z^{-1}JU_1\left[\prod_{k=2}^{h-1} U_k\right]U'U''_{\zeta\xi;x-1}\,\mathrm{diag}(1,\eta)J^{*T}$$

where $U'_{\zeta\xi}$ is a matrix obtained from U' by replacing all of its elements by 0, except the one lying at row ζ and column ξ. $U''_{\zeta\xi;k}$ is obtained from U''_k the same way.

The conditional probability q for bond i in state ξ, given that the bond i–1 in state ζ ($\leq i \leq 2x-1$), is

$$q_{\zeta\xi;i} = \frac{p_{\zeta\xi;i}}{p_{\zeta;i-1}} = \frac{p_{\zeta\xi;i}}{\sum\limits_{\varepsilon} p_{\varepsilon\zeta;i-1}}$$

The conditional probability rests on the assumption that the interdependence of the bond rotation does not extend beyond first neighbors.

In Theodorou's treatment for polypropylene, the conditional probability is modified to take into account long range interactions which gives a more realistic model. The rotational isomeric state conditional probability is then modified as [3],

$$q'_{\zeta\xi;i} = q_{\zeta\xi;i} \frac{\exp\left[-\frac{\Delta U^{LR}_{\xi;i}}{RT}\right]}{\sum\limits_{\xi'} q_{\zeta\xi'} \exp\left[-\frac{\Delta U^{LR}_{\xi;i}}{RT}\right]}$$

where $\Delta U^{LR}_{\xi;i}$ is the increase in long-range interaction energy upon addition of the skeletal carbon i+1 and the substituent of carbon i, if bond i is assigned the rotational state ξ.

Intermolecular forces and potential energy

1) Non-bounded potential energy

It is found that the short-range repulsion forces between two atoms (or two molecules) are proportional to $1/r^6$. The non-bonded potential energy is usually approximated by [10]

$$V(r) = -A/r^6 + B/r^n \qquad (n > 6)$$

This is known as Mie(n,6) model.

The Lenard-Jones potential is given where n is equal to 12,

$$V_{ij} = \left(\frac{a_{ij}}{r_{ij}^{12}}\right) - \left(\frac{c_{ij}}{r_{ij}^{6}}\right)$$

or

$$V_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

where c_{ij} is the London dispersion parameter following the Slater-Kirkwood formula [10] by which the London dispersion energy E_L [11, 12] for unlike molecules or atoms is calculated by

$$E_L = -\frac{3e/h}{2m_e^{1/2}} \frac{\alpha_A \alpha_B}{(\alpha_A/n_A)^{1/2}+(\alpha_B/n_B)^{1/2}} \frac{1}{r^6}$$

i,e

$$c_{ij} = -\frac{3e/h}{2m_e^{1/2}} \frac{\alpha_i \alpha_j}{(\alpha_i/n_i)^{1/2}+(\alpha_j/n_j)^{1/2}} \frac{1}{r^6}$$

where α is polarizability, n the effective number of electrons, and r the distance between interacting atoms.

The constants a_{ij} are assigned to minimize the potential V(r) and

$$a_{ij} = \frac{1}{2} c_{ij} r_{ij}^6$$

Parameter σ_{ij} is the separation of the particles where V(r)=0 and ε_{ij} is the depth of the potential well at the minimum in V(r),

$$\varepsilon_{ij} = \frac{1}{2} \frac{1}{r_{ij}^6} c_{ij},$$

$$\sigma_{ij} = \frac{1}{2^{1/6}} r_{ij}.$$

2) Bonded potential energy

The bonded potential energy is calculated as an intrinsic three fold potential having a barrier of k_ϕ=2.8 kcal mol^{-1} for each skeletal C-C bond [2].

$$V_\phi(\Phi) = \frac{k_\phi}{2} (1-\cos 3\Phi)$$

where ϕ is the bond torsional angle.

Parameters used in energy calculations for polystyrene are listed as follows [7, 8],

Atom	$r^o(Å)$	$\alpha_i(Å^3)$	n_i
C	1.8	0.93	5
H	1.3	0.42	0.9
C^{ar}	1.95	1.23	5

Phenyl group

The distinguishing feature of the phenyl group is that it has a plane of symmetry. The phenyl substituent is confined to the orientations such that its plane is approximately perpendicular to the plane defined by the skeletal bonds flanking the c^{α} to which it is attached. The more detailed analysis justified the mean value of rotation angle of the phenyl group , X, is at 0°.

In our model, we treat the phenyl group as 11 single atoms following Flory's treatment in calculation of conformational energy of polystyrene [8]. The exact calculation avoids the inaccuracy of being an approximation of the phenyl group in the expense of the increment of calculating time and the relatively smaller model.

In future developments, a good approximation of the phenyl group by a relatively much simpler atom-unit(s) is needed in order to decease the computing time such that the model can be reasonably large so that the accuracy of simulation of large deformation, where the model size is also a critical factor [4], can be improved.

Size of cubic model

The cubic model is filled with one single parent chain according to the experimental density of the material.

For polystyrene, the cubic size and the polymerization x of the parent chain has the following volume relationship

$$V = \mathbf{a} \bullet (\mathbf{b} \times \mathbf{c})$$
$$= \frac{1}{\rho N_A} [(2x+1)M_C + (8x+4)M_H]$$

where **a**, **b**, and **c** are edge vectors giving the volume V. ρ is the density of the polymeric system. N_A denotes the Avogadro number, and M_C and M_H are respectively the atomic weight of carbon and hydrogen.

According to the minimum image convention [13] which allows each atom in the center cube to interact at most with one image of another atom either in the center cube or within its 26 neighboring cubes.

The edge of each cube a is decided as

$$a \geq 2r$$

where r is the effective range of L-J potential.

Based on the calculating time and the restriction on the size of the model, the polymerization x can be chosen. The cubic size is usually of the order of 10 Å.

Further development

Theodorou [3] showed that the computer model based on Flory's RIS theory can be used to predict properties in small elastic deformations. Since the repeating methods of *deform-relaxation* was successfully applied to the amorphous metals dealing with plastic deformation [6], it is possible to use this procedure to study the large deformation, the phenomenon of crazing and the formation of microcrack which are two characteristics of brittle polymer materials.

The local structure defects along with atomic level stresses and strains need to be studied.

1. *Atomic stresses (Atomic-level stresses)*

The concept of atomic stresses or the atomic-level stresses were first introduced by K. Huang [14] in his paper dealing with atomic elastic theory of crystalline solids, and was stated by Born and Huang [15].

For a central force model, the atomic interaction is described by a central force potential $\Phi(r_{ij})$, where r_{ij} is the separation of atom i and j.

The $\alpha\beta$ components of the stress tensor of atom i is given,

$$\sigma_{\alpha\beta}(i) = \frac{1}{2\Omega_i} \sum_{\substack{j \\ (j\neq i)}} \frac{\partial \Phi(r_{ij})}{\partial r_{ij}} \frac{r_{ij}^{\alpha} r_{ij}^{\beta}}{r_{ij}}$$

where r_{ij}^{k} is the k^{th} component of vector **r**.

The atomic elastic modulus tensor of the i^{th} atom is defined as

$$C^{\alpha\beta\gamma\xi} = \frac{1}{2\Omega_i} \sum_{\substack{j \\ (j\neq i)}} \left[\frac{1}{r_{ij}} \frac{\partial \Phi}{\partial r}\Big|_{r=r_{ij}} \delta_{\alpha\gamma} + \frac{r_{ij}^{\alpha} r_{ij}^{\gamma}}{r_{ij}^{2}} \left(\frac{\partial^2 \phi}{\partial r^2} - \frac{1}{r} \frac{\partial \Phi}{\partial r} \right)_{r=r_{ij}} \right] r_{ij}^{\beta} r_{ij}^{\xi}$$

where Ω_i in equation () and () is the atom volume such that the total cell volume, V_{cell}, is calculated by the following equation.

$$V_{cell} = \sum_{atoms} \Omega_i$$

Atomic stresses are the quantities which can be used to characterize the deformation, defects and potential energy of the model studied.

2. Structure Defects in Amorphous Materials

The concept of structural defects such as point defects and line dislocation were introduced in the study of crystalline materials.

In the last ten years, structural defects in the amorphous material have been studied [16, 17].

In the study of structure defects of amorphous solids [16], the structural defects are defined as the regions of high stress and low symmetry. By comparing the stresses and symmetry-coeffient distributions of those in the cores of dislocations in crystals, the region consisting of compressive and tensile parts is then defined as a dislocation-like structural defect. A collection of split vacancies which determine a region of lower density under tension is a vacancy-like defect while an interstitial-like defect is a crowded region under compression.

Large concentrations of defects may aggregate and form precipitates (and will form extra lattice plane in crystals). One of the possible results of such motions and aggregations of defects is the formation of the micro-surface which is a critical condition of crazing and the formations of microcracks.

References

1. P. J. Flory , Foundations of the rotational isomeric state theory and general methods for generating configurational averages, *Macromolecules* 7 (1974)
2. P. J. Flory, Statistical Mechanics of Chain Molecules, John Wiley-Interscience, New York (1969)
3. D. N. Theodorou, Molecular Modeling of polymer glasses, Ph.D thesis, Massachusetts Institute of Technology (1985)

4. M. Bishop, D. Ceperley, H. L.Frisch, and M. H.Kloos, Supercomputers in chemistry, ed. P. L. Lykos, I.Shauitt (1980)

5. W. G. Hoover; G. De Lorenzi, B. Moran, J. A. Moriarty and A. J. G. Ladd, Computer-Based Microscopic Description of the Structure and Properties of Materials, ed.J. Broughton; W. Krakow; S. T.Paulelides (1986)

6. K. Maeda and S.Takeuchi, Atomistic process of plastic deformation in a model amorphous metal, *Phi. Mag. A* **44** (1981)

7. U. W. Suter and P. J. Flory, Conformational energy and configurational statistics of polypropylene, *Macromolecules* 7, 765–776 (1975)

8. D. Y. Yoon, P. R. Sundasdrojan, and P. J. Flory, Conformational characteristics of polystyrene, *Macromolecules* **8**, 776 (1975)

9. D. W. Calvin and T. M. Reed III, Mixture Rules for the Mie(n,b) intermolecular pair potential and the Dymond-Alder pair potential, 5. *Chem.phys.* **54**, 3, 3733 (1971)

10. A. Abe, R. L. Jermgan, and P. J. Flory. *J. Am. Chem. Soc.* **88**, 631 (1966)

11. A.Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, John Wiley & Sons (1968)

12. K. S. Pitzer, *Adv. Chem. Phys.* **2**, 59 (1959)

13. D. N. Theodorou and U.W.Suter, Geometrical considerations in model systems with periodic boundaries, *J. Chem. Phys.* **82** (1985)

14. K. Huang, On the atomic theory of elasticity, *Proc. Roy. Soc.* A, 203, (1950)

15. M. Born and K. Huang, Dynamical theory of crystal lattices, Oxford: Clarendon Press, (1954)

16. T.Egami, K. Maeda and V. Vitek, Structural defects in amorphous solids, a computer simulation study, *Phi.Mag A*, **41** (1980)

17. D. Srolovitz, K. Maeda, V. Vitek and T. Egami, Structural defects in amorphous solids, statistical analysis of a computer model, *Phi. Mag. A.* **44** (1981)

Supplement to the Final Technical Report

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CRAZING IN POLYMERIC AND COMPOSITE SYSTEMS

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19 ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The technical report on crazing in polymeric and composite systems encompasses several phases of mesomechanics studies which lead into continuum and non-continuum microdamage mechanics investigations. Based upon the first principles of physics and mechanics and the sciences of the microstructure of materials, this new interdisciplinary research has been quite challenging and very fruitful. As a result new ideas have been introduced in developing new theories and breakthroughs have occurred on several fronts in time dependent deformation, strength theories and damage criteria for solids and composite systems.

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Research Objective

The overall research objectives of this program are to analyze and to obtain a better understanding of the role of crazing in polymeric and composite systems. Following a basic and fundamental consideration of microstructure and its connection with the mechanics of the material system, these interdisciplinary mesomechanics studies are to develop time-dependent mathematical models of crazing as global damage for polymeric solids and composite systems.

Research Summary

The approach used in this program emphasized the study of the damage problem of polymer and composite materials. The strength and fracture behavior of stressed systems has been closely associated with microstructural information. The initiation of crazing, the transition of a craze to crack has been analyzed for a viscoelastic system with time-dependent characteristics. A viscoelastic boundary element method has been employed to analyze the opening displacement and the envelope stress of a crack-induced craze. This quasifracture problem has been successfully studied to give good results comparable with theoretical micromechanics predictions.

The effect of time on breaking stress was also investigated. It was found that Hsiao's statistical absolute reaction rate nonlinear model considerations were more successful for interpreting many general observations.

This statistical model has also been used to study the temperature influence on polymer fracture. The mathematical expression was satisfactorily examined to account for temperature variations at fracture. As a result, a new generalized fracture theory and damage criterion has been initiated and an initial attempt to formulate a general damage theory for simple solids and composites was very encouraging. It appears that this multiphase approach has rapidly achieved the initial goals. The results obtained this far have given very fruitful understanding of the subject matter and the research findings have converged toward a truly mesomechanical investigation of the damage mechanics of composites. Since the research effort has involved many phases of interdisciplinary studies, the available time did not permit the studies to be brought to a conclusion.

Individually published materials showing results are attached herewith. Research papers presented as invited lectures and speeches are listed. Unfinished phases of research are also given as references for possible future continuations of research in this field.

Reprints of published papers (please see Appendix):

IV.1* "NONCONTINUUM CRAZE-CRACK TRANSITION," C.C. Hsiao. American Society of Mechanical Engineers AD-Vol. **12**, *Damage Mechanics in Composites* 25–37 (1987)

V.1 "ANALYSIS OF CRACK-INDUCED-CRAZE IN POLYMERS," B.N. Sun, H.S. Hou, and C.C. Hsiao. *Engineering Fracture Mechanics* **30**(5), 595–607 (1988)

V.2 "ANALYZING POLYMER CRAZING AS QUASIFRACTURE," B.N. Sun and C.C. Hsiao. *Journal of Polymer Science B: Polymer Physics* **26**, 967–979 (1988)

V.3 "TIME-DEPENDENT FRACTURE STRENGTH OF SOLID BODIES," O.M. Ettouney and C.C. Hsiao, *Journal of Applied Physics* **64**(10, pt.1), 4884–4888 (1988)

V.4 "TEMPERATURE VARIATION DURING POLYMER FAILURE," C.C. Hsiao and Y.S. Cheng, *Europhysics Conference Abstracts*, 20th Europhysics Conference on Macromolecular Physics and 3rd Lausanne Polymer Meeting on Physical Mechanisms in Polymer Failure, Lausanne, Switzerland, Vol. **12J** (1988)

V.5 "A NEW GENERALIZED DAMAGE CRITERION FOR POLYMERS," C.C. Hsiao, *Europhysics Conference Abstracts*, 20th Europhysics Conference on Macromolecular Physics and 3rd Lausanne Polymer Meeting on Physical Mechanisms in Polymer Failure, Lausanne, Switzerland, Vol. **12J** (1988)

VI.1 "A NEW DAMAGE CRITERION FOR COMPOSITES," C.C. Hsiao, Y.S. Cheng, S.J. You and Y.H. Yuan, *Proceedings*, 7th International Conference on Composite materials (ICCM VII). International Publishers and Pergamon Press 3, 340 (1989)

VI.2 "KINETIC STRENGTH OF SOLIDS," C.C. Hsiao. *Advances in Fracture Research.* Proceedings, 7th International Conference on Fracture (ICF 7), 2913–2919 (1989)

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Invited lectures and spoken papers:

"UV-IRRADIATED POLYMERS," High Polymer Physics Meeting, American Physical Societ·· New York, March 1987

"MODELING QUASIFRACTURE BEHAVIOR IN VISCOELASTIC MEDIA," International Conference on Fracture and Fracture Mechanics, Shanghai, April 1987

"CRAZING AND MESOMECHANICS," Beijing Materials Research Institute, Peking, May 1987

"COMPOSITES AND MESOMECHANICS," Lanzhou Railway Institute, Lanzhou, P.R. China, May 1987

"LASER AND CRAZING OF POLYMERS," Zhong Shan University, Guangzhou, P.R. China, May 1987

"NONCONTINUUM CRAZE-CRACK TRANSITION," The Winter Annual Meeting of the American Society of Mechanical Engineers, Boston, December 1987

"STRENGTH AND DAMAGE OF POLYMERS," High Polymer Physics Meeting, American Physical Society, March 1988

"DAMAGE MECHANICS," University of Hong Kong, Hong Kong, December 1988

"GENERAL DAMAGE CRITERIA FOR SOLIDS," International Conference on Fracture, Houston, March 1989

"KINETIC STRENGTH OF SOLIDS," International Conference on Fracture, Houston, March 1989

"UNIFIED STRENGTH THEORY FOR ANISOTROPIC SOLIDS AND COMPOSITES," University of Sydney, New South Wales, Australia, August 1989

"KINETIC STRENGTH OF SOLID BODIES," University of New South Wales, New South Wales, Australia, August 1989

"STRENGTH AND DAMAGE OF SOLIDS," University of Newcastle, Newcastle, Australia, August 1989

"TIME-DEPENDENT FRACTURE STRENGTH OF SOLIDS," University of Melbourne, Melbourne, Australia, August 1989

"CRAZING AND DAMAGE OF POLYMERS," Polymer and Composites Group, Victoria, Australia, August 1989

"MICROSTRUCTURE AND MECHANICAL BEHAVIOR OF POLYMERIC SYSTEMS," Aeronautical Research Laboratories, Melbourne, Australia, August 1989

"CRAZING AND MESOMECHANICS OF POLYMERS," University of Auckland, Auckland, New Zealand, August 1989

"VISCOELASTIC BEHAVIOR OF POLYMERIC SYSTEMS," University of Canterbury, Christchurch, New Zealand, August 1989

General content of some of the invited lectures and spoken papers:

"A NEW UNIFIED STRENGTH THEORY FOR ANISOTROPIC SOLIDS AND COMPOSITES": Using an energy approach, a new unified strength theory is developed. The general time and temperature dependent formulation is reducible to almost every existing theory put forward during the past centuries for linear elastic material systems as individual special cases. It is found that the initiation of yielding, the nucleation of crazing, the inception of fatigue cracking, and the propagation of fracture under stress are a result of overcoming the distortional and/or dilatational energy.

"KINETIC STRENGTH OF SOLID BODIES": The kinetic strength of solid bodies has been studied theoretically. Using the statistical absolute reaction rate theory, the nonlinear time-dependent fracture strength can be satisfactorily analyzed. Results thus obtained fit very well with the experimentally determined empirical linear relationship of the logarithm of time-to-break and the fracture strength.

"NONCONTINUUM CRAZE-CRACK TRANSITION": An approach in studying the damage problem of solids and composite material systems is reviewed. It appears highly desirable to investigate the strength and failure behavior of stressed systems by connecting the macro- and micro-mechanics analyses with microstructure of the material body. Starting from the nucleation of craze, the process of transition to a mature crack in an infinite viscoelastic medium under stress is described physically and analytically. Emphasis is placed on the nature of its time dependency. The propagation of both the external and internal craze and crack is analyzed theoretically under a simple state of tension.

"A GENERAL DAMAGE CRITERION FOR SOLID BODIES": A general damage criterion dealing with yielding, crazing and fracturing of solids is introduced. Using a unique free volume concept, damages under both quasi-static and dynamic loading conditions can be analyzed by considering distortional and dilatational variations of the media.

Unfinished research (Please refer to the original Report):

VI.3. "Analyses of Three-Dimensional Crazing in Polymers"

VI.4. "Crazing as Damaging Behavior of Irradiated Polymers"

VI.5. "Propagation of Crack-Induced-Crazing in Unidirectional Composites"

VII.1. "A New General Unified Strength Theory and Damage Criterion for Anisotropic Solids and Composite Systems"

VII.2. "Significance of Critical Energy Theory for Damage of Anisotropic Solids and Composite Systems"

VII.3. "Mechanical Strength and Damage of Polymers and Composites"

VII.4. "Computer Model for Amorphous Polystyrene"

List of Professional Personnel Involved in the Program:

C.C. Hsiao	Principal Investigator
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H.S. Hou	Graduate Research Assistant
O.M. Ettouney	Graduate Student
Y.S. Cheng	Research Fellow
S.J. You	Graduate Research Assistant
Y.H. Yuan	Graduate Research Assistant
M.A. Morales	Graduate Student
R.J. Lippert	Graduate Student

IV. 1.

NON-CONTINUUM CRAZE-CRACK TRANSITION

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ABSTRACT

An approach studying the damage problem of polymeric and composite material systems is reviewed. It appears highly desirable to investigate the strength and fracture behavior of stressed solid systems by combining microstructural information with macro- mechanical analysis.

Starting from the initiation of crazes, the process of transition of a craze to crack in an infinite viscoelastic medium under stress is described. The actual physical change of a craze into a crack is considered. Emphasis is placed on the nature of its time dependency. The enlargement of both craze and crack is analyzed under a simple state of tension. Suggestions on future research upon temperature influence on crazing and craze-crack interactions are also given.

NOMENCLATURE

A,B	material constants
a_n	integer constants ($-\infty < n < \infty$)
a(t)	time-dependent length to high stress level σ_2
b(t)	time-dependent crack length measured from center of symmetry
c(t)	time-dependent craze-crack length measured from center of symmetry
$C_b(t)$	time-dependent material creep compliance function
$\dot{D}_f(t)$	rate of energy dissipation of craze fibril domains
d(x,t)	time- and position-dependent diameter of craze fibril domains
d_1	average diameter of fibril domain under craze envelope stress σ_1
d_2	average diameter of fibril domain under craze envelope stress σ_2
E(t)	relaxation modulus
e_{ij}	deviatoric strains
f	fraction of integrity of microstructural system
$G_1(t-\tau)$	time-dependent deviatoric relaxation modulus
$G_2(t-\tau)$	time-dependent dilatational relaxation modulus
$\dot{H}_c(t)$	rate of energy absorption of quadrantal craze
I_1, I_2	constants
$J_2(\xi-\eta)$	time dependent bulk creep compliance function
K_1, K_2, K_3, K_4	differential or integral functions
$K_b = \omega_b \exp[-U/RT + \beta\psi(t)]$	rate coefficient of broakage
$K_r = \omega_r \exp[-U/RT - \gamma\psi(t)]$	rate coefficient of reformation
$\dot{K}_f(t)$	rate of kinetic energy of craze fibril domains
n	integers
n_i, n_j	unit vectors (i, j = 1, 2 or 3)
P(t)	time-dependent load

dP	infinitesimal elemental vector in reference frame X_K (K = 1, 2 or 3)
dp	infinitesimal elemental vector in current frame x_k (k = 1, 2 or 3)
q	craze-crack system depth measured from center of symmetry
R	universal gas constant
S	magnitude of deviatoric stress tensor
S	deviatoric stress tensor
s	Laplace parameter
S_{ij}	deviatoric stresses
$\dot{S}(t)$	rate of creation of craze fibril domain surface
T	absolute temperature
t	real time
t_a	time when a(t) reaches position x
t_b	time-to-break
t_c	craze initiation time
t_f	craze-crack transition time
t_h	time when b(t) reaches position x
t_n	nucleus incubation time
t_x	time for tip of craze-crack system to reach position x
t_2	period of time fibril domains subjected to stress σ_2
U	activation energy
$\dot{U}_f(t)$	rate of strain energy absorption of craze fibril domains
V_f	volume fraction of craze fibril domains
$u_{i,j}$	displacement gradients
w(x,t)	craze opening displacement measured from center of symmetry
$w_0(x,t) \equiv u_z(x,o,t),\ \lvert x\rvert < c(t)$.	opening displacement measured from center of symmetry of craze-crack system as defined
$x \equiv x_1$	coordinate along first coordinate axis
X_K	coordinates in reference frame (K = 1, 2 or 3)
x_k	coordinates in current frame (k = 1, 2 or 3)

$z \equiv x_3$	third coordinate axis
α_o	constant linear thermal coefficient of expansion
$\beta,\ \gamma$	positive parameters
δ_{ij}	delta function
Γ_b, Γ_c	material constants
ϵ	orientation strain ($-1 < \epsilon < \infty$)
ϵ_{kl}	strain tensor (k, l = 1, 2 or 3)
θ, ϕ	spherical coordinates
$\theta(T)$	temperature function
$\lambda(x,t)$	time- and position-dependent draw ratio
λ_1	draw ratio beyond craze mid-section under stress σ_1
λ_{m1}	draw ratio of craze mid-section at stress level σ_1
λ_{m2}	draw ratio of craze mid-section at stress level σ_2
ν	strain ratio
$\xi = t\phi(T)$, $\eta = \tau\phi(T)$	shift times
n	strain ratio
ρ	density of the probability distribution function of molecular orientation
σ	applied stress
$\sigma_o(T,t)$	constant temperature, time-dependent stress
σ_I, σ_{II}	principal stresses
σ_1, σ_2	craze envelope stress levels
σ_b	tensile strength or fracture strength
σ_c	craze envelope stress
σ_{ij}	stress tensor (i, j = 1, 2 or 3)
$\dot{\sigma}_{ii}$	time derivative of the isotropic stress tensor
σ_{max}	maximum breaking stress
σ_{min}	minimum breaking stress
τ	time or dummy parameter
$\Phi(x, t)$	stress function at spatial position x and time t

$\phi(T)$	temperature-time shift function
Ψ	axial stress of an element
$d\omega$	solid angle
ω_b	frequency of motion in breaking process
ω_r	frequency of motion in reforming process

PRELIMINARIES AND INTRODUCTION

For a long time, the analyses and prediction of the mechanical strength behavior of engineering components have been dependent mostly upon the application of continuum theories. This is true even in failure studies. Elasticity, viscoelasticity, plasticity and linear elastic fracture mechanics have dominated much of the analytical investigation in solid mechanics. Failure criteria for continuous media are considered to be independent with respect to the integrity of the media. There is no introduction of noncontinuum damage mechanics based upon microstructural behavior, and discrete interactions among discontinuous flaws are not predictable.

Recently, however, a new research direction has emerged to connect microscopic material behavior with macroscopic structural mechanics. This is motivated primarily by the strong desire to design the constitution and configuration of the microstructure of material systems for obtaining required macromechanical properties and functions. In doing so, the integrity of the media is included in failure criteria as well as in the constitutive description. Micromechanisms and their interactions are taken into consideration in analyses aside from their time and temperature dependencies.

In failure investigations of solids and composite material systems, an important and challenging problem in science and engineering has been the attempt to understand the strength and fracture behavior of stressed solid systems. Either continuum or noncontinuum method of approach has been used to study the problem. The continuum damage mechanics approach deals with the phenomenological behavior of matrix cracking in fiber-reinforced composites using quantities such as stress, strain, strain rate and temperature fields. The noncontinuum approach deals with the individual micro-damages such as minute crazes and cracks formed in the matrix together with the matrix-fiber interfaces in composites. Usual field quantities appropriate to the problem as well as unusual parameters are introduced to effect a satisfactory solution. During such a course of investigation, both micro- and macro-structural information is connected. This noncontinuum approach relies on the mode of damage and micromechanism. Aside from usual parameters, the ultimate results can depend upon other quantities such as a function of the fraction of integrity and/or a distribution function of molecular orientation, etc. The following gives an example concerning a noncontinuum micromechanics and craze-crack transition behavior.

Since the first publication of the pioneer work on crazing,[1] there was an inadvertent attempt to connect the microstructure of the polymer medium with its macroscopic behavior. However, little attention has been given to make this connection for many decades.

One of the first analyses of the growth of crazing was modeled as a continuum theory. Under a critical tensile stress the linearly elastic material initiates crazes which are rate insensitive.[2] Several other analyses using elasticity theory have also appeared more recently.[3,4] Similar to the analysis of a craze, many craze-related crack problems have been investigated in viscoelastic media.[5-10] The intention of these studies was to take care of the energy dissipation which takes place in the viscoelastic bodies not considered in the elastic theory. The time-dependent size and shape of cracks in linearly viscoelastic isotropic continuum media have been analyzed. No microstructural nature is considered however. Subsequently, approximate methods of analysis have been presented and illustrated with a failure zone to obtain viscoelastic stresses and displacements for elastic solutions. In the analysis, in order to satisfy the developed governing equations, the failure zone in the elastic problem is modified to meet the traction boundary condition for the crack faces. In general, the connection between the mechanics of the problem and the noncontinuum microstructural nature is not made in these investigations. Therefore, in the following example a noncontinuum craze-crack transition is analyzed in light of the actual microstructural behavior and the mechanics of the problem. Equations governing the rupture of the fibril domain structure in the middle of the craze envelope surfaces subject to a uniform tension is considered for an isolated craze in an infinite viscoelastic polymer sheet. Solutions yield both information on the time dependent craze-crack transition and the displacement field around the craze-crack envelope profile describing the shape of the craze-crack region. Before this is done relevant noncontinuum information is reviewed. Justifications and significance of using the noncontinuum microstructure are described.

TIME DEPENDENT DEFORMATION AND MOLECULAR ORIENTATION

By incorporating microstructural information, the deformation of a material system may be analyzed under stresses with the help of classical continuum theory. For some polymeric and composite systems, the deformation processes may be characterized to contain a molecular orientation mechanism with a microporosity sensitive to time and temperature.

A realistic medium may be represented by a system of microstructural elements which translate and rotate under stressing. As shown in Figure 1, an elemental vector **dP** in the reference frame X_K (K = 1, 2, or 3) transforms to **dp** in the current frame x_k (k = 1, 2 or 3) under a time-dependent load **P**(t). Then the stress tensor σ_{ij} at any point can be calculated under certain conditions.[11]

$$\sigma_{ij}(\epsilon_{kl},T,t) = \int \rho(\theta,\phi,\epsilon_{kl}) \cdot f(\theta,\phi,\epsilon,T,t)\, \Psi(\theta,\phi,\epsilon,T,t) n_i n_j \, d\omega \,, \qquad (1)$$

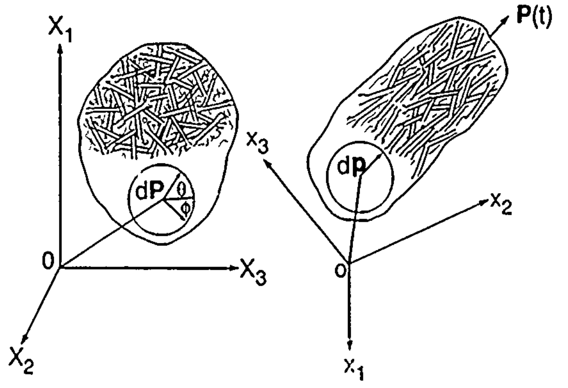


Fig. 1 Molecular Entanglement and Orientation in Deformation

where ϵ_{kl} is the strain tensor,

T	is the absolute temperature,
t	is time,
ρ	is the density of the probability distribution function of molecular orientation,
θ, ϕ	are spherical coordinates,
f	is the fraction of integrity of the microstructional system,
ϵ	is the orientation strain ($-1 < \epsilon < \infty$),
Ψ	is the axial stress in an element,
n_i, n_j	are unit vectors, and
$d\omega$	equals $\sin\theta d\theta d\phi$ representing the solid angle from which statistical expectation may be evaluated.

Since the stresses are functions of the orientation strain, it is likely that the constitutive behavior will be greatly affected. A simple illustration is shown in Figure 2 where the nonlinear deformational behavior of an isotropic continuum medium must be modified by the molecular orientation behavior to give a more realistic combined constitutive description. This no doubt will affect the further response of the material system to stressing such as the initiation of crazes and the stability or instability of the system.

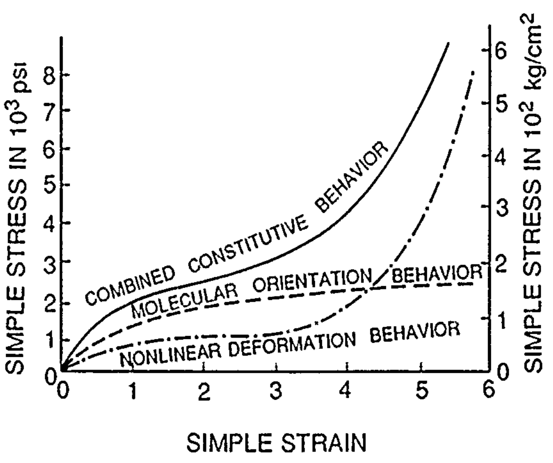


Fig. 2 Simple Stress-Strain Constitutive Behavior

ENERGY STATE, TEMPERATURE AND CRAZE INITIATION

At a constant temperature, the stability of the homogeneous deformation of a real material system under a simple uniform tension will eventually be upset at some time when a specific energy state of the microstructural system develops. The possible responses may be described with the help of Figure 3. Under load, the stability or instability of a material system may best be determined by its free energy state. The material system readjusts its microstructural configuration to maintain its lowest energy state until certain dominating characteristics develop. After an incubation period is reached the material system may deform in shear primarily as a result of the rotational motion of certain microstructures. Thus, a simple shearing band develops in the system. The material system may develop cracks as a result of a basically translational motion of the microstructure including possibly the slipping and rupturing of molecular bonds. This may be the simple cracking of a material system. When a complex kinetic situation occurs, both the rotational and translational motion of the microstructure may take place. Crazing may develop as a result.

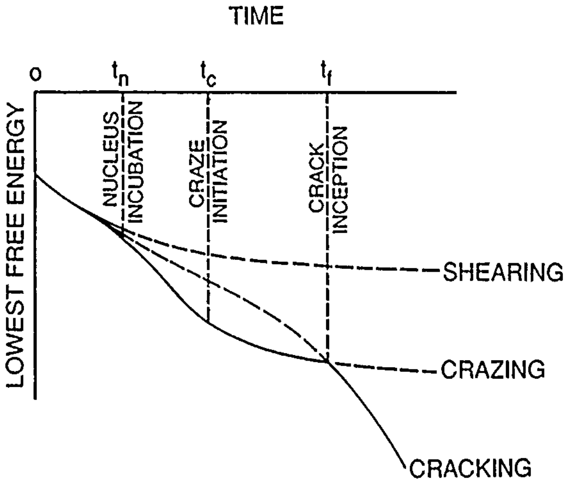
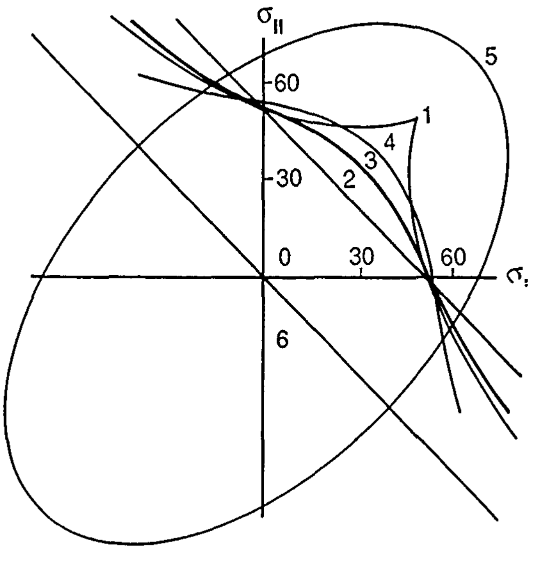


Fig. 3 Lowest Free Energy State and Deformation Behavior

For a two-dimensional craze, the isochronous biaxial locus for craze initiation is given in Figure 4. Various criteria put forward to date are plotted for comparison. Detailed information can be found in an earlier reference.[12] Only the three-dimensional craze initiation criterion is given below in a series form with a_n as an integer constant and n an integer.



Stress in MPa

Biaxial locus for criteria of craze initiation in polymers by:
1. Sternstein and Ongchin,
2. Bowden and Oxborough,
3. New Criterion,
4. Argon,
5. Distortion strain energy, and
6. 45° reference line

Fig 4 Biaxial Locus for Criteria of Craze Initiation in Polymers

$$S(x_k, T, t) \geq \sum_{n=-\infty}^{\infty} a_n[3\alpha_0\Theta(T) + \int_{-\infty}^{t} J_2(\xi-\eta)\dot{\sigma}_{ii}(x_k,\tau)\,d\tau]^n \qquad (2)$$

where S is the magnitude of the deviatoric stress tensor **S** which must overcome an intrinsic flow resistance, a_n are constants, α_0 is the constant linear thermal coefficient of expansion, $\Theta(T)$ is the temperature function, $J_2(\xi - \eta)$ is the bulk creep compliance function with $\xi = t\phi(T)$ and $\eta = \tau\phi(T)$ as shift times defined by the "temperature-time shift" principle for "thermorheologically simple" viscoelastic media and $\dot{\sigma}_{ii}$ is the time derivative of the isotropic stress tensor. This three-dimensional craze initiation criterion is reducible to any of the other criteria by introducing appropriate values for a_n. In Figure 4 this new criterion is represented by line 3 for the two-dimensional situation. This line reduces to each of the other curves from 1 through 5 when appropriate values of a_n and n are introduced.

The influence of temperature motion on craze-initiation is also plotted in Figure 5 together with the applied stress for the polystyrene material system computed with $a_0 = -30$ MN/m^2, $a_{-1} = 0.3$ MN/m^2 and $a_1 = 0$.

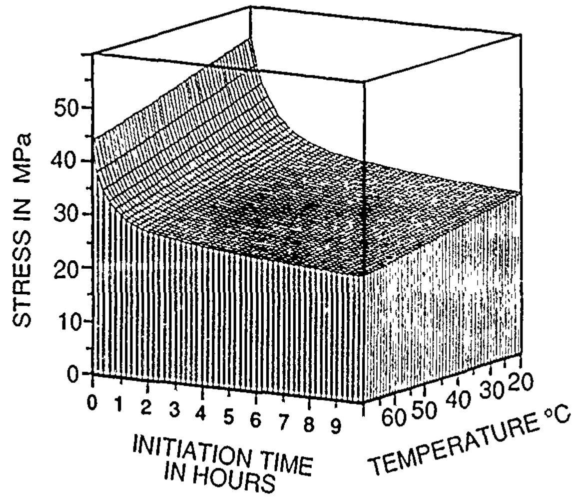


Fig. 5 Stress, Temperature Effects on Craze Initiation in Polymers

MICROSTRUCTURE AND MECHANICAL STRENGTH

Based upon the microstructural behavior and the dynamic nature of molecular motion, the fraction of integrity can be determined and utilized to establish a fracture criterion for a material system. Subsequently the connection between the microstructure and the macromechanical strength can be made. This has been done by means of the statistical theory of the absolute reaction rate. Not only can the microstructural orientation and the rupture of the microscopic structural units be incorporated but their reformation can also be included in the theory to obtain the time-dependent mechanical strength particularly for long times as illustrated in Figure 6.[11,13-15] This tensile strength which is the fracture strength as a function of time has been well established as shown. The tensile strength of a stressed solid material system for both short or long times tends to level off as shown. This means that the tensile strength becomes independent of time for very short times as well

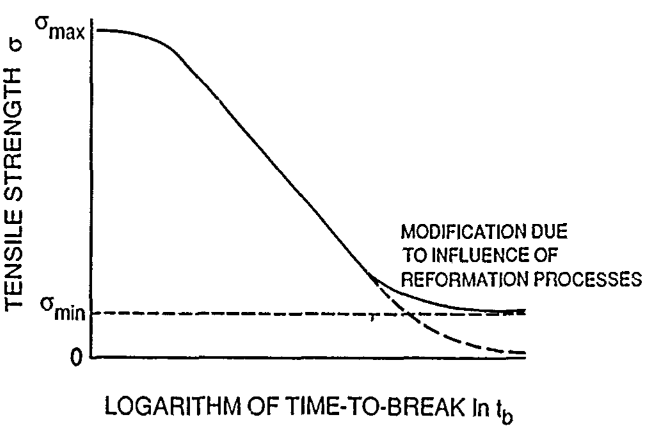


Fig. 6 Microstructural Orientation and Reformation Effects on a Time-Dependent Mechanical Strength

as for very long times. In between these times, the tensile strength is linearly proportional to the logarithm of time. The temperature effect on the time-dependent mechanical strength is given in Figure 7 to show that temperature is an important entity in this complex situation which must be taken into consideration in the analysis for any material system.

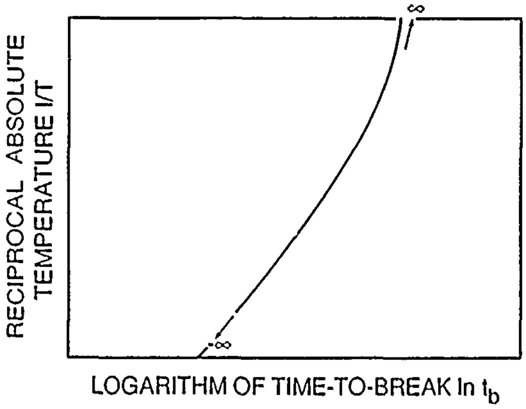


Fig. 7 Temperature Effects on Time-Dependent Mechanical Strength

Consider a material system composed of a large number of randomly oriented similar molecular units or elements which elongate and rotate in a stress field. In order to formulate a temperature- and time-dependent failure criterion for such a material system, one can use the quantity f(t), the time-dependent fraction of integrity. By calculating its time rate of change as follows:

$$\dot{f} = K_r(1-f) - K_b f \tag{3}$$

where $K_r = \omega_r \exp[-U/RT - \gamma\Psi(t)]$ is the rate coefficient of reformation of the disconnected units and $K_b = \omega_b \exp[-U/RT + \beta\Psi(t)]$, the rate coefficient of breakage of the connected elements, ω_r and ω_b are respectively the frequencies of motion with respect to forming and breaking processes of these units, U is the activation energy, R is the universal gas constant, and γ and β are positive parameters which modify the true axial stress $\Psi(t)$ in each elemental unit.

The failing of a material system is when f approaches zero. In these formulations, K_r and K_b, are both functions of temperature and the true stress in individual elements. Once a stress σ is applied to the material system, the energy state is altered and the time-to-break t_b can be calculated.

The fracture strength, the statistical mean strength in the vicinity of any point in the system, has been analyzed and found to be proportional to the modulus of individual elements, their length and the number of the elements per unit volume. For an oriented system, the fracture strength is a function of deformation as briefly reviewed in the previous section. For a fully oriented system[11] under a constant applied stress σ, we may write

$$\Psi(t)f(t) = \sigma . \tag{4}$$

The functional relationship between Ψ and t is

$$\Psi = -\frac{\Psi^2}{\sigma}[K_r(1-\frac{\sigma}{\Psi}) - K_b\frac{\sigma}{\Psi}] . \tag{5}$$

Integration results in the time-to-break t_b. With zero initial time

$$t_b = \int \frac{d\Psi}{\Psi[K_b + K_r(1-\Psi/\sigma)]} . \tag{6}$$

Usually near fracture, K_r becomes unimportant, and the time-to-break may be approximated to

$$t_b = \exp(U/RT) \int \frac{d\Psi}{\omega_b \Psi \exp(\beta\Psi)} , \tag{7}$$

which can further be simplified to

$$t_b = A\exp(-B\sigma) \tag{8}$$

with A and B as material constants.

Now let us consider the craze problem as shown in Figure 8. Under a temperature and time dependent stress $\sigma_o(T,t)$ a three-dimensional craze may develop from the surface of a material body. In general the microstructure on the surface of the material body is composed of a network of highly oriented fibril domains drawn out of the envelope profile and separated by cavities. This combined structure propagates along the surface of the material body and penetrates into the body as indicated respectively by c(T,t) and q(T,t) which are measured from the center of craze at the origin 0. The stress at any point in the material is designated as $\sigma(x_1,x_2,x_3,T,t)$ and the craze envelope stress by $\sigma_c(x_1,x_2,x_3,T,t)$ as shown.

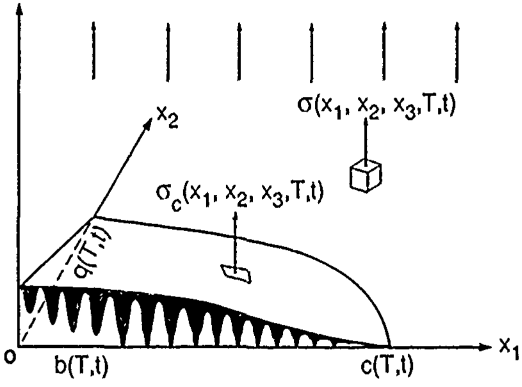


Fig. 8 Microstructure of a Three-Dimensional Craze-Crack System

A strong interest has been the determination of the displacement field since it is not easily measured. This noncontinuum feature is easily seen in Figure 9, in which the randomly oriented microstructure is being drawn into

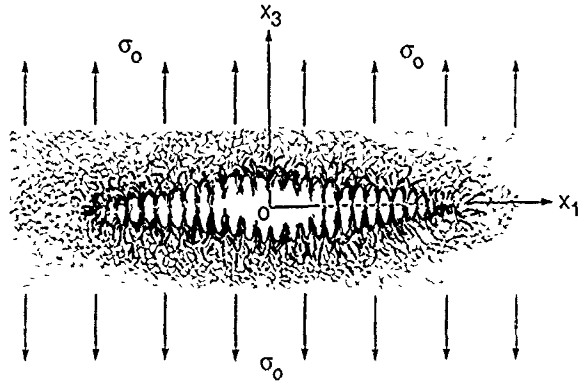


Fig. 9 Microstructural Formation of a Two-Dimensional Craze-Crack System

highly oriented fibril domains. A schematic diagram of a two-dimensional craze is given in Figure 10 to show the pertinent quantities. For simplicity in sequel x_3 is replaced by z and x_1, by x.

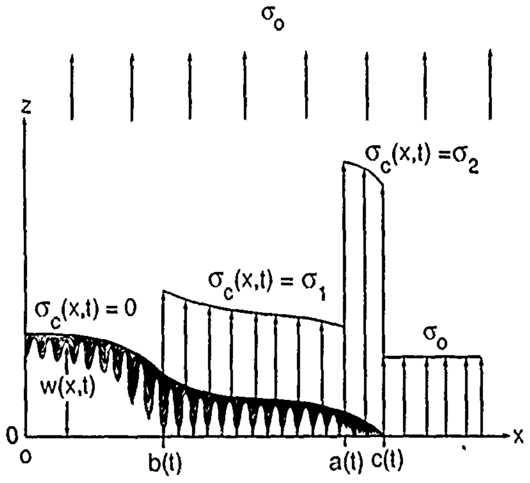


Fig. 10 An Idealized Two-Dimensional Craze-Crack System with Assumed Step Envelope Stress Distribution

ANALYSIS OF CRAZE-CRACK TRANSITION

Considering this two-dimensional model, an analysis can be made to obtain the time dependent displacement field and the craze-crack lengths by incorporating the microstructural behavior into the macromechanics problem.

Starting from the highly oriented fibril domain structure in the craze region, the required time-to-break t_b is calculable based upon a perfectly oriented molecular system under a constant stress σ.[11,15] A general curve t_b vs. σ is given in Figure 6. The maximum applied stress is indicated by σ_{max}. With reformation processes considered, the tensile strength of the material system begins to deviate from the dotted curve. There exists a minimum strength value σ_{min} for which t_b goes to infinity asymptotically.[14] Therefore for a given medium there exists a corresponding curve between t_b and the applied constant stress σ. When the applied stress varies with time, one can use the linear summation damage rule which states that the same number of damages accumulate during identical time intervals. Thus the time-to-break is determinable by the equation:[16]

$$\int_0^{t_b} \frac{dt}{t_b[\sigma(t)]} = 1 . \qquad (9)$$

By adopting this microstructural behavior, the opening displacement w(x,t), the craze-crack system length c(t) and the crack length b(t) in this craze-crack transition problem can be calculated. To facilitate the possibility of obtaining numerical solutions, a three-step envelope stress distribution, as shown in Figure 10, is introduced:

$$\sigma_c(x, t) = \begin{cases} o & o < x < b(t) , \\ \sigma_1 & b(t) < x < a(t) , \\ \sigma_2 & a(t) < x < c(t) . \end{cases} \qquad (10)$$

It is hoped that this assumed step stress function will yield good approximations in both the displacement field and the lengths of the craze-crack system.[1]

With the three-step envelope stress function, the stress sustained by the fibril domains in the thin mid-section where under certain conditions, failure has been observed to occur more often, is

$$\begin{cases} \sigma = \lambda_{m2}\sigma_2 & a(t) < x < c(t) , \\ \sigma = \lambda_{m1}\sigma_1 & b(t) < x < a(t) , \end{cases} \qquad (11)$$

where $\lambda_{m2}\sigma_2$ is the true stress born by the fibril domains and λ_{m2} is the draw ratio at the stress region σ_2. Similarly $\lambda_{m1}\sigma_1$ and λ_{m1} denote the corresponding quantities under region σ_1.

As discussed earlier, under large stresses, the time-to-break t_b can be obtained by first dropping K_r in (3) to get (8), then introducing (11) in (9), one can obtain:

$$t_b = A\exp(-B\lambda_{m1}\sigma_1) - t_2\{\exp[B(\lambda_{m2}\sigma_2 - \lambda_{m1}\sigma_1)] - 1\} \qquad (12)$$

where t_2 is the period when the fibril domains experience the higher envelope stress σ_2.

To review briefly the time-dependent viscoelastic problem, the opening displacement measured from the center of symmetry of the craze-crack system in a viscoelastic polymer sheet can be obtained by using the well known correspondence principle in linear viscoelasticity.

The field equations are:

$$\sigma_{ij,j}(x,z,t) = o , \qquad (13)$$

$$\epsilon_{ij}(x,z,t) = \frac{1}{2}[u_{i,j}(x,z,t) + u_{j,i}(x,z,t)] , \quad (14)$$

$$S_{ij}(t) = \int_{-\infty}^{t} G_1(t-\tau)de_{ij}(\tau) , \quad (15)$$

$$\sigma_{ij}(t) = \int_{-\infty}^{t} G_2(t-\tau)d\epsilon_{ij}(\tau) , \quad (16)$$

where σ_{ij} is the stress tensor, ϵ_{ij}, the strain tensor, $u_{i,j}$, the displacement gradients, G_1 and G_2 are respectively the deviatoric and dilatational relaxation moduli of the original bulk medium, and the deviatoric stresses and strains are respectively

$$S_{ij}(t) = \sigma_{ij}(t) - \frac{1}{3}\delta_{ij}\sigma_{kk}(t) , \quad (17)$$

$$e_{ij}(t) = \epsilon_{ij}(t) - \frac{1}{3}\delta_{ij}\epsilon_{kk}(t) , \quad (18)$$

with i, j and k = x or z denoting dummy variables in two-dimensional problems. The boundary conditions are described as:

$$\sigma_{zx}(x,o,t) = o , \qquad |x| < c(t) \quad (19)$$

$$\sigma_{zz}(x,o,t) = \sigma_c(x,t) , \quad |x| < c(t) \quad (20)$$

$$\left.\begin{array}{l} \sigma_{zz}(x,z,t) = \sigma_o(t) , \\ \sigma_{xx}(x,z,t) = o , \\ \sigma_{xz}(x,z,t) = o , \end{array}\right] \text{ as } (x^2+z^2) \dashrightarrow \infty . \quad (21)$$

The opening displacement $w_o(x,t)$ is defined by

$$w_o(x,t) = u_z(x,o,t) , \qquad |x| < c(t) . \quad (22)$$

To solve this viscoelastic problem. The Laplace transform with respect to time is applied to all of the field equations and the boundary conditions. The solution to the transformed equation can be found by using the well established complex variable conformal mapping method or the complex variable stress function method for elastic medium.

The time dependent solution of the problem is obtained by Laplace inversion. This solution is valid only if the boundary conditions are independent of time, i.e., c(t), b(t) and $\sigma_c(x,t)$ remain unchanged. These restrictions can be removed by using a sequence of loading and unloading steps,[17] which yields,

$$w_o(x,t) = C_b(o)\Phi(x,t) + \int_0^t \dot{C}_b(t-\tau)\Phi(x,\tau)d\tau , \quad (23)$$

where

$$\Phi(x,t) = \sigma_o\sqrt{c^2-x^2} - \frac{2}{\pi}\int_0^c \sigma_c(\xi,t)\,\ln(c+\sqrt{c^2-\xi^2})d\xi$$

$$+\frac{2}{\pi}\int_0^x \sigma_c(\xi,t)\,\ln(x+\sqrt{x^2-\xi^2})d\xi$$

$$+\frac{2}{\pi}\int_x^c \sigma_c(\xi,t)\,\ln\xi d\xi , \quad (24)$$

$$C_b(t) = L^{-1}\,[(2(2\overline{G}_1+\overline{G}_2)) / (s^2\overline{G}_1(\overline{G}_1+2\overline{G}_2))] \quad (25)$$

with L^{-1} designating the Laplace inversion and barred quantities being in Laplace domains.

If the strain ratio ν is constant, $C_b(t)$ reduces to

$$C_b(t) = L^{-1}\,[(2(1 - s^2\nu^2)) / s^2\overline{E}] , \quad (26)$$

where E is the relaxation modulus of the original unoriented bulk polymer medium.

Taking into consideration the thickness of the primordial layer from which the fibril domain structure has been pulled out, the actual opening displacement of the system becomes

$$w(x,t) = C_b(o)\Phi(x,t) + \int_0^t \dot{C}_b(t-\tau)\Phi(x,\tau)d\tau$$

$$+ \int_{t_x}^{t} \frac{\dot{w}(x,\tau)}{\lambda(x,\tau)}d\tau , \quad (27)$$

where t_x is the time when the tip of the craze-crack system first reaches the point x, λ is the draw ratio. Since the midsection is relatively thin in a craze, the λ function can be taken as

$$\lambda(x,t) = \begin{cases} \lambda_1 , & b(t) < x < a(t) \\ \lambda_{m2} , & a(t) < x < c(t) , \end{cases} \quad (28)$$

where λ_1 is the draw ratio outside the mid-section under the envelope stress σ_1. The opening displacement finally is obtained as

$$w(x,t) = \frac{\lambda_{m2}}{\lambda_{m2}-1}[C_b(o)\Phi(x,t)$$

$$+ \int_0^t \dot{C}_b(t-\tau)\Phi(x,\tau)d\tau] , \quad \text{for } a(t) < x < c(t) , \quad (29)$$

$$w(x,t) = \frac{\lambda_1}{\lambda_1-1}[C_b(o)\Phi(x,t) + \int_0^t \dot{C}_b(t-\tau)\Phi(x,\tau)d\tau]$$

$$+ (\frac{1}{\lambda_{m2}} - \frac{1}{\lambda_1})w(x,t_a) , \qquad \text{for } b(t) < x < a(t) , \quad (30)$$

$$w(x,t) = C_b(o)\Phi(x,t) + \int_0^t \dot{C}_b(t-\tau)\Phi(x,\tau)d\tau$$

$$+\left(\frac{1}{\lambda_{m2}}-\frac{1}{\lambda_1}\right)w(x,t_a)+\frac{1}{\lambda_1}w(x,t_h),$$

$$\text{for } o < x < b(t), \qquad (31)$$

where t_a and t_h respectively denote the times when a(t) and b(t) arrive at the point x.

CRAZE AND CRACK LENGTHS

With regard to the length of the craze-crack system and that of the crack, suppose that the fibril domain nucleation rate at the craze tips is proportional to the growth velocity $\dot{c}(t)$ of the system. Then the energy rate required for the growth of craze tip is $\Gamma_c\dot{c}(t)$ and that for the crack tip is $\Gamma_b\dot{b}(t)$, where Γ_c and Γ_b are material constants. Based upon the assumption that the rate of energy required for drawing the fibrils out of the craze surface envelope is proportional to the rate of creation of the new fibril domain surface $\dot{S}(t)$, using the proportionality constant Γ_s, the following local energy balance equation can be written as:

$$\dot{H}_c(t) = \Gamma_c\dot{c}(t) + \Gamma_b\dot{b}(t) + \Gamma_s\dot{S}(t)$$

$$+ \dot{U}_f(t) + \dot{D}_f(t) + \dot{K}_f(t) \qquad (32)$$

where $\dot{H}_c(t)$ is the energy absorption rate of the quadrantal portion of the craze system, $\dot{U}_f(t)$ is the strain energy absorption rate of fibril domains, $\dot{D}_f(t)$ is the energy dissipation rate by the craze fibrils, and $\dot{K}_f(t)$ is the rate of kinetic energy due to the motion of the craze fibril domains. $\dot{U}_f$, $\dot{D}_f$ and $\dot{K}_f$ are negligible when compared with the other rate quantities in the quasi-static conditions. With this simplification and the terms expressed by elementary parameters defined earlier, the following equations can be established. Since the stress each fibril domain sustains is $\lambda\sigma_c$ which equals σ_c/V_f if V_f is the volume fraction:

$$\dot{H}_c(t) = \int_o^c \sigma_c(x,t)\,\frac{\partial w(x,t)}{\partial t}\,dx, \qquad (33)$$

$$\dot{S}(t) = \int_o^c 4\,\frac{V_f(x,t)}{d(x,t)}\,\frac{\partial w(x,t)}{\partial t}\,dx, \qquad (34)$$

where d(x,t) is the time and position dependent diameter of craze fibril domains. Now using these, Equation (32) becomes an implicit nonlinear differential equation of the craze-crack system length c(t) and the crack length b(t) as follows:

$$\int_o^c \left(\sigma_c - 4\,\frac{\Gamma_s V_f}{d}\right)\frac{\partial w(x,t)}{\partial t}\,dx = \Gamma_c\dot{c} + \Gamma_b\dot{b}. \qquad (35)$$

This implicit differential equation has three unknown quantities, a(t), b(t) and c(t) to be determined. In order to solve this equation, some subsidiary equations are necessary. One of them is that[17] the craze envelope stress $\sigma_c(x,t)$ must balance the applied external load corresponding to an applied simple tension σ_o to ensure that the stress field within the uncrazed bulk material is finite everywhere for all times t. In mathematical form this means:

$$\int_o^c \frac{\sigma_c(x,t)}{\sqrt{c^2(t)-x^2}}\,dx = \frac{\pi}{2}\sigma_o. \qquad (36)$$

When the three-step envelope stress function (10) is substituted in, it yields:

$$a(t) = c(t)\sin\left(\frac{\pi}{2}\,\frac{\sigma_2-\sigma_o}{\sigma_2-\sigma_1} - \frac{\sigma_1}{\sigma_2-\sigma_1}\sin^{-1}\frac{b(t)}{c(t)}\right). \qquad (37)$$

The other equation is from the consideration of the nature of the failure of the craze material, which obviously provides a relation between the craze-crack system and crack lengths,

$$b(t) = c\,(t - t_b). \qquad (38)$$

It should be noted that the time-to-break t_b is spatially dependent and it is evident that

$$b(t) = c\,[t - t_b(b(t))]. \qquad (39)$$

RESULTS AND DISCUSSION

Generally speaking, c(t) and b(t) can be obtained as functions of time by solving Equations (35), (37) and (39). But it is still rather complicated because of the unusual form of Equation (39).

If the craze-crack system and the crack propagate steadily without drastically change in their propagating speeds, Equation (39) can be simplified to the following form

$$b(t) = c(t) - t_b\dot{c}(t), \qquad (40)$$

where t_b has been evaluated and displayed as Equation (12), i.e.,

$$t_b = A\exp(-B\lambda_{m1}\sigma_1)$$

$$- t_2\{\exp[B(\lambda_{m2}\sigma_2 - \lambda_{m1}\sigma_1)] - 1\}.$$

Usually, the distance c(t) - a(t) is relatively small since it is associated with the region of stress concentration. Thus t_2 can be expressed as

$$t_2 = (c - a)/\dot{c}. \qquad (41)$$

Using the envelope stress profile proposed earlier, Equation (24) turns out to be

$$\Phi = \frac{1}{\pi}[(\sigma_2-\sigma_1)x\ln\frac{a\sqrt{c^2-x^2} - x\sqrt{c^2-a^2}}{a\sqrt{c^2-x^2} + x\sqrt{c^2-a^2}}$$

$$+ \sigma_1 x\ln\frac{b\sqrt{c^2-x^2} - x\sqrt{c^2-b^2}}{b\sqrt{c^2-x^2} + x\sqrt{c^2-b^2}}$$

$$- (\sigma_2 - \sigma_1) a \ln \frac{\sqrt{c^2-x^2} - \sqrt{c^2-a^2}}{\sqrt{c^2-x^2} + \sqrt{c^2-a^2}}$$

$$- \sigma_1 b \ln \frac{\sqrt{c^2-x^2} - \sqrt{c^2-b^2}}{\sqrt{c^2-x^2} + \sqrt{c^2-b^2}}] . \qquad (42)$$

Since the product of the average fibril domain diameter and the envelope stress has been found to be constant, that is, $d_1\sigma_1 = d_2\sigma_2 =$ constant, thus let

$$d(x, t) = \begin{cases} d_1, & b(t) < x < a(t), \\ d_2, & a(t) < x < c(t), \end{cases} \qquad (43)$$

and noting that $V_f = 1/\lambda$ and Equation (32) then, by substitution, Equation (35) becomes

$$(\sigma_2 - \frac{4\Gamma_s}{d_2\lambda_{m2}}) \int_a^c \frac{\partial w}{\partial t}\, dx$$

$$+ (\sigma_1 - \frac{4\Gamma_s}{d_1\lambda_1}) \int_b^a \frac{\partial w}{\partial t}\, dx = \Gamma_c\dot{c} + \Gamma_b\dot{b} . \qquad (44)$$

Since $\Phi(c, t) = o$, obviously,

$$\int_a^c \frac{\partial w}{\partial t} dx = \frac{\lambda_{m2}}{\lambda_{m2}-1} \{C_b(o)[\dot{a}\Phi(a,t)$$

$$+ \frac{d}{dt} \int_a^c \Phi(x,t)dx]$$

$$+ \int_a^c \dot{C}_b(o)\Phi(x,t)dx$$

$$+ \int_a^c \int_o^t \ddot{C}_b(t-\tau)\Phi(x,\tau)d\tau dx \} , \qquad (45)$$

$$\int_b^a \frac{\partial w}{\partial t} dx = \frac{\lambda_1}{\lambda_1-1} \{C_b(o) [\dot{b}\Phi(b,t) - \dot{a}\Phi(a,t)$$

$$+ \frac{d}{dt} \int_b^a \Phi(x,t)dx]$$

$$+ \int_b^a \dot{C}_b(o)\Phi(x,t)dx$$

$$+ \int_b^a \int_o^t \ddot{C}_b(t-\tau)\Phi(x,\tau)d\tau dx \} . \qquad (46)$$

Introducing the notations

$$\Phi_{ac} = \int_a^c \Phi(x,t)dx , \qquad (47)$$

$$\Phi_{ba} = \int_b^a \Phi(x,t)dx , \qquad (48)$$

and substituting them into (44), we have

$$K_1\dot{a}(t) + K_2\dot{b}(t) + K_3\dot{c}(t) + K_4 = o , \qquad (49)$$

where

$$K_1 = C_b(o)[(I_2 - I_1)\Phi(a,t) + I_2\frac{\partial \Phi_{ac}}{\partial a} + I_1\frac{\partial \Phi_{ba}}{\partial a}] , \qquad (50)$$

$$K_2 = C_b(o)\{ I_2\frac{\partial \Phi_{ac}}{\partial b} + I_1[\Phi(b,t) + \frac{\partial \Phi_{ba}}{\partial b}]\} - \Gamma_b , \qquad (51)$$

$$K_3 = C_b(o)(I_2\frac{\partial \Phi_{ac}}{\partial c} + I_1 \frac{\partial \Phi_{ba}}{\partial c}) - \Gamma_c , \qquad (52)$$

and

$$K_4 = \dot{C}_b(o)(I_2\Phi_{ac} + I_1\Phi_{ba})$$

$$+ I_2 \int_o^t \ddot{C}_b(t-\tau)\Phi_{ac}d\tau + I_1 \int_o^t \ddot{C}_b(t-\tau)\Phi_{ba}d\tau , \qquad (53)$$

with I_1 and I_2 being constants, and

$$I_1 = (\sigma_1 - \frac{4\Gamma_s}{d_1\lambda_1}) \frac{\lambda_1}{\lambda_1-1} , \qquad (54)$$

$$I_2 = (\sigma_2 - \frac{4\Gamma_s}{d_2\lambda_{m2}}) \frac{\lambda_{m2}}{\lambda_{m2}-1} . \qquad (55)$$

The explicit forms of those quantities in expressions of K's are given in the Appendix.

The calculations should be divided into two steps. First, the original craze propagates during the absence of a crack. This can be calculated by simply setting $b(t) = o$ in Equations (38) and (44), which degenerates into the case discussed earlier.[17] After certain time elapses, the fibril domains first produced in the mid-section of the craze breaks down and crack commences. Second, the crack comes into play and the Equations (38), (41), (42) and (44) must be used to calculate simultaneously the propagations for both the craze-crack system and the crack.

Now to illustrate the changes of a craze-crack system in polystyrene, a Voigt solid is taken as an example. The material properties are taken to be[18-23]

$$
\begin{aligned}
J(t) = \{29 &+ 5.09[1-\exp(-t)] + 2.32[1-\exp(-t/10)] \\
&+ 6.59[1-\exp(-t/10^2)] + 12.72[1-\exp(-t/10^4)] \\
&+ 0.71[1-\exp(-t/10^5)] + 14.71[1-\exp(-t/10^6)] \\
&+ 1.02[1-\exp(-t/10^7)]\} \cdot 10^{-5}\ \mathrm{m^2/MN},
\end{aligned}
$$

$A = \exp(11)$ secs, $d_1 = 20$ nm,

$B = 0.05\ \mathrm{m^2/MN}$, $d_2 = 10$ nm,

$\lambda_1 = 2.0$, $\Gamma_s = 0.125\ \mathrm{J/m^2}$,

$\lambda_{m1} = 2.5$, $\Gamma_c = 0.085\ \mathrm{J/m^2}$,

$\lambda_{m2} = 4$, $\Gamma_b = 300\ \mathrm{J/m^2}$.

ν for polystyrene is 0.395, a constant, and the applied stress is considered to be 36 MN / m^2, that is: $\sigma_0 = 36$ MN / m^2. In addition, based upon some experimental evidence, σ_1 and σ_2 are assumed to be respectively 40 MN / m^2 and 80 MN / m^2 for numerical calculations.

The normalized length of the craze-crack system and that of the crack are shown in Figure 11, where the normalization is made with respect to the initial length of the craze-crack system. The opening displacements at different times are plotted in Figure 12.

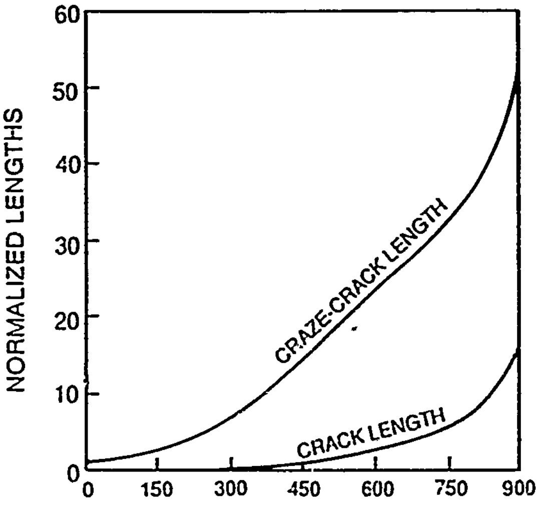


Fig. 11 Time-Dependent Crack and Craze-Crack System Lengths

For ease of visualization, the normalized craze length as a function of time is also given in Figure 13. The non-linear nature of the craze behavior is self-evident.

As can be seen from the calculations, both the velocities of the craze-crack system and that of the crack become larger and larger. Thus further calculation is not accurate since the unsteady propagation gives rise to irregular growth, branching and/or bifurcation. These complex phenomena are yet to be considered in the future analyses.

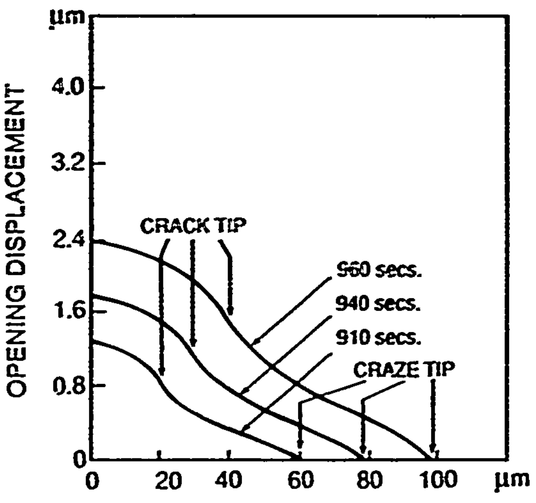


Fig. 12 Nonlinear Crack and Craze-Crack Length Behavior

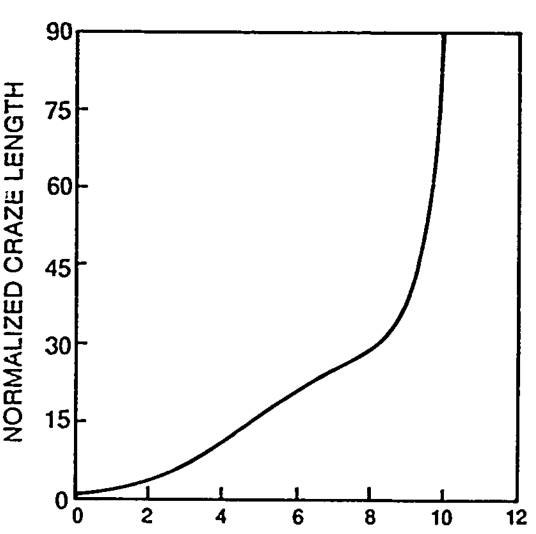


Fig. 13 Nonlinear Behavior of Normalized Craze Length

REMARKS AND SUGGESTIONS

From the review of the connection between microstructure and macromechanics as well as the analysis of the craze-crack transition it is seen that, in general, the complete fracture processes take time to develop and mature. Depending upon the degree of energy absorption by the microstructure of a medium, shear flow, craze or crack may occur. If craze occurs first, then the transition from craze to crack is likely to be highly nonlinear. Results are important in studying the time-dependent strength and fracture behavior of polymeric and composite systems. By averaging all the microscopic behavior specific in each molecular orientation, a fracture criterion may be established to analyze the time and deformation dependent breaking strength of an oriented polymer solid. Utilizing spherical functions and the double Fourier series expansion, the statistical microscopic behavior in the vicinity of a point in an oriented medium may be converted into several symmetric tensorial terms. Then the time-to-break can be synthesized and incorporated in calculating the macroscopic behavior. By taking into account the individual values of the directional fraction of integrity, the fracture time as well as the most probable direction of fracture initiation within any volume element in the medium can be predicted. However, results thus obtained governs only the localized behavior of a material. For a layered composite system, the interactions among craze-crack regions must also be determined. Perhaps a joint distribution function of the characteristic parameters can be introduced to obtain the final analytical result of the strength and fracture of a composite system. In addition, since the material systems are viscoelastic, measurements of temperature fields in and around a craze-crack system are extremely important in connecting the properties of the microstructure and the analysis of the energy dissipation of the macromechanical behavior.

APPENDIX

Substituting Equation (42) into (47) and (48), yields

$$\int_b^a \Phi dx = \frac{1}{\pi}\{[\,(\sigma_2-\sigma_1)a\sqrt{c^2-a^2}$$

$$+\sigma_1 b\sqrt{c^2-b^2}\,](\sin^{-1}\frac{a}{c}-\sin^{-1}\frac{b}{c})$$

$$+\frac{1}{2}(2\sigma_1-\sigma_2)(a^2+b^2)\ln\frac{a\sqrt{c^2-b^2}-b\sqrt{c^2-a^2}}{a\sqrt{c^2-b^2}+b\sqrt{c^2-a^2}}$$

$$-(2\sigma_1-\sigma_2)ab\ \ln\frac{\sqrt{c^2-b^2}-\sqrt{c^2-a^2}}{\sqrt{c^2-b^2}+\sqrt{c^2-a^2}}$$

$$+2(\sigma_1-\sigma_2)a^2\ \ln\frac{a}{c}+2\sigma_1 b^2\ \ln\frac{b}{c}\}, \qquad \text{(A1)}$$

$$\int_a^c \Phi dx = \frac{1}{\pi}\{[(\sigma_2-\sigma_1)\ a\sqrt{c^2-a^2}+\sigma_1 b\sqrt{c^2-b^2}\,]\cos^{-1}\frac{a}{c}$$

$$-\frac{1}{2}\sigma_1(a^2+b^2)\ln\frac{a\sqrt{c^2-b^2}-b\sqrt{c^2-a^2}}{a\sqrt{c^2-b^2}+b\sqrt{c^2-a^2}}$$

$$+ab\sigma_1\ \ln\frac{\sqrt{c^2-b^2}-\sqrt{c^2-a^2}}{\sqrt{c^2-b^2}+\sqrt{c^2-a^2}}$$

$$+2(\sigma_2-\sigma_1)a^2\ \ln\frac{a}{c}\}. \qquad \text{(A2)}$$

Differentiating (A1) and (A2) yields

$$\frac{\partial\Phi_{ba}}{\partial a}=\frac{1}{\pi}[(\sigma_2-\sigma_1)(\sin^{-1}\frac{a}{c}-\sin^{-1}\frac{b}{c})\frac{c^2-2a^2}{\sqrt{c^2-a^2}}$$

$$+(\sigma_2-\sigma_1)(b\frac{\sqrt{c^2-b^2}}{\sqrt{c^2-a^2}}-a-4a\ln\frac{a}{c})$$

$$-(\sigma_2-2\sigma_1)(a\ln\frac{a\sqrt{c^2-b^2}-b\sqrt{c^2-a^2}}{a\sqrt{c^2-b^2}+b\sqrt{c^2-a^2}}$$

$$-b\ln\frac{\sqrt{c^2-b^2}-\sqrt{c^2-a^2}}{\sqrt{c^2-b^2}+\sqrt{c^2-a^2}})], \qquad \text{(A3)}$$

$$\frac{\partial\Phi_{ba}}{\partial b}=\frac{1}{\pi}[\sigma_1(\sin^{-1}\frac{a}{c}-\sin^{-1}\frac{b}{c})\frac{c^2-2b^2}{\sqrt{c^2-b^2}}$$

$$-\sigma_1(a\frac{\sqrt{c^2-a^2}}{\sqrt{c^2-b^2}}-b-4b\ln\frac{b}{c})$$

$$-(\sigma_2-2\sigma_1)(b\ln\frac{a\sqrt{c^2-b^2}-b\sqrt{c^2-a^2}}{a\sqrt{c^2-b^2}+b\sqrt{c^2-a^2}}$$

$$-a\ln\frac{\sqrt{c^2-b^2}-\sqrt{c^2-a^2}}{\sqrt{c^2-b^2}+\sqrt{c^2-a^2}})], \qquad \text{(A4)}$$

$$\frac{\partial\Phi_{ba}}{\partial c}=\frac{1}{\pi}\{[(\sigma_2-\sigma_1)\frac{a}{\sqrt{c^2-a^2}}+\sigma_1\frac{b}{\sqrt{c^2-b^2}}]\cdot$$

$$(\sin^{-1}\frac{a}{c}-\sin^{-1}\frac{b}{c})c$$

$$+(\sigma_2-\sigma_1)\frac{a^2}{c}-\sigma_1\frac{b^2}{c}+\frac{ab}{c\sqrt{c^2-a^2}\sqrt{c^2-b^2}}\cdot$$

$$[(\sigma_2-\sigma_1)b^2-\sigma_1 a^2-(\sigma_2-2\sigma_1)c^2]\}, \qquad \text{(A5)}$$

$$\frac{\partial\Phi_{ac}}{\partial b}=\frac{1}{\pi}[(\sigma_2-\sigma_1)(\frac{c^2-2a^2}{\sqrt{c^2-a^2}}\cos^{-1}\frac{a}{c}+a+4a\ln\frac{a}{c})$$

$$-\sigma_1 a\ln\frac{a\sqrt{c^2-b^2}-b\sqrt{c^2-a^2}}{a\sqrt{c^2-b^2}+b\sqrt{c^2-a^2}}$$

$$+\sigma_1 b\ln\frac{\sqrt{c^2-b^2}-\sqrt{c^2-a^2}}{\sqrt{c^2-b^2}+\sqrt{c^2-a^2}}, \qquad \text{(A6)}$$

$$\frac{\partial\Phi_{ac}}{\partial b}=\frac{\sigma_1}{\pi}(\frac{c^2-2b^2}{\sqrt{c^2-b^2}}\cos^{-1}\frac{a}{c}+a\frac{\sqrt{c^2-a^2}}{\sqrt{c^2-b^2}}$$

$$-b\ln\frac{a\sqrt{c^2-b^2}-b\sqrt{c^2-a^2}}{a\sqrt{c^2-b^2}+b\sqrt{c^2-a^2}}$$

$$+a\ln\frac{\sqrt{c^2-b^2}-\sqrt{c^2-a^2}}{\sqrt{c^2-b^2}+\sqrt{c^2-a^2}}), \qquad \text{(A7)}$$

$$\frac{\partial\Phi_{ac}}{\partial c}=\frac{1}{\pi}\{[(\sigma_2-\sigma_1)\frac{a}{\sqrt{c^2-a^2}}+\sigma_1\frac{b}{\sqrt{c^2-b^2}}]c\cos^{-1}\frac{a}{c}$$

$$-(\sigma_2-\sigma_1)\frac{a^2}{c}-\sigma_1\frac{ab\sqrt{c^2-a^2}}{c\sqrt{c^2-b^2}}\}. \qquad \text{(A8)}$$

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REFERENCES

1. Hsiao, C. C. and Sauer, J. A., "On Crazing of Linear High Polymers," Journal of Applied Physics, Vol. 21, No. 11, Nov. 1950, pp. 1071-1083.

2. Knight, A. D., "Stress Crazing of Transparent Plastics. Computed Stresses at a Nonvoid Craze Mark," Journal of Polymer Science, Part A, Vol. 3, 1965, pp. 1845-1857.

3. Warren, W. A., "Stress and Displacement Fields at the Tip of a Craze Containing a Crack," Polymer Engineering and Science, Vol. 24, No. 10, July 1984, pp. 814-819.

4. Walton, J. R. and Weitsman, Y., "Deformations and Stress Intensities Due to a Craze in an Extended Elastic Material," Journal of Applied Mechanics, Vol. 51, March 1984, pp. 84-92.

5. Williams, M. L., "Initiation and Growth of Viscoelastic Fracture," International Journal of Fracture Mechanics, Vol. 1, No. 4, 1965, pp. 292-310.

6. Willis, J. R., "Crack Propagation in Viscoelastic Media," Journal of Mechanics and Physics of Solids, Vol. 15, No. 4, 1967, pp. 229-240.

7. Graham, G. A. C., "The Correspondence Principle of Linear Viscoelasticity Theory for Mixed Boundary Value Problems Involving Time-Dependent Boundary Regions," Quarterly Applied Mathematics, Vol. 26, No. 2, 1968, pp. 167-174. "Two Extending Crack Problems in Linear Viscoelasticity Theory," Vol. 27, No. 4, 1969, pp. 497-507.

8. McCartney, L. N., "Crack Propagation, Resulting from a Monotonic Increasing Applied Stress, in a Linear Viscoelastic Material," International Journal of Fracture, Vol. 13, No. 5, Oct. 1977, pp. 641-654.

9. Schapery, R. A., "A Theory of Crack Initiation and Growth in Viscoelastic Media," International Journal of Fracture, I. Theoretical Development, Vol. 11, No. 1, Feb. 1975, pp. 141-159. II. Approximate Methods of Analysis, Vol. 11, No. 3, June 1975, pp. 369-388. III. Analysis of Continuous Growth, Vol. 11, No. 4, Aug. 1975, pp. 549-562.

10. Schapery, R. A., "A Method for Predicting Crack Growth in Nonhomogeneous Viscoelastic Media," International Journal of Fracture, Vol. 14, No. 3, June 1978, pp. 293-309. "Correspondence Principles and a Generalized J Integral for Large Deformation and Fracture Analysis of Viscoelastic Media," Vol. 25, 1984, pp. 195-223.

11. Hsiao, C. C. and Moghe, S. R., "Characterization of Random Microstructural Systems," Proceedings of the 1969 International Conference on Structure, Solid Mechanics and Engineering Design in Civil Engineering Materials, Southampton, England, John Wiley, London, Part I, 1971, pp. 95-103.

12. Chern, S. S. and Hsiao, C. C., "A Generalized Time-Dependent Theory on Craze Initiation in Viscoelastic Media," Journal of Applied Physics, Vol. 57, No. 6, March 1985, pp. 1823-1834.

13 Hsiao, C. C., "Fracture," Physics Today, Vol. 19, No. 3, March, 1966, pp. 49-53.

14. Kausch von Schmeling, H. H., Mohge, S. R. and Hsiao, C. C., "Influence of Reforming Processes on the Fracture Strength of Solids," Journal of Applied Physics, Vol. 38, No. 1, Jan. 1967, pp. 201-204.

15. Moghe, S. R., Kawatate, K., Cheung, J. E. and Hsiao, C. C., "Mechanical Breakdown of Oriented Solids under Time Dependent Loads," Proceedings of the Fifth International Congress on Pheology, Vol. 1, Oct. 7-11, 1968, Kycto, Japan, 1969, pp. 595-606.

16. Kuksenko, V. S. and Tamuzs, V. P., Fracture Micromechanics of Polymer Materials, Martinus Nijhoff Publishers, Hague, Boston, London, 1981, Chapter 7.

17. Chern, S. S. and Hsiao, C. C., "A Time Dependent Theory of Crazing Behavior in Polymers," Journal of Applied Physics, Vol. 53, No. 10, Oct. 1982, pp. 6541-6551.

18. Kramer, E. M., "Craze Fibril Formation and Breakdown," Polymer Engineering and Science, Vol. 24, No. 10, July 1984, pp. 761-769.

19. Doll, W., "Kinetics of Crack Tip Craze Zone Before and During Fracture," Polymer Engineering and Science, Vol. 24, No. 10, July 1984, pp. 798-808.

20. Verheulpen-Heymans, N., "Craze Failure by Midrib Creep," Polymer Engineering and Science, Vol. 24,. No. 10, July 1984, pp. 809-813.

21. Williams, J. G., "Modelling Crack Tip Failure Mechanisms in Polymers," Metal Science, Aug-Sept. 1980, pp. 344-350.

22. Chan, T., Donald, A. M., Kramer, E. J., "Film Thickness Effects on Craze Micromechanics," Journal of Material Science, Vol. 16, 1981, pp. 676-686.

23. Zhang, Z. D., Chern, S. S. and Hsiao, C. C., "Propagation of Crazing in Viscoelastic Media," Journal of Applied Physics, Vol. 54, No. 10, Oct. 1983, pp. 5568-5576.

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V. 1.

ANALYSIS OF CRACK-INDUCED-CRAZE IN POLYMERS

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Abstract—In this paper, the viscoelastic boundary element method is used to estimate the opening displacement and the envelope stress on the surface of an isolated crack-induced-craze system. To predict the propagation history of both the crack and the craze in a polymer sheet, the material properties of the glassy polymers are represented by a generalized linear viscoelastic model. In the calculation, the energy absorption criterion is utilized to determine the initial breaking time and the propagation rate. A sequence of numerical calculations of crack-induced-craze propagation by means of the boundary element method are carried out. Results are compared with the theoretical micromechanics predictions. Good agreements are obtained. This investigation illustrates that the three-step envelope stress profile is reasonably adequate for use in analysing polymer quasifracture problems. The stress concentration phenomenon, neglected on the Dugdale model, is taken into consideration in the present work.

INTRODUCTION

THE QUASIFRACTURE and fracture behaviors of a crack-induced-craze system in glassy polymers have been investigated extensively by many researchers both theoretically and experimentally up to now[1–8]. Generally speaking, the crack-induced-craze model in micromechanics accentuates the opening displacement, the envelope stress distribution around the interfaces of a craze, and especially the propagation processes of the craze and the crack. For some of the studies[5–7] the opening displacement profile has been determined experimentally first, from which the envelope stress distribution was evaluated by some analytical methods such as Fourier transform, whereas others obtain the envelope stresses based upon experimental observations first, then the opening displacement profile analytically. Some scientists[6, 9] considered that the yield property beyond the crack tip would determine the cracking and crazing properties, thus the Dugdale model was employed. Although the Dugdale model is thought to be able to predict the overall effect, it is questionable whether it is good enough in representing the true behavior of cracking and crazing properties in glassy polymers. Based on a number of experimental observations and theoretical analyses[6, 7], Hsiao *et al.* proposed the stress step-distribution model some years ago[2], which seems more reasonable and accurate in representing the properties of the region behind the craze tips.

Until now quite a lot of investigations on this subject matter have been reported, among which most were done by an experimental or analytical method. Papers using numerical methods for predicting the cracking and crazing behaviors have also appeared. Bevan[10, 11] studied the craze micromechanics by using linear boundary element method, in which the craze at crack tip was modeled by linear springs with constant stiffness. However, the linear elasticity and constant stiffness are not accurate enough to represent the properties of crack-induced-craze system in glassy polymers since it is well known that glassy polymers behave viscoelastically rather than elastically, and the drawing process is the dominant mechanism in polymer crazing. Therefore, some scientists considered the time dependent crack-craze propagation, such as Chern and Hsiao[2], McCartney[12] and Schapery[13] who appplied the linear viscoelastic model for studying the craze or crack propagation, and Schapery[14], also studied the crack growth in nonhomogeneous viscoelastic media for opening crack model. Some others[15, 16] investigated the nonlinear quasifracture properties using finite element method, and the time-dependent behavior of a craze using a viscoelastic boundary element method. In these studies, the polymer material around the crack or craze has been regarded as viscoelastic represented by a generalized Kelvin model. The relationship between the tractions and the displacement of fibril domains in a craze was represented by a convolution integral. Using the correspondence principle in linear viscoelasticity and the boundary element method, the time-dependent opening displacement field and the stress distribution along the craze surface envelope have been calculated numerically.

In this article, the viscoelastic boundary element method is utilized to study the propagation of a crack-induced-craze system. Meanwhile, the opening displacement profile and the envelope stresses on the craze interface surface have been obtained for different propagation steps. For comparison, the theoretical analysis using an energy balance method was formulated, with a three-step stress distribution for calculating the propagation of the crack-induced-craze system. The opening displacement profile of the crack-craze contour was also evaluated. Because of the change of the boundary conditions during the propagation of both the craze and the crack, Salamon's[17] superposition principle of a step-like propagation has been applied to this problem, and a numerical calculation sequence of the boundary element method has been derived. Comparing the numerical and analytical results, good agreement has been obtained. It appears that the step distribution of the envelope stress used in the analysis is a good approximation suitable in dealing with glassy polymers. The viscoelastic boundary element method has the advantage of ease in preliminary preparation, economical in computing time, and the required accuracy for studying the crack-induced-craze system propagation problem may be achieved without much difficulty.

THEORETICAL CONSIDERATIONS

Craze is filled with load bearing highly oriented fibril domains and cavitated networks formed by continuous flowing of the bulk polymer during the crazing process. Based upon some experimental observations[18, 19] and the craze model developed earlier[2], referring to a central fixed (x_1, x_3) coordinate system, an idealized symmetric crack-induced-craze system in a constant simple stress field σ_0 is shown in Fig. 1. Figure 2 shows $c(t)$ as the half-length of the crack-craze system and $a(t)$, the half-length of the crack only at time t. The stresses acting on the interfaces are called the envelope stresses with notation $\sigma_c(x_1, t)$ as a function of position and time. The half distance $w(x_1, t)$ between two craze or crack interfaces is known as the half opening displacement.

The half opening displacement of the crack-induced-craze system in a viscoelastic polymeric sheet can be obtained by using the correspondence principle in linear viscoelasticity theory[20]. The field equations and the constitutive relations are:

$$\sigma_{ij,j}(x_1, x_3, t) = 0, \tag{1}$$

$$\epsilon_{ij}(x_1, x_3, t) = \frac{1}{2}[U_{i,j}(x_1, x_3, t) + U_{j,i}(x_1, x_3, t)], \tag{2}$$

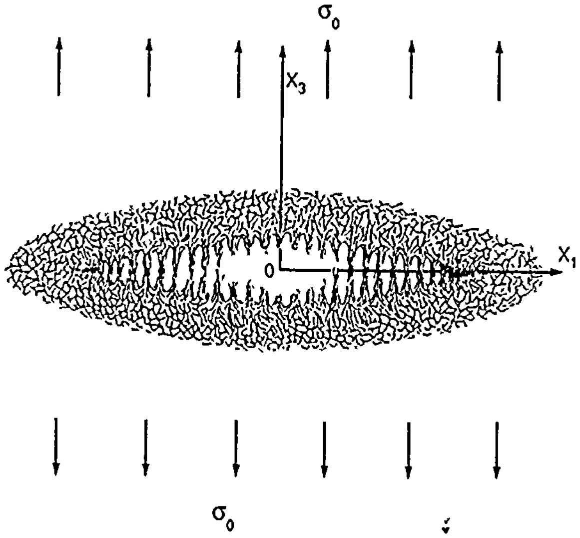

Fig. 1. Schematic fibrillar structure of a two-dimensional crack-induced craze system.

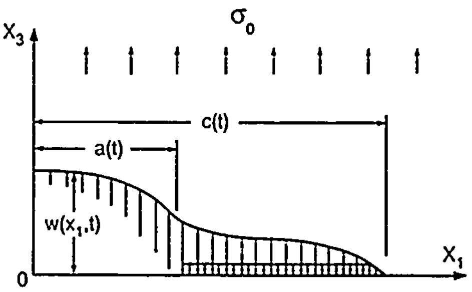

Fig. 2. A two-dimensional quadrantal crack-induced-craze system.

$$e_{ij}(t)=\int_{-\infty}^{t} J_1(t-\tau)\frac{\partial S_{ij}(\tau)}{\partial \tau}\,\mathrm{d}\tau, \tag{3}$$

$$\epsilon_{kk}(t)=\int_{-\infty}^{t} J_2(t-\tau)\frac{\partial \sigma_{kk}(\tau)}{\partial \tau}\,\mathrm{d}\tau, \tag{4}$$

where σ_{ij} is the stress tensor, ϵ_{ij} is the strain tensor, $U_{i,j}$ the displacement gradients, and J_1 and J_2 are respectively the shear and isotropic creep compliance functions of the original bulk medium.

$$S_{ij}(t)=\sigma_{ij}(t)-\frac{1}{3}\,\delta_{ij}\sigma_{kk}(t), \tag{5}$$

$$e_{ij}(t)=\epsilon_{ij}(t)-\frac{1}{3}\,\delta_{ij}\epsilon_{kk}(t), \tag{6}$$

with i, j and $k=1, 3$ denoting dummy variables. The boundary conditions are,

$$\sigma_{31}(x_1,0,t)=0, \qquad |x_1|<c(t), \tag{7}$$

$$\sigma_{33}(x_1,0,t)=\sigma_c(x_1,t), \qquad |x_1|<c(t), \tag{8}$$

$$\left.\begin{array}{ll}\sigma_{33}(x_1,x_3,t)=\sigma_0(t) & (9)\\ \sigma_{11}(x_1,x_3,t)=0 & (10)\\ \sigma_{13}(x_1,x_3,t)=0 & (11)\end{array}\right\}\quad \text{as } (x_1^2+x_3^2)\to\infty.$$

The opening displacement $w_0(x_1,t)$ is defined as

$$w_0(x_1,t)=U_3(x_1,0,t), \qquad |x_1|<c(t). \tag{12}$$

To solve this viscoelastic problem, the Laplace transform of the field equations and the boundary conditions is applied to reduce the time dependency. Then the solution to the transformed equations can be found by using Muskhelishvili's complex variable conformal mapping method[21] or Westergaard's complex variable stress function method[22] for an elastic medium when $c(t)$, $a(t)$ and $\sigma_c(x,t)$ remain unchanged with respect to time[23].

The time dependent solution of the original problem is obtained by a Laplace inversion. This solution is valid only if the boundary conditions are independent of time as mentioned earlier. These shortcomings can be surmounted by using a superposition method, i.e. a sequence of loading and unloading steps[17, 24], which yields,

$$w_0(x_1,t)=C_b(0)\Phi(x_1,t)+\int_0^t \dot{C}_b(t-\tau)\Phi(x_1,\tau)\,\mathrm{d}\tau, \tag{13}$$

where

$$\Phi(x_1, t) = \sigma_0\sqrt{c^2 - x_1^2} - \frac{2}{\pi}\int_0^c \sigma_c(\eta, t)\ln\left(c + \sqrt{c^2 - \eta^2}\right)\mathrm{d}\eta + \frac{2}{\pi}\int_0^{x_1} \sigma_c(\eta, t)\ln\left(x_1 + \sqrt{x_1^2 - \eta^2}\right)\mathrm{d}\eta + \frac{2}{\pi}\int_{x_1}^{c} \sigma_c(\eta, t)\ln\eta\,\mathrm{d}\eta, \tag{14}$$

and with an assumed constant strain ratio v, L^{-1} being the Laplace inversion:

$$C_b(t) = L^{-1}\frac{2(1 - s^2v^2)}{s^2\bar{E}(s)}, \tag{15}$$

where E is the relaxation modulus of the bulk polymer and $\bar{E}(s)$ represents the same in the Laplace domain s.

Taking into consideration the thickness of the primordial layer from which the fibril domain structure has been pulled out, the actual opening displacement of the system becomes[25, 26]:

$$w(x_1, t) = C_b(0)\Phi(x_1, t) + \int_0^t \dot{C}_b(t - \tau)\Phi(x_1, \tau)\,\mathrm{d}\tau + \int_{t_{x_1}}^{t} \frac{\dot{w}(x_1, \tau)}{\lambda(x_1, \tau)}\mathrm{d}\tau, \tag{16}$$

where t_{x_1} is the time when the crack-craze-system tip first reaches the point x_1, and λ is the draw ratio. The values of λ are found to be virtually unchanged along the periphery of the craze[8, 27–31], with only a slight increase in the central region and near the craze tip. Therefore, λ can be considered as a constant and the opening displacement reduces to:

$$w(x_1, t) = \frac{\lambda}{\lambda - 1}\left[C_b(0)\Phi(x_1, t) + \int_0^t \dot{C}_b(t - \tau)\Phi(x_1, \tau)\,\mathrm{d}\tau\right], \quad \text{for } a(t) \le x_1 \le c(t), \tag{17}$$

$$w(x_1, t) = C_b(0)\Phi(x_1, t) + \int_0^t \dot{C}_b(t - \tau)\Phi(x_1, \tau)\,\mathrm{d}\tau + \frac{1}{\lambda}\,w(x_1, t_a), \quad \text{for } 0 \le x_1 \le a(t), \tag{18}$$

where t_a denotes the time when the crack tip arrives at the point $x_1 = a$.

The crack and craze lengths can be obtained by considering the energy balance. The energy absorbed by the craze[32] is spent to nucleate fibril domains near the craze tips, to pull fibrils out of the craze envelope surface and to break the fibril boundles[4]. With the supposition that the fibril nucleation rate at the craze tips is proportional to the system growth velocity $\dot{c}(t)$[33] the energy rate necessary for craze tip growth is $\Gamma_c\dot{c}(t)$. Similarly, the energy rate required for the crack tip growth is $\Gamma_a\dot{a}(t)$, where Γ_c and Γ_a are material constants. Based upon the assumption that the energy rate required for drawing fibrils out of the craze envelope surface is proportional to the new fibril domain surface creation rate $\dot{S}(t)$, and use the proportionality constant Γ_s, we have the following local energy rate balance equation:

$$\dot{H}_c(t) = \Gamma_c\dot{c}(t) + \Gamma_a\dot{a}(t) + \Gamma_s\dot{S}(t) \tag{19}$$

where $\dot{H}_c(t)$ is the energy absorption rate of the quadrantal system. Here the strain energy, energy dissipation and kinetic energy have been neglected since during steady state they are negligible compared with the other rate quantities. With this simplification and the terms defined earlier, it follows that[2, 3, 32–34]

$$\dot{H}_c(t) = \int_0^c \sigma_c(x_1, t)\frac{\partial w(x_1, t)}{\partial t}\mathrm{d}x_1, \tag{20}$$

$$\dot{S}(t)=\int_0^c 4\frac{V_f(x_1,t)}{d(x_1,t)}\frac{\partial w(x_1,t)}{\partial t}\,dx_1. \tag{21}$$

where V_f is the volume fraction of the crazed polymer and d is the diameter of the individual fiber domains.

Substituting into (19) results in

$$\int_0^c\left(\sigma_c-4\frac{\Gamma_s V_f}{d}\right)\frac{\partial w(x_1,t)}{\partial t}\,dx_1=\Gamma_c\dot{c}+\Gamma_a\dot{a}. \tag{22}$$

BOUNDARY ELEMENT CALCULATION

The viscoelastic boundary element method is applied to a polymer sheet with an isolated crack-induced-craze centrally located. The sheet is subjected to a unit step tension stress $\sigma_0 H(t)$, where $H(t)$ is the unit step function of time t. The material properties of the bulk polymer around the crack-induced-craze system is considered to be linearly viscoelastic. The constitutive equation can be expressed by convolution integrals eqs (3) and (4). For a linear viscoelastic polymer, a very convenient expression for the creep compliance $J(t)$ is obtainable by using a generalized Kelvin model[2, 35, 36] composed of a series of Voigt elements as described below:

$$J(t)=J_0+\sum_{i=1}^{n}J_i(1-e^{-t/\tau_i}), \tag{23}$$

where J_0 and J_i are constants and τ_i, retardation times. Since some experimental results[32] have shown that the strain ratio $\nu(t)$ remains virtually unchanged for long creep times, the viscoelastic relaxation modulus $E(t)$ can be shown to be of the following form:

$$E(t)=L^{-1}\left[\frac{1}{s^2\bar{J}(s)}\right]=L^{-1}\left[s\left(J_0+\sum_{i=1}^{n}J_1\frac{1}{1+s\tau_i}\right)\right]^{-1}, \tag{24}$$

where the bar indicates Laplace transform and L^{-1}, Laplace inversion. Taking into consideration of the fibril structure of the craze beyond the crack tip, the two opposite interfaces of the craze region are connected by the fibrillar structure as shown in Fig. 2, which is formed by a fibrillation process due to the advances of the crack. These connections are capable of transmitting load and can sustain large deformations. The stress state of an individual fibril domain is considered as an uniaxial tension. The relationship between the traction $T_3(x_1, t)$ and the opening displacement $U_3(x_1, t)$ of the crack-induced-craze system can be shown as follows:

$$\begin{aligned}T_3(x_1,t)&=-\int_{-\infty}^{t}K(x_1,t-\tau)\frac{\partial U_3(x_1,\tau)}{\partial\tau}\,d\tau\\&=K(x_1,0)U_3(x_1,t)+\int_0^t\dot{K}(x_1,t-\tau)U_3(x_1,\tau)\,d\tau,\end{aligned} \tag{25}$$

$$\text{on } x_1<c \text{ and } x_3=0,$$

where $K(x_1, t)$ is the stiffness per unit area on the craze surface and $K(x_1, 0)$, the initial value of $K(x_1, t)$ at x_1. Using the molecular orientation theory[16], the stiffness turns out to be:

$$K(x_1,t)=L^{-1}\left[\frac{K(x_1,0)J_0}{s^2\bar{J}(s)}\right]. \tag{26}$$

It should be noted that the drawing process is the main mechanism of craze thickening. Thus

$K(x_1, t)$ here is not stiffness in the usual sense. It must take the drawing process into consideration.

The traction $T_3(x_1, t)$ acting along the craze envelope becomes

$$T_3(x_1, t) = -L^{-1}[sK(x_1, s)U_3(x_1, s)]. \tag{27}$$

Because of the symmetry of the problem, only a quarter of the uniform sheet of width B, length L is considered in the boundary element calculation. The boundary conditions around the quadrantal sheet with isolated crack-induced-craze system are:

$$\begin{cases} T_3(x_1, t) = 0, \\ T_1(x_1, t) = 0, \end{cases} \qquad 0 \le x_1 \le a(t),\ x_3 = 0, \tag{28}$$

$$\begin{cases} T_3(x_1, t) = -\displaystyle\int_0^t K(x_1, t-\tau)\frac{\partial U_3(x_1, \tau)}{\partial \tau}\,\mathrm{d}\tau, \\ T_1(x_1, t) = 0, \end{cases} \qquad a(t) \le x_1 \le c(t),\ x_3 = 0, \tag{29}$$

$$\begin{cases} U_3(x_1, t) = 0, \\ T_1(x_1, t) = 0, \end{cases} \qquad c(t) < x_1 \le B,\ x_3 = 0, \tag{30}$$

$$\begin{cases} T_1(x_1, t) = 0, \\ T_3(x_3, t) = 0, \end{cases} \qquad x_1 = B,\ 0 \le x_3 \le L, \tag{31}$$

$$\begin{cases} T_1(x_1, t) = 0, \\ T_3(x_1, t) = \sigma_0 H(t), \end{cases} \qquad 0 \le x_1 \le B,\ x_3 = L, \tag{32}$$

$$\begin{cases} U_1(x_3, t) = 0, \\ T_3(x_3, t) = 0, \end{cases} \qquad x_1 = 0,\ 0 \le x_3 \le L. \tag{33}$$

As the crack-craze-system propagates, new crack and craze surfaces are created. The associated energy release rate is

$$\dot{D}(t) = \Gamma_a \dot{a}(t) + \Gamma_c \dot{c}(t), \tag{34}$$

where Γ_a and Γ_c represent, respectively, the coefficients of fracture work for crack and crack-induced-craze, and $\dot{a}(t)$ and $\dot{c}(t)$ are, respectively, the crack and the system propagation rates. The energy absorption rate for the crack-induced-craze system is expressed by eq. (19). The energy absorption criterion claims that

$$\dot{D}(t) = \dot{H}_c(t),$$

$$\text{i.e. } \Gamma_a \dot{a}(t) + \Gamma_c \dot{c}(t) = \int_a^c \sigma_c(x_1, t)\frac{\partial \dot{U}_3(x_1, t)}{\partial t}\,\mathrm{d}x_1. \tag{35}$$

In addition, sometimes the constant crack opening displacement criterion can be used as the propagation criterion of the crack-induced-craze system. However, these two criteria are the same if the deformation associated with the crack tip is fixed with respect to time, a situation which occurs when the applied stress is constant. Thus both the crack and the craze propagate at the same velocity[37]. In this case, the opening displacement of the crack-induced-craze system is of the form:

$$U_3(x_1, t) = f[x_1 - c(t)], \tag{36}$$

which means that the shape of the crack and that of the craze are conserved during the propagation, i.e.

$$\frac{\mathrm{d}U_3}{\mathrm{d}t} = -\dot{c}(t)f'[x_1 - c(t)]. \tag{37}$$

If the envelope stress is considered as the following step functional distribution:

$$\sigma_c = \begin{cases} \alpha_1\sigma_0 & a(t) \le x_1 \le b(t), \\ \alpha_2\sigma_0 & b(t) < x_1 \le c(t), \end{cases} \tag{38}$$

where $c(t)$-$b(t)$ is a small quantity representing the stress growth at the craze tip, then in the analysis, the energy absorption criterion formula (35) will be:

$$\Gamma_a\dot{a}(t) + \Gamma_c\dot{c}(t) = \int_a^b \alpha_1\sigma_0\frac{\partial U_3}{\partial t}\,\mathrm{d}x_1 + \int_b^c \alpha_2\sigma_0\frac{\partial U_3}{\partial t}\,\mathrm{d}x_1, \tag{39}$$

$$\Gamma_a + \Gamma_c = \sigma_0[\alpha_1 U_3(a, t) - (\alpha_1 - \alpha_2)U_3(b, t)], \tag{40}$$

where $U_3(a, t) = U_3(x_1, t)|_{x_1=a}$ and $U_3(b, t) = U_3(x_1, t)|_{x_1=b}$, are the opening displacements of the crack tip and the craze tip, respectively. Noting that $U_3(b, t) \ll U_3(a, t)$, eq. (40) becomes:

$$U_3(a, t) = \frac{\Gamma_a + \Gamma_c}{\sigma_0\alpha_1}, \tag{41}$$

which is the constant crack opening displacement criterion in linear fracture mechanics. Therefore, in the theoretical and numerical analyses of the propagation of crack-induced-craze system, either the energy absorption criterion or the crack opening displacement criterion may be applied to determine the propagation rates at different times.

The viscoelastic boundary element method for analysing crack-induced-craze system in polymers has been described in detail in an earlier study[16]. Using the correspondence principle in linear viscoelasticity theory, a series of transformed simultaneous algebraic equations can be solved. The displacement U_k and traction T_k on the boundary involving the crack-craze surface can be obtained in the Laplace domain. Based upon Schapery's collocation numerical method[38] for Laplace inversion, the components of the stress and displacement fields at any point can be represented for the fixed time t by the series:

$$F(t) = C_0 + C_1 t + \sum_{m=1}^{M} A_m\,\mathrm{e}^{-b_m t}, \tag{42}$$

with C_0, C_1, A_m and b_m being constants. Taking the Laplace transformation of eq. (42) and multiplying by the transform parameter s yield:

$$s\bar{F}(s) = C_0 + \frac{C_1}{s} + \sum_{m=1}^{M}\frac{A_m}{1 + \dfrac{b_m}{s}}, \tag{43}$$

where $F(s)$ designates the Laplace transform of a time function $F(t)$. When time t goes to infinity the function $F(t)$ should remain finite. Therefore the constant c_1 has to be chosen as zero. After a sequence of s_k $(k = 1, 2, \ldots M + 1)$ is selected, the constants C_0 and A_m can be calculated by the viscoelastic boundary element method, and the opening displacement U_{3_j} and the envelope stress T_{3_j} on the jth boundary element of crack-craze system surface for time t become

$$U_{3_j} = D_{0j} + \sum_{m=1}^{M} D_{m_j}\,\mathrm{e}^{-\alpha_m t}, \tag{44}$$

$$T_{3j} = G_{0j} + \sum_{m=1}^{M} G_{m_j}\,\mathrm{e}^{-\beta_m t}. \tag{45}$$

Substituting the above two equations into the energy absorption criterion (35) for fracture, the breaking or the initial propagation time t of the crack-craze system for discreted boundary elements will be of the form:

$$t_b = \frac{l_T(\Gamma_a + \Gamma_c)}{\sum_{j=1}^{N} \left(T_{3j} - 4\frac{V_f}{d_f}\right) \frac{\mathrm{d}U_{3j}}{\mathrm{d}t}\, l_j}, \tag{46}$$

where l_T is the length of the boundary element on the crack tip and l_j the jth element length on the crack-craze system, U_{3j} and T_{3j} are respectively the displacement and the envelope stress on jth boundary element of the crack-craze system surface before propagation. After the commencement of the propagation of the crack-craze system, both the boundary shape and the boundary conditions will change as a function of time. Therefore, the numerical solutions U_{3j} and T_{3j} are not valid for propagating crack-craze system because the linear viscoelastic correspondence principle can only be applied to the problem with time independent boundary conditions. These restrictions can be removed by a generalized method of superposition principle, which uses stepwise development boundary conditions formulized by Salamon[17]. This method is utilized here to deal with the changing boundary conditions. A time dependent function $F(t)$ after n steps in the time interval $t_n < t < t_{n+1}$ may be expressed as follows:

$$F(t) = \sum_{i=1}^{N-1} \{F_i[r_i, (t - t_i)] - F_i[r_i, (t - t_{i+1})]\} + F_n[r_n, (t - t_n)], \tag{47}$$

where r_i is some critical linear dimension and F the solution, i.e. the opening displacement or the traction, which can be solved by the linear viscoelastic correspondence principle in the ith time step, t_n and t_{n+1} are the nth and the $(n+1)$th time steps. Similarly, the envelope traction T_{3j} and the displacement U_{3j} on jth element of the crack-craze system after the nth element propagates can be written as:

$$\begin{aligned} U_{3j}^{(n)} = {} & \sum_{i=1}^{M} D_{ij}^{(1)}(\mathrm{e}^{-\alpha_i t_1} - 1)\, \mathrm{e}^{-\alpha_i(t_2+t_3+\cdots+t_n)} \\ & + \sum_{i=1}^{M} D_{ij}^{(2)}(\mathrm{e}^{-\alpha_i t_2} - 1)\, \mathrm{e}^{-\alpha_i(t_3+t_4+\cdots+t_n)} + \cdots\cdots \\ & + \sum_{i=1}^{M} D_{ij}^{(n-1)}(\mathrm{e}^{-\alpha_i t_{n-1}} - 1)\, \mathrm{e}^{-\alpha_i t_n} \\ & + \sum_{i=1}^{M} D_{ij}^{(n)}\, \mathrm{e}^{-\alpha_i t_n} + D_{0j}^{(n)}, \end{aligned} \tag{48}$$

$$\begin{aligned} T_{3j}^{(n)} = {} & \sum_{i=1}^{M} G_{ij}^{(1)}(\mathrm{e}^{-\beta_i t_1} - 1)\, \mathrm{e}^{-\beta_i(t_2+t_3+\cdots+t_n)} \\ & + \sum_{i=1}^{M} G_{ij}^{(2)}(\mathrm{e}^{-\beta_i t_2} - 1)\, \mathrm{e}^{-\beta_i(t_3+t_4+\cdots+t_n)} + \cdots\cdots \\ & + \sum_{i=1}^{M} G_{ij}^{(n-1)}(\mathrm{e}^{-\beta_i t_{n-1}} - 1)\, \mathrm{e}^{-\beta_i t_n} \\ & + \sum_{i=1}^{M} G_{ij}^{(n)}\, \mathrm{e}^{-\beta_i t_n} + G_{0j}^{(n)}. \end{aligned} \tag{49}$$

According to the principle, the calculation procedures are expounded as follows. The first step is to calculate the coefficients D_{ij} and G_{ij} on the jth element using the viscoelastic boundary element method, in which the length of crack is a_1 and that of the crack-craze system c_1. Then substituting D_{ij} and G_{ij} $(i = 0, 1, \ldots M)$ into eq. (35) the transition or the initial breaking time can be obtained. After that, both crack and craze propagate a distance of one element length for the steady state propagation case. Correspondingly the boundary conditions on the craze surface will shift forward by a length of one element. The second step is the calculation of D_{ij} and G_{ij} ($i = 0, 1, \ldots M$) on the jth element using the same viscoelastic boundary element method. But at this time the length of crack is $a_1 + l$ and that of system $c_1 + l$, where l is the length of an element. Substituting these coefficients, together with D_{ij} and G_{ij}, into eqs (25) and (26), the opening displacement U_{3j} of the system surface, the envelope traction T_{3j} can be obtained. The breaking time t for the system to propagate to the next element can again be calculated from the energy absorption criterion eq. (35). The same procedure continues to be iterated until the system grows to the nth element. At that time, the coefficients D_{ij} and G_{ij} are evaluated. And the opening displacement U_{3j} and the envelope stress T_{3j} on the jth element can be obtained at time t_n.

RESULTS

A quarter of the sheet used in the calculation using the boundary element method has unit thickness, width $B = 500$ μm and length $L = 600$ μm. The initial lengths of the system and the craze are taken to be $c(0) = 98$ μm and $a(0) = 38$ μm respectively. The total number of the boundary elements is 155 with the smallest element of the length 4 μm located on the craze surface. The mesh construction is shown in Fig. 3, where the elements around the craze tip are drawn in an enlarged scale. The surface of the crack-induced-craze system is divided into 23 boundary elements. Beyond the craze tip there are 10 elements in 40 μm span.

The viscoelastic material properties are represented by a generalized Kelvin model (23) with other material constants taken to be as follows:

$$n = 4,$$

$$J_0 = 4.17 \times 10^{-4}\ \mathrm{m^2/MN},$$

$$J_1 = 0.71 \times 10^{-4}\ \mathrm{m^2/MN},$$

$$J_2 = 0.62 \times 10^{-4}\ \mathrm{m^2/MN},$$

$$J_3 = 0.43 \times 10^{-4}\ \mathrm{m^2/MN},$$

$$J_4 = 0.31 \times 10^{-4}\ \mathrm{m^2/MN},$$

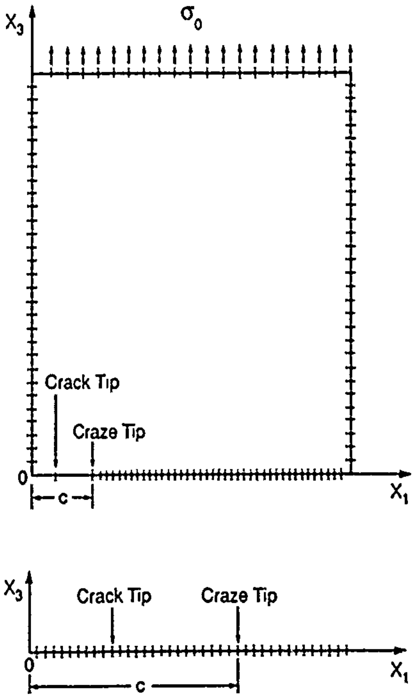

Fig. 3. Boundary element mesh with craze tip shown in an enlarged scale.

$$\nu = 0.3,$$
$$\tau_1 = 1.0\,\text{h},$$
$$\tau_2 = 10.0\,\text{h},$$
$$\tau_3 = 80.0\,\text{h},$$
$$\tau_4 = 110.0\,\text{h},$$
$$\Gamma_c = 0.3\,\text{J/m}^2,$$
$$\Gamma_a = 2.72\,\text{J/m}^2,$$
$$\alpha_1 = 1.21,$$
$$\alpha_2 = 2.58.$$

The following quantities occurring in the calculations of theoretical method are also used[39–41]:

$$\lambda = 2,$$
$$\Gamma_s = 0.231\,\text{J/m}^2,$$
$$d = 4.4\,\text{nm},$$

which represent the properties of polycarbonate. The applied stress is $\sigma_0 = 37.4\,\text{MN/m}^2$.

The first kind of calculation is based upon the stiffness distribution shown in Fig. 4. Correspondingly, the instantaneous opening displacement of the crack-induced-craze system is plotted in Fig. 5 against the distance measured from the center of crack. The data points indicating the experimental observations[6, 8], triangles represent the theoretical solutions, and the solid curve is the result obtained by the boundary element method. Initially the distribution of the stress normal to the surface is shown in Fig. 6.

When the applied constant stress σ_0 is maintained, the opening displacement of the system increases as a result of creep and the drawing of the fibril domains. According to the energy absorption criterion, the craze-crack transition time $t_b = t_1$ can be determined numerically. Then the crack-craze system propagates steadily and the case that the crack and the system have the same velocity[9] is considered here. During the calculation of the propagation rate the stiffness on the craze-surface is shifted stepwise by one element. Figure 7 shows the time dependent normalized lengths of the crack-induced-craze system, where the points are obtained by the boundary element method and the solid line is calculated by theoretical method. As can be seen from the figure, the propagation rate at the steady state is almost constant. After a certain period of time, both the crack and the system propagation rates increase drastically. The opening displacement profile of the crack-craze system as a function of time is shown in Fig. 8. The

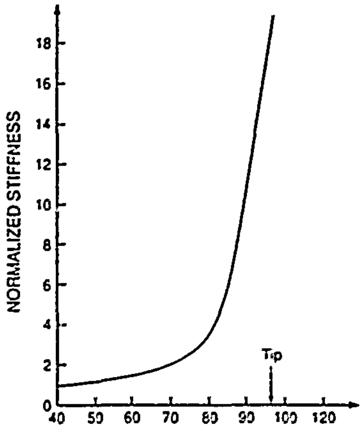

Fig. 4. Stiffness distribution in craze region.

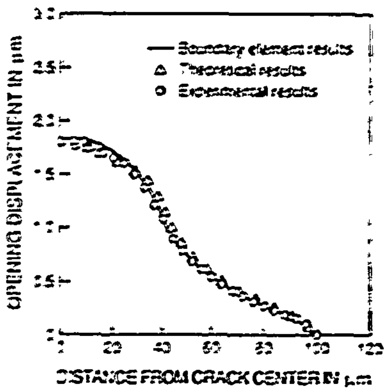

Fig. 5. Opening displacement profile of crack-craze system.

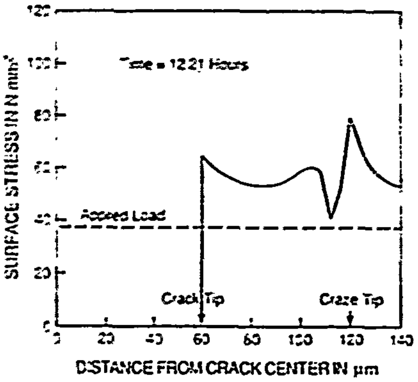

Fig. 6. Initial envelope stress on surface of craze region.

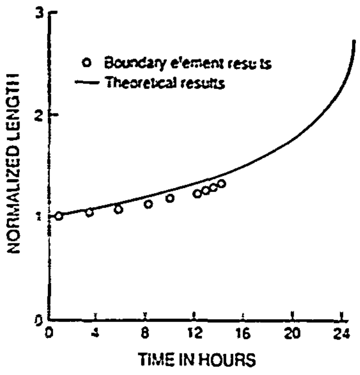

Fig. 7. Time dependent normalized length of crack-induced-craze system.

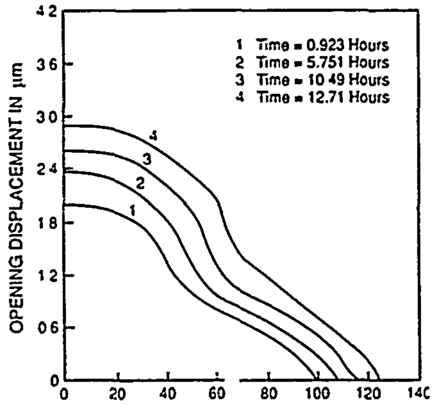

Fig. 8. Opening displacement of crack-craze system at several time steps.

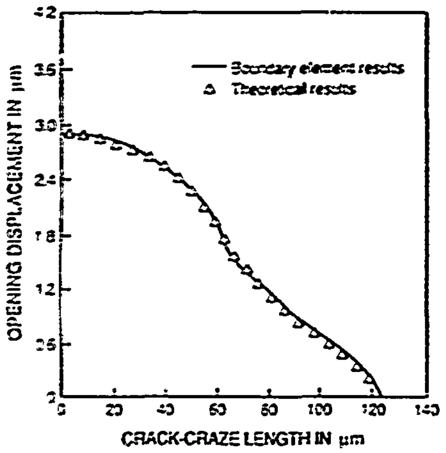

Fig. 9. Comparison of opening displacements by boundary element method and theoretical analysis.

opening displacement profiles at different times exhibit somewhat similar shape. Figure 9 shows the comparison between the results obtained by the boundary element method and the analytical results at time $t = 12.21$ h. A very good agreement is obtained. Figure 10 shows the envelope stress distribution in the craze region.

The closeness between the theoretical results and those obtained by the boundary element method in Figs 5, 7 and 9 connotes that the boundary element results are generally in good agreement with the analytical results. The accuracy depends on the mesh construction and the type of element used. Constant elements used in the boundary element calculation procedure yield satisfactory results in this case. The use of higher order elements, such as first and second order elements, or much smaller elements would improve the accuracy. The stress distribution on the craze surface has almost the same shape and magnitude throughout the propagation. In fact, it has been suggested that the Dugdale model is not fully adequate for analysis in describing the craze envelope stress. Nevertheless, the analytical formulation using the three-step distribution function has been shown to be a reasonable and good approximation for analysing the isolated crack-craze system. As can be seen in Figs 6 and 10, there is a deep stress minimum just behind the tip of the craze. This characteristic feature persisted during the course of this investigation. This is somewhat similar to the results obtained earlier using the finite element method. Two extreme values in the envelope stress distribution have occurred. Like in the present case a minimum envelope stress is located at some point behind the craze tip where the stiffness gradient changes sharply and a maximum one occurs at the tip. Both of these extremes have been obtained by either analytical or experimental methods[1, 2, 42, 43, 44]. It is hoped that this phenomenon will be studied further to acquire a better understanding of its behavior with respect to the crack-craze system.

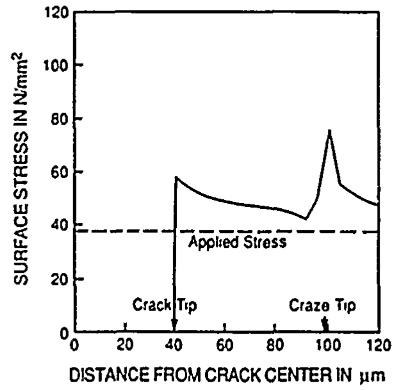

Fig. 10. Envelope stress on craze surface at time = 12.21 h.

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REFERENCES

[1] S. S. Chern and C. C. Hsiao, *J. appl. Phys.* **52**, 5994 (1981).
[2] S. S. Chern and C. C. Hsiao, *J. appl. Phys.* **53**, 6541 (1982).
[3] Z. D. Zhang, S. S. Chern and C. C. Hsiao, *J. appl. Phys.* **54**, 5568 (1983).
[4] S. S. Chern and C. C. Hsiao, *Proc. ICF6*, New Delhi, India, p. 2603 (1984).
[5] B. D. Lauterwasser and E. J. Kramer, *Phil. Mag.* **A39**, 469 (1979).
[6] Wen-chou V. Wang and E. J. Kramer, *J. Mater. Sci.* **17**, 2013 (1982).
[7] E. H. Andrews, *Development in Polymer Fracture*—1, p. 78. Applied Science Publishers Ltd, London (1979).
[8] A. M. Donald and E. J. Kramer, *J. Mater. Sci.* **16**, 2977 (1981).
[9] Elio Passaglia, *Polymer* **23**, 754 (1982).
[10] L. Bevan, *J. Polym. Sci. Phys.* **19**, 1759 (1981).
[11] Idem, *J. appl. Polym. Sci.*, **27**, 4263 (1982).
[12] L. N. McCartney, *Int. J. Fracture* **13**, 641 (1977); **14**, 547 (1978).
[13] R. A. Schapery, *Int. J. Fracture* **11**, 141, 369, 549 (1975).
[14] R. A. Schapery, *Int. J. Fracture* **14**, 293 (1978).
[15] B. N. Sun and C. C. Hsiao, *J. appl. Phys.* **57**, 170 (1985).
[16] B. N. Sun and C. C. Hsiac, to be published.
[17] M. D. G. Salamon, *Advances in Rock Mechanics*, Part B, National Academy of Science, (1974).
[18] P. Beahan, M. Bevis and D. Hull, *J. Mater. Sci.* **8**, 162 (1972).
[19] X. C. Lu, C. G. Fan and T. Z. Qian, *Proc. ICF Int. Symp. Fracture Mech.*, Beijing, p. 1075 (1983).
[20] R. M. Christensen, *Theory of Viscoelasticity—An Introduction*. Academic Press, New York (1971).
[21] N. I. Muskhelishvili, *Some Basic Problems of Mathematical Theory of Elasticity*, p. 340. Noordhoff, Gronigen, The Netherlands (1953).
[22] H. M. Westergaard, *J. appl. Mech.* **6**, 49 (1939).
[23] N. V. Heymans and J. C. Bauwens, *J. Mater. Sci.* **11**, 7 (1976).
[24] H. K. Mueller, Ph.D thesis, California Institute of Technology (June, 1968).
[25] J. Murray and D. Hull, *J. Mater. Sci.* **6**, 1277 (1971).
[26] S. S. Chern, Univ. of Minn., Mpls, Minn., Ph.D thesis (Aug 1983).
[27] A. M. Donald and E. J. Kramer, *J. Polym. Sci. Phys.* **20**, 1129 (1982).
[28] T. Chan, A. M. Donald and E. J. Kramer, *J. Mater. Sci.* **16**, 676 (1981).
[29] R. P. Kambour, *J. Polym. Sci., Part A* **2**, 4165 (1964).
[30] H. G. Krenz *et al. J. Mater. Sci.* **11**, 2198 (1976).
[31] E. J. Kramer *et al.*, *J. Polym Sci. Phys.* **16**, 349 (1978).
[32] S. S. Pang, Z. D. Zhang, S. S. Chern and C. C. Hsiao, *J. Folym. Sci. Phys.* **23**, 683 (1985).
[33] S. S. Chern and C. C. Hsiao, *J. appl. Phys.* **53**, 6541 (1982).
[34] H. H. Kaush and M. Dettermaier, *Polym. Bull.* **3**, 565 (1980).
[35] A. J. Stavarman, F. Schwarzl, *Die Physik der Hochpolymeren* (Edited by H. A. Stuart). Springer, Berlin (1965).
[36] Z. Rigbi, *Appl. Polym. Symposia*, No. 5, p. 1 (1967).
[37] P. Trassaert, R. Schirrer, *J. Mater. Sci.* **18**, 3004 (1983).
[38] R. A. Schapery, *U.S. Natl Congr. appl. Mech.*, p. 1075 (1961).
[39] A. M. Donald and E. J. Kramer, *J. Polym. Sci. Phys.* **20**, 899 (1982).
[40] E. J. Kramer, *Polym. Engng Sci.* **24**, 761 (1984).
[41] N. V. Heymans, *Polym. Engng Sci.* **24**, 809 (1984).
[42] J. C. Newman, Jr, *AIAA J.* **13**, 1017 (1975).
[43] J. C. Newman, Jr., *ASTM STP* **56**, 637 (1977).
[44] E. J. Kramer, *Advances in Polymer Science*, Vols. 52/53, *Crazing in Polymers 1*. Springer, Berlin, Heidelberg (1983).

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V. 2.

Analyzing Polymer Crazing as Quasifracture

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Synopsis

This paper deals with a viscoelastic boundary element method for analyzing a polymer quasifracture usually called a craze in polymers. A time-dependent boundary stiffness is considered on the quasifracture envelope surface. The viscoelastic property of the glassy polymer is represented by a generalized Kelvin model with multiple retardation times. According to the linear viscoelastic correspondence principle, the associated elasticity solution can be solved by applying the general integral boundary element method. Then the viscoelastic solution in the time domain can be obtained by applying a collocation Laplace inversion transformation. Using these methods, the quasifracture problem composed of an isolated craze opening with time-dependent stiffness traction in a stressed rectangular plate is analyzed. The displacement profile and the stress distribution around the craze envelope surface are computed.

INTRODUCTION

The craze or quasifracture behavior of glassy polymers has been studied recently by many scientists using theoretical and/or experimental methods.[1-3] Only a few papers reported the linear elastic quasifracture behavior using numerical methods. Bevan[4] applied both the elastic finite-element method and boundary-element method with linear boundary condition for investigating the craze problem. Recently, using the nonlinear finite element method, the stress distribution around the envelope surface and the displacement profile associated with a craze have been reported.[5] However, since the boundary element method has currently become a powerful technique for solving boundary value problems, including some nonlinear ones, it is worthy of utilization, since it has several advantages over the finite-element method. The number of unknowns in the calculation system depends only on the boundary discretization rather than upon the discretization of the whole volume of the material body as in the finite element method. The singular kernels in the integral equations weigh the unknown quantities near a singular point more heavily than those far away, and the resultant matrices are generally well behaved. The physical quantities obtained by differentiation of the primary variables such as the stresses obtained from displacements are determined pointwise inside and on the body. Thus there is less chance to have discontinuities. This is especially important in problems having viscoelastic deformations and, in particular, viscoelastic fracture mechanics problems.[6] In addition, this method takes less computing time and yields greater accuracy than those problems analyzed using the finite element method under somewhat similar situations. Therefore, in the case wherein highly localized stresses may exist, more elements can be introduced so that any possible singularities will not be suppressed by the analysis. Since the quasifracture

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behavior of crazing is important for studying engineering plastics and polymer composites, in this paper a viscoelastic boundary-element method for analyzing polymer quasifracture and determining the displacement field has been developed. In this attempt, emphasis is placed on the procedural development of the method. The measured displacement field obtained earlier has been employed[3] in the computation.

It is well known that glassy polymers behave viscoelastically. Using the correspondence principle in the linear theory of viscoelasticity, the quasifracture behavior of a polymer can be calculated from the solution of an associated elasticity problem by means of a numerical method; then inversion yields the required time-dependent response. Therefore, in this paper the boundary element method is applied to solve the associated elasticity problem in the Laplace domain. By applying the numerical Laplace inversion technique developed by Schapery[7] and Cost,[8] the associated elasticity solution can be transformed from the Laplace domain back into the time domain. There are several reports dealing with the use of the viscoelastic boundary element method. For simple specific viscoelastic models, Kusama and Mitsui[9] developed an improved collocation method and applied the boundary element method to solve a Kelvin viscoelastic model. Rizzo and Shippy[10] used the direct boundary integral method to solve a standard linear viscoelastic model. Wang and Crouch[11] applied the displacement discontinuity boundary element method and collocation inversion technique to solve a rock mechanics problem represented by a Burgers model. In this paper the general boundary element method together with the collocation inversion technique is used to solve an isolated quasifracture having a generalized Kelvin model behavior with multiple retardation times. In using such a method, the prescribed boundary condition may be either the displacements or the tractions. For a quasifracture problem the boundary condition on the craze envelope surface is prescribed in a stiffness form. By considering the molecular orientation mechanism[12] of the craze fibril domains, the boundary displacement of a craze envelope surface may be represented by a convolution integral. Then the displacement field and the stress distribution along a craze surface envelope can be calculated in several time steps. It is interesting to show that the calculated stress distribution along the craze envelope surface did not change very much with respect to initial zero time and several hundred hours.

FUNDAMENTAL BOUNDARY VALUE PROBLEM

The governing equations for the quasifracture boundary value problem are the equilibrium equations in terms of the stress components σ_{ij}, relations between displacements, u_i and strain components ϵ_{ij} together with a set of constitutive equations. The stress and displacement fields must satisfy the prescribed boundary conditions on the craze envelope surface and other boundaries. They are, in a rectangular coordinate system $(0 - x_1, x_2, x_3)$,

$$\sigma_{ij,j}(x_1, x_3, t) = 0, \tag{1}$$

$$\epsilon_{ij}(x_1, x_3, t) = \tfrac{1}{2}\left[u_{i,j}(x_1, x_3, t) + u_{j,i}(x_1, x_3, t)\right]. \tag{2}$$

The constitutive equations can be written in integral form as

$$e_{ij(t)} = \int_{-\infty}^{t} J(t-\tau)\frac{\partial S_{ij}(\tau)}{\partial\tau}\,d\tau, \tag{3}$$

$$\epsilon_{kk(t)} = \int_{-\infty}^{t} B(t-\tau)\frac{\partial \sigma_{kk}(\tau)}{\partial\tau}\,d\tau, \tag{4}$$

where $J(t)$ and $B(t)$ are, respectively, the shear and bulk creep compliances; σ_{kk} and ϵ_{kk} are, respectively, the hydrostatic stresses and strains by implying the summation convention. S_{ij} and e_{ij} are, respectively, the deviatoric components of stress tensor σ_{ij} and strain tensor ϵ_{ij} and are related to other stress and strain components as follows:

$$S_{ij} = \sigma_{ij} - \tfrac{1}{3}\delta_{ij}\sigma_{kk}, \tag{5}$$

$$e_{ij} = \epsilon_{ij} - \tfrac{1}{3}\delta_{ij}\epsilon_{kk}, \tag{6}$$

where δ_{ij} are delta functions.

In a linear viscoelastic polymer, a very good approximation[3,13,14] for the tensile creep compliance $D(t)$ is obtainable using a generalized Kelvin model composed of a series of Voigt elements, or simply it can be mathematically represented in the following form:

$$D(t) = D_0 + \sum_{\eta=1}^{n} D_\eta\left[1 - \exp\left(-\frac{t}{\tau_\eta}\right)\right], \tag{7}$$

where D_0 and D_η are constants and τ_η are discrete retardation times. Now if one adopts the notation and definition that

$$\bar{f}(x_1, x_3, s) = \int_0^\infty f(x_1, x_3, t)\, e^{-st}\,dt, \tag{8}$$

where $\bar{f}(x_1, x_3, s)$ is the Laplace transform of the time-dependent function $f(x_1, x_3, t)$ with s as the Laplace parameter, then it can be shown that the shear and bulk creep compliance functions can be obtained through Laplace inversion:

$$J(t) = \mathrm{L}^{-1}(\bar{J}(s)) = \mathrm{L}^{-1}[(1 + s\bar{\nu}(s))\bar{J}(s)], \tag{9}$$

$$B(t) = \mathrm{L}^{-1}(\bar{B}(s)) = \mathrm{L}^{-1}[(1 - 2s\bar{\nu}(s))\bar{B}(s)], \tag{10}$$

where $\bar{\nu}(s)$ is the Laplace transform of the time-dependent strain ratio. It is to be noted that in analyzing a problem involving the time-dependent viscoelasticity, $\nu(t)$ is time dependent. The quantity Poisson's ratio in the classical theory of elasticity is meaningless in viscoelastic behavior; thus $\nu(t)$ is termed the *strain ratio*. Experimental results[15] have shown that the strain ratio $\nu(t)$ became approximately a constant for long creep times. With this information,

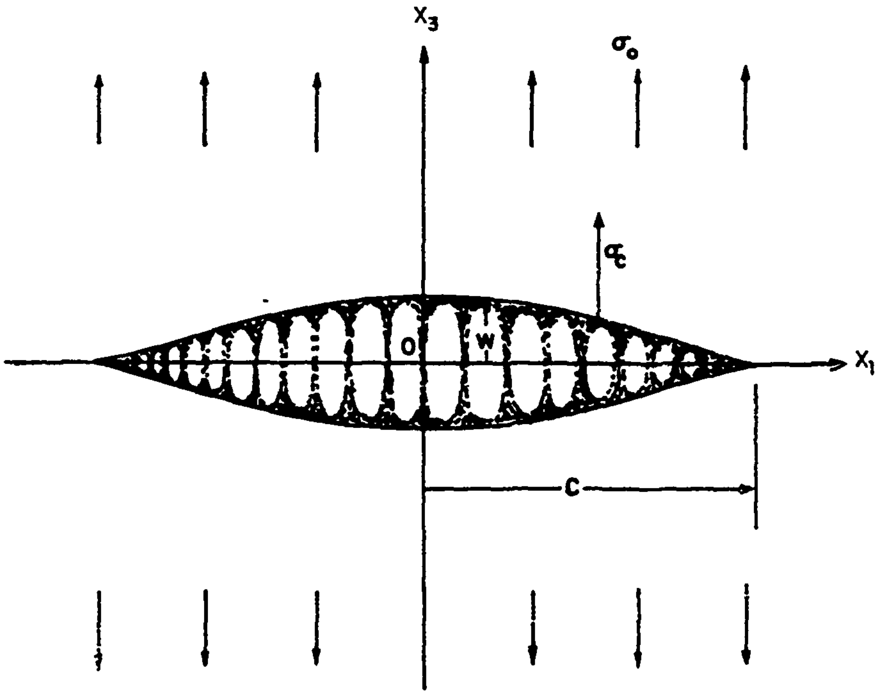

Fig. 1. Schematic diagram of a two-dimensional craze.

the viscoelastic tensile relaxation modulus function $E(t)$ can be shown as

$$E(t) = \mathbf{L}^{-1}\left[\frac{1}{s^2\bar{D}(s)}\right] = \mathbf{L}^{-1}\left[\frac{1}{s\left(D_0 + \sum_{\eta=1}^{n} D_\eta \frac{1}{\tau_\eta s + 1}\right)}\right]. \tag{11}$$

In the craze region, oriented molecular domains and voids are formed as shown schematically in Figure 1. Since the domains are composed of groups of connected fibrils of molecules, they bear load and are subjected to large deformations. When a craze elongates, its displacement field in the direction of stressing also increases. Although a part of the contribution of the displacement field is due to the creeping of the fibril domains, the major contribution comes as a result of the drawing of the molecules from the bulk of the polymer. This drawing mechanism coupled with a simultaneous neckdown of the fiber domains dominates the local crazing behavior composed of the molecular orientation mechanism and the formation of pores. A local strain field ϵ ($-1 < \epsilon < \infty$ defined as $\lambda - 1$, where λ is the draw ratio) identifies the degree of molecular orientation termed the *orientation strain* and has been found essentially constant[2,3,16] throughout the craze length as it is intimately associated with the natural draw ratio of the polymer. During the process of deformation, individual fibril domain is considered to be under uniaxial tension. Under a uniaxial stress $\sigma_{33}(x_1, t)$, a corresponding small strain $\epsilon_{33}(x_1, t) \ll \epsilon(x_1, t)$, the orientation strain, of a fibril domain will occur. The relationship between the small strain and the tensile stress of each fibril domain at x_1 is

$$\sigma_{33}(x_1, t) = \int_{-\infty}^{t} E_f(x_1, t - \tau)\frac{\partial \epsilon_{33}(x_1, \tau)}{\partial \tau}\, d\tau, \qquad \text{on } x_1 \le c,\ x_3 = 0, \tag{12}$$

where $E_f(t)$ is the viscoelastic tensile relaxation modulus of the fibril domain while the orientation strain ϵ contributes no additional stress. In preparation for computation using the boundary element method, the traction $T_3(x_1, t)$ acting on the craze envelope at x_1 may be written as follows:

$$\begin{aligned} T_3(x_1, t) &= \int_{-\infty}^{t} K(x_1, t-\tau) \frac{\partial U_3(x_1, \tau)}{\partial \tau}\, d\tau \\ &= K(x_1, 0) U_3(x_1, t) + \int_0^t \dot{K}(x_1, t-\tau) U_3(x_1, \tau)\, d\tau, \end{aligned}$$

$$\text{on } x_1 \leq \text{c},\ x_3 = 0, \qquad (13)$$

where $U_3(x_1, t)$ is the opening displacement measured from the horizontal center line of symmetry of the craze corresponding to $\epsilon_{33}(x_1, t)$ at the boundary of the craze envelope at x_1[2,12] as the thickness of the primordial layer is small as compared with U_3. By writing

$$K(x_1, t) = \frac{E_f(x_1, t)}{U_3(x_1, 0)}, \qquad (0 \leq t < \infty), \qquad (14)$$

it becomes the stiffness per unit area of a craze fibril domain. $K(x_1, 0) = K(x_1, t)|_{t=0}$ is the initial stiffness at x_1. Now we use the convolution integral relationship (13) as the boundary condition on the craze envelope. The tensile creep compliance $D_f(t)$ of a fibril domain can be found. By referring to the molecular orientation theory,[12] the tensile relaxation modulus $E_f(\epsilon)$ of a fibril domain may be represented as follows:

$$E_f(\epsilon) = C(\epsilon) E, \qquad (15)$$

where, as stated before, ϵ, the orientation strain, is essentially a constant. Thus, $C(\epsilon)$, being a function of the orientation strain, is also a constant, and E is the modulus of elasticity of the original polymer medium. Therefore, if the time dependency is introduced as given in the following equation:

$$E_f(\epsilon, t) = C(\epsilon) E(t), \qquad (16)$$

both the nature of molecular orientation and the time-dependent viscoelastic behavior of the moduli are preserved. In the Laplace domain, we treat $C(\epsilon)$ as constant:

$$\bar{E}_f(\epsilon, s) = C(\epsilon) \bar{E}(s), \qquad (17)$$

and

$$s^2 \bar{E}(s) \bar{D}(s) = 1. \qquad (18)$$

For individual fibril domains a similar relationship may be written as

$$s^2 \bar{E}_f(s) \bar{D}_f(s) = 1, \qquad (19)$$

where $\overline{D}_f(s)$ is the tensile creep compliance function of the fibril domain in the Laplace s domain. Solving for $\overline{D}_f(s)$, one gets

$$\overline{D}_f(s) = C^{-1}(\epsilon)\left[s^2\overline{E}(s)\right]^{-1}, \tag{20}$$

or

$$\overline{D}_f(s) = C^{-1}(\epsilon)\overline{D}(s). \tag{21}$$

Thus after inversion

$$D_f(t) = C^{-1}(\epsilon)D(t). \tag{22}$$

At position x_1, let us write

$$D_f(x_1, t) = C^{-1}(x_1, \epsilon)\, D(t) = C^{-1}(x_1, \epsilon)\left\{D_0 + \sum_{\eta=1}^{n} D_\eta\left[1 - \exp(-t/\tau_\eta)\right]\right\}, \tag{23}$$

where

$$C^{-1}(x_1, \epsilon) = D_f(x_1, 0)/D_0 \tag{24}$$

is a spatial parameter. Then the stiffness becomes

$$K(x_1, t) = \mathbf{L}^{-1}\left[\frac{\overline{E}_f(x_1, s)}{U_3(x_1, 0)}\right] = \mathbf{L}^{-1}\left[\frac{K(x_1, 0)\, D_0}{s^2\overline{D}(s)}\right]. \tag{25}$$

And the traction $T_3(x_1, t)$ acting on the craze envelope surface is

$$T_3(x_1, t) = \mathbf{L}^{-1}\left[s\overline{K}(x_1, s)\overline{U}_3(x_1, s)\right]. \tag{26}$$

According to the correspondence principle in linear viscoelasticity, we can transfer the boundary value problem of quasifracture into the s domain merely by replacing the elastic parameters by their corresponding time-dependent viscoelastic parameters in the Laplace domain s as follows:

$$\begin{aligned} &E \to s\overline{E}(s),\\ &K \to K(x_1, 0)\, D_0/s^2\overline{D}(x_1, s),\\ &(T_i)_0 \to (\overline{T}_i)_0(s) = (T_i)_0/s,\\ &(U_i)_0 \to (\overline{U}_i)_0(s) = (U_i)_0/s, \end{aligned} \tag{27}$$

where $(T_i)_0$ and $(U_i)_0$ are, respectively, the prescribed constant boundary traction and displacement at point i. Once the associated elasticity solution is obtained, then the Laplace numerical inversion will yield the time-dependent solution of the problem.

CALCULATING PROCEDURE

In order to solve the associated elasticity problem, the general integral boundary element method may be applied. The detailed investigation of these methods and others may be found in the literature.[17–19] For simplicity only one approach is utilized, and the basic formulation for the linear elasticity problem is described here. In the two-dimensional elastic continuum R with boundary Γ, which is assumed to be isotropic without body force, the governing equation may be obtained from pages 125 and 126 of Ref. 17 as follows:

$$C^i U_l^i + \int_\Gamma T_{lk}^* U_k \, d\Gamma = \int_\Gamma U_{lk}^* T_k \, d\Gamma, \qquad (k, l = 1 \text{ or } 3) \tag{28}$$

where $C^i = 1/2$ for point i when it becomes a boundary point on a smooth boundary, U_{lk}^* is the displacement in the k direction due to a unit force acting in the l direction at point i, U_k is the displacement at any point on the boundary Γ in the k direction, T_k is the traction at any point on the boundary Γ in the k direction, and T_{lk}^* is the traction in the k direction due to a unit force acting in the l direction at point i. The fundamental solutions for the two-dimensional isotropic plane strain problem are easily written following the equations given on pages 126 and 141 of Ref. 17. They are

$$U_{lk}^* = \frac{1}{8\pi G(1-\nu)}\left[(3-4\nu)\,\delta_{lk}\ln\left(\frac{1}{r}\right) + \frac{\partial r}{\partial x_l}\cdot\frac{\partial r}{\partial x_k}\right],$$

$$T_{lk}^* = \frac{-1}{4\pi(1-\nu)r}\left\{\frac{\partial r}{\partial n}\left[(1-2\nu)\,\delta_{lk} + 2\frac{\partial r}{\partial x_l}\frac{\partial r}{\partial x_k}\right]\right.$$
$$\left. -(1-2\nu)\left[\frac{\partial r}{\partial x_l}n_k - \frac{\partial r}{\partial x_k}n_l\right]\right\}, \tag{29}$$

where G and ν are elastic shear modulus and Poisson's ratio, respectively, n_l is the outward normal to the boundary, and r is the distance from the load point to the point under consideration. Equation (29) is known as Kelvin's singular solution due to a point load in an infinite elastic medium.

At first, the boundary Γ was divided into N elements with assumed constant values of U_k and T_k in each element. By applying the viscoelastic correspondence principle, the following equations are obtained in the Laplace domain:

$$C^i \overline{U}_l^i + \sum_{q=1}^{N}\int_{\Gamma_q} \overline{T}_{lk}^* \overline{U}_k \, d\Gamma = \sum_{q=1}^{N}\int_{\Gamma_q} \overline{U}_{lk}^* \overline{T}_k \, d\Gamma, \qquad \begin{matrix}(k, l = 1 \text{ or } 3)\\ (q = 1, 2, \ldots, N).\end{matrix} \tag{30}$$

As shown above, there are $2N$ simultaneous algebraic equations. When $2N$ boundary tractions and boundary displacements are given, another $2N$ unknown boundary tractions and boundary displacements can be obtained. For some boundary elements, beginning α, say, such as Γ_q $(q = \alpha, \ldots, N)$, on which the stiffness boundary condition was prescribed, equation (30) becomes

$$C^i\bar{U}_l^i + \sum_{q=1}^{\alpha-1} \int_{\Gamma_q} \bar{T}_{lk}^* \bar{U}_k \, d\Gamma + \sum_{q=\alpha}^{N} \int_{\Gamma_q} (\bar{T}_{lk}^* - K_k \bar{U}_{lk}^*) \bar{U}_k \, d\Gamma$$

$$= \sum_{q=1}^{\alpha-1} \int_{\Gamma_q} \bar{U}_{lk}^* \bar{T}_k \, d\Gamma, \qquad (q = 1,2 \ldots \alpha \ldots N). \tag{31}$$

By solving the above simultaneous algebraic equations, we can obtain the values $\bar{U}_k$ and $\bar{T}_k$ successively for discrete values in the Laplace domain. Based upon the thermodynamic principle, Schapery[7] developed a collocation method for numerical Laplace transform inversion. This method shows that the components of stress and displacement at any point can be represented by a series $F(t)$ defined as follows:

$$F(t) = C_1 + C_2 t + \sum_{m=1}^{M} A_m e^{-b_m t}, \tag{32}$$

where C_1, C_2, A_m, and b_m are constants. Taking the Laplace transform of eq. (32) and multiplying by the transform parameter s gives

$$s\bar{F}(s) = C_1 + \frac{C_2}{s} + \sum_{m=1}^{M} \frac{A_m}{1 + b_m/s}. \tag{33}$$

When time t goes to infinity, the function $F(t)$ should be finite. Therefore, the constant C_2 is chosen to be zero. In order to determine the constants in this equation, a value for M and a sequence of values of s must be selected, i.e.:

$$s = s_\beta, \qquad (\beta = 1,2,\ldots, M+1), \tag{34}$$

Based upon Schapery's suggestion, the relationship between s and t is $s = 1/2t$. The M values of b_m are taken to be the first $M + 1$ values of s. Then eq. (33) can be written

$$s_\beta \bar{F}(s_\beta) = C_1 + \sum_{m=1}^{M} \frac{A_m}{1 + b_m/s_\beta}, \qquad (\beta = 1,2,\ldots, M, M+1), \tag{35}$$

which is a set of $M + 1$ linear algebraic equations with $M + 1$ unknowns C_1 and A_m solvable using standard procedures. The guidelines for selecting the discrete values of s can be found in Rizzo and Shippy.[10]

BEHAVIOR OF A CRAZE

According to the aforementioned theory and method, an illustration is provided by calculating the displacement field in the neighborhood of a hole in a linear viscoelastic infinite plate. The load applied was expressed as a step function. The contour of the circular hole was divided into 24 boundary elements as shown in Figure 2. The radial displacements calculated by either the viscoelastic boundary element method or an analytical solution are shown in Figure 3. The radius of the hole is 3 m. The applied internal pressure is 100 MN/m^2. For linear viscoelastic behavior the tensile creep compliances of the

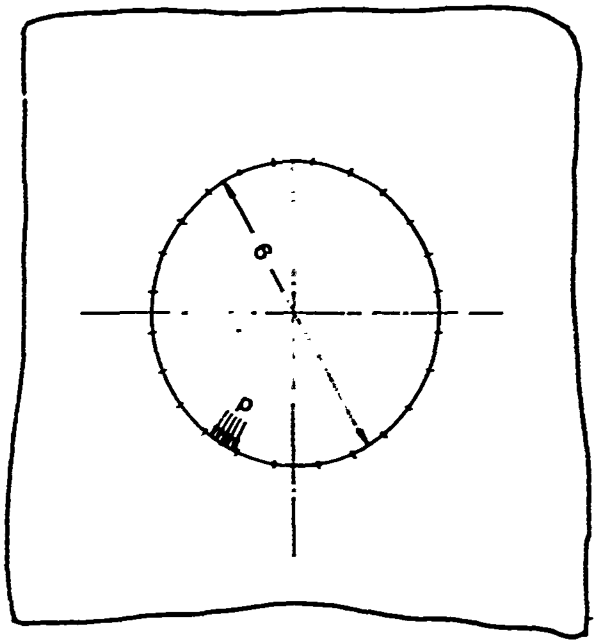

Fig. 2. Mesh division for viscoelastic infinite plate with a hole.

material was represented by a generalized Kelvin model with multiple retardation times, as shown below:

$D_0 = 0.238 \times 10^{-3}\ \text{m}^2/\text{MN}$, $\nu = 0.33$,

$D_1 = 0.071 \times 10^{-3}\ \text{m}^2/\text{MN}$, $\tau_1 = 1\ \text{h}$,

$D_2 = 0.062 \times 10^{-3}\ \text{m}^2/\text{MN}$, $\tau_2 = 10\ \text{h}$,

$D_3 = 0.045 \times 10^{-3}\ \text{m}^2/\text{MN}$, $\tau_3 = 80\ \text{h}$,

$D_4 = 0.031 \times 10^{-3}\ \text{m}^2/\text{MN}$, $\tau_4 = 110\ \text{h}$.

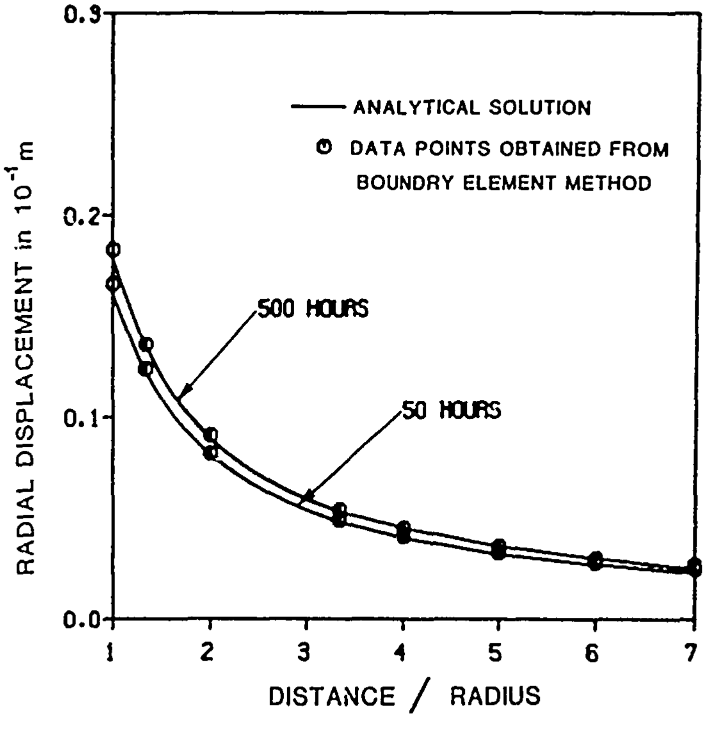

Fig. 3. Radial displacement of viscoelastic infinite plate with a hole.

As seen in Figure 3, the data computed by the viscoelastic boundary element method produced excellent agreement with the analytical results obtained by transforming the classical elasticity solution of a circular hole in an infinite plate into a time-dependent solution in linear viscoelasticity using the well-known correspondence principle.

Now for studying the quasifracture, an idealized symmetrical craze in a constant stress field has been considered. The craze basic structure was represented by a slit with fiber domains distributed along the craze envelope boundary. The distance between the top and the bottom craze envelopes has been referred to as the craze-opening displacement measured from the center of symmetry. The stress acting on the interface of the craze was referred to as the craze envelope stress. The total craze length considered was 2 mm; thus, $c = 1$ mm, which is usually referred to as the craze length measured from the center of a craze. The width of plate was $B = 11.2$ mm, and the length of the plate was $L = 14$ mm, with unit thickness throughout. Because of symmetry, a quarter of the plate containing an isolated quasifracture was divided into 58 boundary elements as shown in Figure 4. The properties of the bulk material were again represented by a generalized Kelvin model. The tensile creep compliances D_m and retardation times τ_m were the same as before. The shape of the applied stress p_0 was a unit step function $H(t)$ modified to 42 N/mm^2.

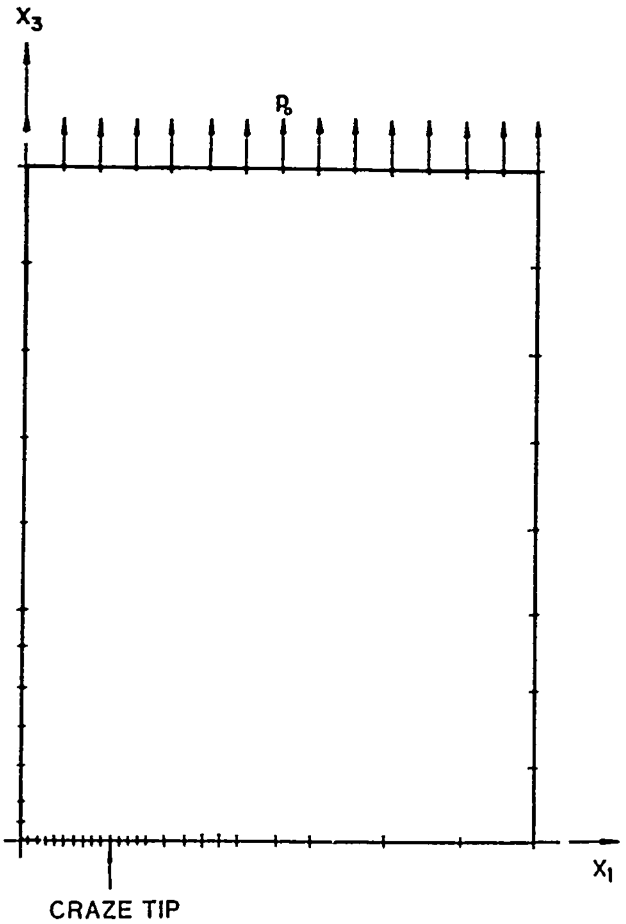

Fig. 4. Mesh division for a quarter plate with a craze.

The boundary conditions used on the plate are

$$\left.\begin{aligned} T_3(x_1,t) &= \int_0^t K(x_1,t-\tau)\frac{\partial U_3(x_1,\tau)}{\partial \tau}\,dt \\ T_1(x_1,t) &= 0 \end{aligned}\right\} \qquad (x_1 \le c,\ x_3 = 0), \tag{36}$$

$$\left.\begin{aligned} U_3(x_1,t) &= 0 \\ T_1(x_1,t) &= 0 \end{aligned}\right\} \qquad (c \le x_1 \le B,\ x_3 = 0), \tag{37}$$

$$\left.\begin{aligned} T_1(x_3,t) &= 0 \\ T_3(x_3,t) &= 0 \end{aligned}\right\} \qquad (x_1 = B, 0 \le x_3 \le L), \tag{38}$$

$$\left.\begin{aligned} T_1(x_1,t) &= 0 \\ T_3(x_1,t) &= p_0 H(t) \end{aligned}\right\} \qquad (0 \le x_1 \le B,\ x_3 = L), \tag{39}$$

$$\left.\begin{aligned} U_1(x_3,t) &= 0 \\ T_3(x_3,t) &= 0 \end{aligned}\right\} \qquad (x_1 = 0, 0 \le x_3 \le L). \tag{40}$$

Initially by using the finite element method and considering the molecular orientation of the fibril domains in the quasifracture,[4] the initial instantaneous craze-opening displacement $U_3(x_1, 0)$ and the craze envelope stress $\sigma_c(x_1, 0)$ were calculated. They agreed fairly well with the experimental results. Subsequently the instantaneous stiffness $K(x_1, 0)$ was calculated and $K(x_1, t)$ determined from expression (25). In applying the viscoelastic boundary ele-

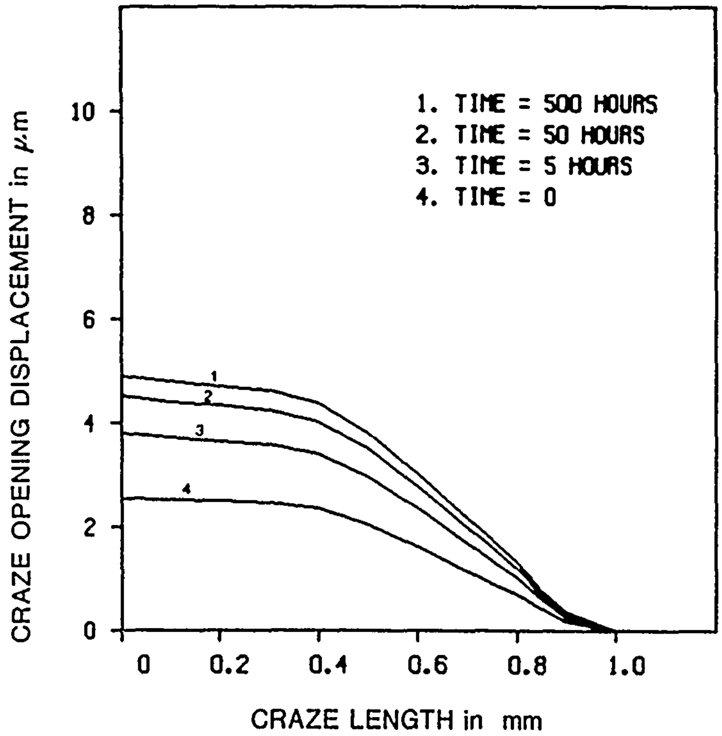

Fig. 5. Creep opening displacement of the craze surface.

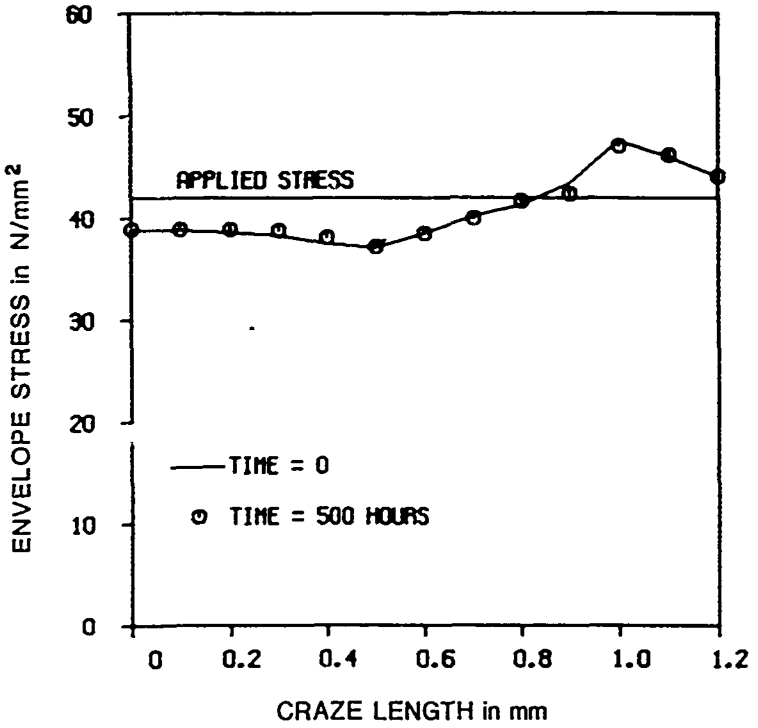

Fig. 6. Comparison of stress distribution of craze surface in time = 500 h and time = 0.

ment method, the values of the s parameter were selected ranging from 10^{-3} to 10^2, and time t was chosen as $1/2s$ as given earlier.[7-10] Figure 5 shows the opening displacement $U_3 = w$ between the quasifracture envelope surfaces versus the distance from the center of craze for various times corresponding to 500, 50, 5, and 0 h. It is seen that the quasifracture opening displacement increases as time increases at a rate which is relatively high from 0 to 50 h. Beyond 50 h it changes slowly. However, it is interesting to find that the stress distribution remains constant as shown in Figure 6. These results indicate that the craze quasifracture behavior can be successfully analyzed using this viscoelastic boundary element method.

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References

1. S. S. Chern and C. C. Hsiao, *J. Appl. Phys.*, **52**, 5994 (1981).
2. S. S. Chern and C. C. Hsiao, *J. Appl. Phys.*, **53**, 6541 (1982).
3. B. D. Lauterwasser and E. J. Kramer, *Philos. Mag. A*, **39**, 469 (1979); *Philos. Bull.*, **3**, 565 (1980).
4. L. Bevan, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 1759 (1981); *J. Appl. Polym. Sci.*, **27**, 4263 (1982).
5. B. N. Sun and C. C. Hsiao, *J. Appl. Phys.*, **57**, 170 (1985).
6. S. Mukherjee, *Boundary Element Methods in Creep and Fracture*, Applied Science Publishers, London, 1982.
7. R. A. Schapery, *U.S. Nat. Congr. Appl. Mech.*, 1075 (1961).
8. T. L. Cost, *AIAA J.*, **2**, 2157 (1964).
9. T. Kusama and Y. Mitsui, *Appl. Math. Model.*, **6**, 285 (1982).
10. F. J. Rizzo and D. J. Shippy, *SIAM J. Appl. Math.*, **21**, 321 (1971).

11. Y. G. Wang and S. L. Crouch, 23rd U.S. Symposium Rock Mechanics, Berkeley, California, *Issues in Rock Mechanics*, ed. by R. E. Goodman and F. Heuze, American Society of Mineral Engineering, New York, N.Y., 1982, p. 704.

12. C. C. Hsiao, *J. Appl. Phys.*, 30, 1942 (1959); *J. Polym. Sci.*, 44, 71 (1960); in *Fracture Processes in Polymeric Solids*, B. Rosen, Ed., Interscience, New York, 1964, p. 529.

13. H. H. Kausch and M. Dettermaier, *Polym. Bull.*, 3, 565 (1980).

14. A. J. Staverman and F. Schwarzl, in *Die Physik der Hochpolymeren*, H. A. Stuart, Ed., Springer-Verlag, Berlin, 1965, p. 1.

15. Z. Rigbi, *Appl. Polym. Symp.*, 1 (1967).

16. A. M. Donald, E. J. Kramer, and R. A. Bubeck, *J. Polym. Sci.-Polym. Phys. Ed.*, 20, 1129 (1982).

17. C. A. Brebbia and S. Walker, *The Boundary Element Techniques in Engineering*, Newnes-Butterworths, London, 1980, p. 120.

18. P. K. Banerjee and R. Butterfield, *Boundary Element Methods in Engineering Science*, McGraw-Hill, 1981, p. 78.

19. T. V. Hromadka II, and Chintu Lai, *The Complex Variable Boundary Element Method in Engineering Analysis*, Springer-Verlag, New York, 1987, p. 28.

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Time-dependent fracture strength of solid bodies

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Time-dependent fracture strength of solid bodies

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Statistical theories in fracture kinetics constitute a very important role in investigating the fracture strength of solids and their utilization in modern engineering. In this paper, a review of some of the recent concepts and models is provided. The main concern is the effect of the breaking stress on the time-to-break. Based upon the consideration of the fraction of integrity of a medium, a number of models have been evaluated and compared. Two basic considerations used for evaluation and comparison are Zhurkov's empirical kinetic relationship and Hsiao's statistical absolute reaction rate model. Other considerations reducible from these two are also given for comparison. Using a well-known numerical analysis method, it appears that the nonlinear mathematical consideration is more realistic in describing the time-dependent fracture strength behavior of a medium over any linear ones. The computed results seem to fit reasonably well with the general observations.

INTRODUCTION

Under load the time-dependent fracture processes of solid bodies can be characterized in several stages: first is the nucleus incubation overlapping with an apparent homogeneous deformation of the material body, followed by either the instable possible craze inception[1,2] or simply a direct crack formation. Eventually, either craze-crack transition[3] takes place or crack propagation results. Thus, fracture occurs. These feature behaviors depend on many factors, such as temperature, time, composition, and microstructural configuration of the medium, as well as environmental conditions. Many investigators in the past[4-19] have studied and interpreted the time-dependent fracture phenomenon of solids. It has been shown experimentally that the logarithm of time-to-break has been found to be linearly related to the applied uniaxial simple tension for a large number of solids, as shown in Fig. 1, ranging from seconds to months. Zhurkov[20] represented this linear relationship between the logarithm of time-to-break t_b and the applied tensile stress σ, as follows:

$$t_b = t_0 \exp[(U - \gamma\sigma)/kT], \tag{1}$$

where k is the Boltzmann constant, T is the absolute temperature, and t_0, U, γ are constants. However, there is deviation from this empirical linearity, as shown in Fig. 2, when either large or small applied stresses are involved in the experimental measurement. This deviation was not clearly mentioned or considered for any material system by Zhurkov. The present report addresses this point by taking into account the nonlinear behavior of the system based on the statistical theory of the absolute reaction rate.[21-23] The mathematical model used is a matrix of oriented microelements representing primary and/or secondary bonding forces embedded randomly in an arbitrary matrix domain. The fraction of unbroken microelements, identifying the fracton of integrity of the system as "f," and its rate of change is as follows:

$$f = \frac{df}{dt} = K_r(1 - f) - K_b f, \tag{2}$$

where

$$K_r = \omega_r \exp(-U/RT - \rho\psi),$$
$$K_b = \omega_b \exp(-U/RT + \beta\psi), \tag{3}$$

with K_r and K_b as the rate of reformation of broken and breakage of unbroken microelements, respectively, ω_r and ω_b as the frequency of motion of the broken and unbroken microelements, respectively, and U,β, and ρ as material constants. They are positive definite. R is the universal gas constant, and $\psi(t) = \sigma(t)/f(t)$ as the axial stress subjected by the individual microelements of an oriented material system. This statistical model on the rate theory of fracture has strong physical implications. It deals with thermally activated atomic-bonding formation and breakage processes as the

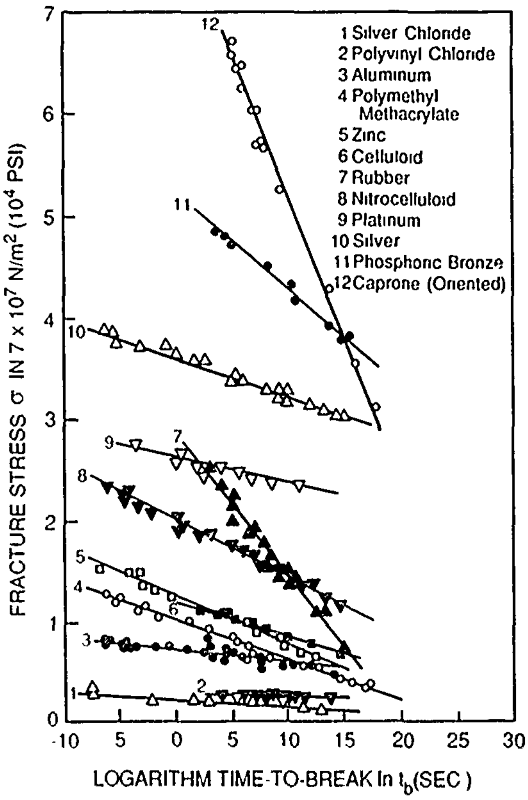

FIG. 1. Time-dependent fracture strength for solids (after Zhurkov).

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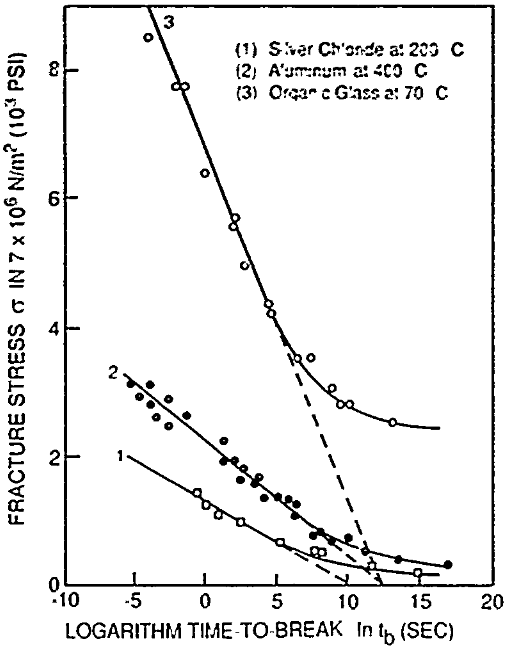

FIG. 2. Fracture stress vs logarithm time-to-break, after Hsiao and Zhurkov.

fundamental kinetic mechanisms of fracture initiation and propagation. In this atomic level, the theory is valid for metallic, ceramic, and polymeric material systems. For either crystalline or amorphous materials, the behavior of the broken and intact bonds may be different and the rates of breaking and mending are also considered different.

Based upon the analyses of Hsiao, this rate theory well describes the stress, temperature dependence of the time-to-break for a large number of crystalline and amorphous solids at different temperatures, and for a wide range of applied high and low stresses. This will be seen through the following analysis and interpretations under constant stressed conditions. To explore these characteristics, expressions (2) and (3) are solved for a limiting value of $\psi(t)$, where $\psi(t_b) = \psi_b$ for a constant applied stress σ, then

$$\psi(t_b) = \sigma/f(t_b), \tag{4}$$

to give

$$\ln\frac{2\sigma}{\psi_b} + \omega_b \exp\left(-\frac{U}{RT}\right)\exp(2\beta\sigma)\exp(\ln t_b) = 0. \tag{5}$$

This turns out to be not only satisfactory for the observed middle range of stresses as Zhurkov has reported but also consistent with very small stress behavior as shown in Fig. 2. In addition, it also yields information on fracture for very high stresses and very short durations as will be seen later.

For relatively large values of σ, within the observed mid-stress range, Eq. (5) may be approximated by

$$\exp(2\beta\sigma) \gg \ln(2\sigma/\psi_b). \tag{6}$$

Equation (5) is then solved to show a linear relationship between the logarithm of time-to-break t_b and the constant applied stress σ, then

$$\sigma = (1/2\beta)(U/RT - \ln \omega_b t_b), \tag{7}$$

and

$$t_b = (1/\omega_b)\exp(U/RT - 2\beta\sigma), \tag{8}$$

which is similar to Eq. (1) given by Zhurkov. Equation (5) can be rewritten to give

$$t_b = \frac{1}{\omega_b}\left(\ln\frac{\psi_b}{2\sigma}\right)\exp\left(\frac{U}{RT} - 2\beta\sigma\right). \tag{9}$$

Comparing Eq. (1) with (9), it can be recognized that t_0 in (1) can be a function of the applied stress σ instead of being a constant as suggested by Zhurkov.

To determine the influence of reforming processes on the fracture strength, Hsiao and co-workers[19,21,23] used Eqs. (2) and (4) to obtain an expression for the average rate of stressing on the unbroken microelements in the mathematical model

$$\frac{d\psi}{dt} = \psi\left[\Omega_b \exp(\beta\psi) - \left(\frac{\psi}{\sigma} - 1\right)\Omega_r \exp(-\rho\psi)\right], \tag{10}$$

where Ω_b and Ω_r are constants associated, respectively, with ω_b and ω_r, as well as some other quantities independent of stress.

An expression for the fracture stress and the time-to-break behavior was then evaluated to give

$$\frac{d(\ln \Omega_b t_b)}{d(\beta\sigma)} = -1 - (\beta\sigma)^{-1}. \tag{11}$$

Figure 3 shows a qualitative representation of Eq. (11) with high and low stresses of fracture bounded. This behavior is nonlinear which deviates from the linear behavior of Zhurkov's Eq. (1). It should also be noted that in Eq. (2) if $K_r = 0$, the curve will have steeper slopes[22] (see Fig. 4).

THE FRACTION OF INTEGRITY f

The integrity of a material body may be described, in addition to other dominant quantities such as stress, strain, elastic modulus, etc., by a measure of the material's damage under stress, or its opposite, the fraction of integrity f.

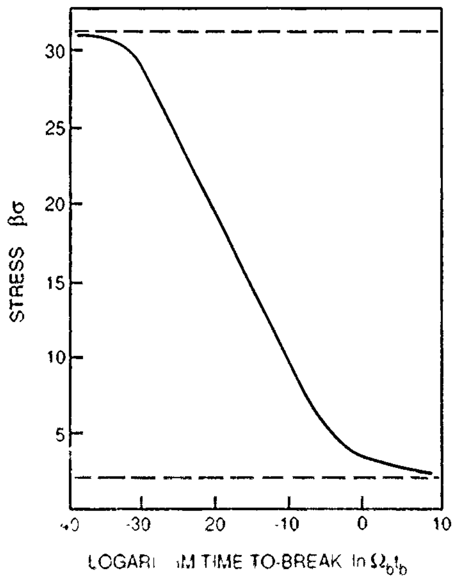

FIG. 3 Qualitative stress-dependent time-to-break

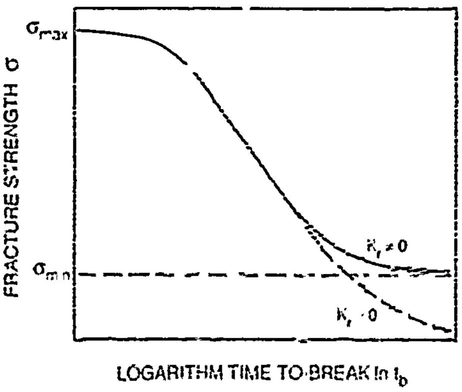

FIG. 4. Time-dependent strength of solids under simple tension.

Changes in the velocity of ultrasound propagation in the material, its density, volume of deformation, and other characteristics are used to establish the degree of damage in a material system. Most often, a quantity D is identified with the density of microcracks in the vicinity of the examined point or with the relative quantity of the broken bonds. During the loading process the value of D varies within the limits [0,1]. In general, the rate of damage $\dot{D}$ is a function of many arguments,[24] such as stresses σ_{ij}, stress rates $\dot{\sigma}_{ij}$, strains ϵ_{ij}, strain rates $\dot{\epsilon}_{ij}$, time t, and other parameters.

$$\dot{D} = \dot{D}(\sigma_{ij},\dot{\sigma}_{ij},...,\epsilon_{ij},\dot{\epsilon}_{ij},...,t,D,A_i), \tag{12}$$

where A_i are material constants. In a simple state of stressing, $\dot{D}$ can be expressed as

$$\dot{D} = \dot{D}(\sigma,D), \tag{13}$$

where σ represents an applied simple tension. An expression for f can be formulated similar to that given in (13), since $f = 1 - D$,

$$\dot{f} = \dot{f}(\sigma,f). \tag{14}$$

As illustrated earlier, Hsiao[19] used the statistical theory of the absolute reaction rate and obtained an expression for the fraction of integrity f as shown in Eq. (2). Then, he introduced an approximate solution for f (during the loading process) in the form

$$f = 1 + A\,\exp(Bl\epsilon_{mn}e_m e_n), \tag{15}$$

where

$$K_b/K_r = A\,\exp(Bl\epsilon_{mn}e_m e_n),$$

$\epsilon_{mn}s_m s_n$ is the scalar strain in individual elements in the deformation process, e_m and e_n are unit vectors, A and B are constants, and l is the length of each microelement.

The fraction of integrity f may be used to describe the behavior of a specific medium during the loading process. This qualitative factor can be of tremendous help in closed loop control systems to predict points of instability and fracture In general, it may be used to follow the behavior of a medium under loading conditions. Initially, the fraction of integrity f decreases slowly as time increases, then it falls, first gradually for some time and finally sharply near the time to break. This relationship is a highly nonlinear one. To illustrate this schematically, Fig 5 shows the variation of the fraction of integrity f vs time t This theoretical curve may also be represented by Eq. (15) in the following manner:

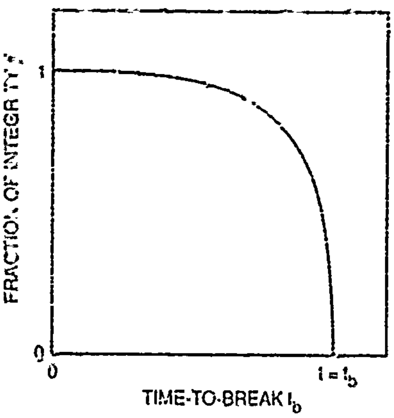

FIG. 5. Qualitative representation of fraction of integrity f vs time t.

$$\text{at } t = 0, f = 1 \quad \text{for which} \quad A\,\exp(Bl\epsilon_{mn}e_m e_n) = 0,$$

and

$$\text{at } t = t_b, f = 0 \quad \text{and} \quad A\,\exp(Bl\epsilon_{mn}e_m e_n) = -1.$$

Kuksenko and Tamuzs[24] did use an expression for f as a function of time t, stress σ, and constants a and n, i.e.,

$$f = (1 - at\sigma^n)^{1/n}. \tag{16}$$

It was not clear from the author's description what was the origin of Eq. (16). However, by expanding and simplifying Eq. (2), a similar expression as (16) can be obtained. If Eq. (16) is differentiated, the following expression is obtained:

$$\dot{f} = -(a/n)f(\sigma/f)^n. \tag{17}$$

Also, the same authors did introduce another expression for f based on a model that utilizes a statistical overstress distribution and a kinetic theory of strength[24];

$$\dot{f} = f^2/\{t_0(\sigma\gamma/kT)\exp[(U - \sigma\gamma/f)/kT]\}, \tag{18}$$

or

$$\dot{f} = -\frac{f^2}{(t_0\sigma\gamma/kT)}\exp\left(-\frac{U}{kT} + \frac{\sigma\gamma}{fkT}\right). \tag{19}$$

The main disadvantage of the theory, as has been mentioned in their analysis, is the assumption that the stress concentration around the broken bonds can be disregarded. For this reason, the theory is unable to account for the fact that final fracture begins in the presence of a considerable number of unbroken, highly overstressed bonds. The theory limits itself with modeling of breaking of a bundle of fibers.

COMPUTATION AND DATA

For comparison, the previously mentioned expressions have been evaluated with the help of a computer package called dynamic system simulation (DYSYS).[25] DYSYS was developed over a period of years at MIT for the simulation of dynamic systems. Its key function is the solution of the appropriate differential equations describing a system It uses a fourth order Runge-Kutta integration to obtain an appropriate solution to the differential equation.

As has been mentioned earlier, the main objective of this report is to assess the validity of the different expressions developed for describing the time-dependent fracture strength of solids. This, in turn, would enable one to select the most appropriate theory for describing the fracture behavior of a medium. The empirical relationship and the theoretical mathematical models that have been used in this evaluation are: Zhurkov's kinetic relationship, Eq. (1); Hsiao's statistical absolute reaction rate considerations, Eqs. (2), (7), (9), and (11); and Kuksenko and Tamuzs' kinetic expressions, Eqs. (16), (17), and (19). Data were collected and plotted for ease of comparison of polymeric systems[19,20,22–24] as discussed and illustrated in the following section.

RESULTS AND DISCUSSION

Variations of the breaking strength with respect to the logarithm of time-to-break are shown in Fig. 6 for various expressions: (1) Eq. (7) (after Hsiao[19]) was plotted with $\beta = (0.041\times10^{-7}$ in.^{2}/lb) 0.285×10^{-4} m^2/N, $U/RT = 65$, and $\omega = 1.778\times10^{-6}$ rad/s, (2) and (3) Eq. (1) (after Zhurkov[20]) was plotted for $kT/\gamma = 13.629$ N/m^2 with two different values for U/γ, as designated. Each of the three curves shows a linear relationship between the logarithm of time-to-break and the applied fracture stress and thus is not realistic for very short or long time load applications. It should also be noted that, for the purpose of clear illustration and comparison, different constants have been used for different expressions. However, the linear relationship between the logarithm of time-to-break and the fracture stress has not been altered.

In Fig. 7, the variation of stress versus logarithm of time to-break is plotted for an organic glass at 70 °C using Eqs. (7) and (9) or (11) with $\beta = 0.0027\times10^{4}$ m^2/N(0.00324$\times10^{7}$ in ^{2}/lb) over a long period of time. Equation (9) or (11) gives essentially a nonlinear relationship between fracture stress and the logarithm of time-to-break with partial linearity behavior Three stages are recognized during the time span: At the beginning, when the stresses are very high, the time-to-break is very short and the relationship approaches a nearly constant fracture stress independent of time As the stress decreases, the curve exhibits a straight line having a constant slope with increasing logarithm of time-to-break. Finally, as the stress becomes very low, the stress-time relationship takes a nonlinear behavior again with the magnitude of stress decreasing considerably as the logarithm of time-to-break approaches to infinity. On the other hand, Eq. (7) gives only a linear relationship between fracture stress and the logarithm of time-to-break for the range of time indicated without any nonlinear behavior beyond. From these curves, it is seen that Eq. (9) or (11) obtained from the consideration of the statistical theory of the absolute reaction rate does give a more realistic behavior for a medium under load.

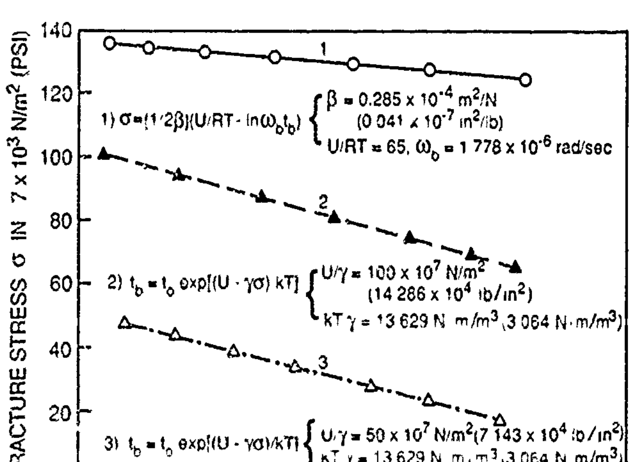

FIG. 6. Variation of stress vs logarithm time-to-break for polymeric systems

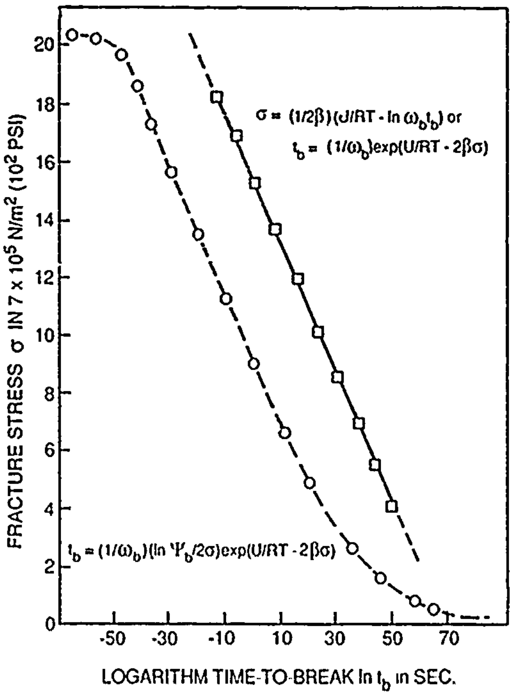

FIG. 7. Fracture stress vs time-to-break for organic glass at 70 °C.

Similarly for the same polymer medium, in Fig. 8, the variation of the fraction of integrity f vs time t for several different expressions is shown: (1) the simplified form of Eq. (2) with $K_r = 0$ (after Hsiao[22,23]) and Eq. (19) (after Kuksenko and Tamuzs[24]); (2) and (4) the original form of Eq. (2) with $K_r \neq 0$ and $\beta\sigma = 5$ and 7, respectively, and finally (3) shows Eq. (17) (after Kuksenko and Tamuzs[24]) with given data as labeled. It is clear that Eq. (2) with $K_r \neq 0$ is the most sensitive one for describing a nonlinear behavior of a medium during the loading process. On the other hand, Eq. (2) with $k_r = 0$ and also Eq. (19), shown together on top of Fig. 8, are not sensitive at all and show only a linear straight line behavior while Eq. (17) seems to be a variation of Eq. (2) and does behave similarly. However, it is not clearly defined how the determination of the constants in the expression a and n can be made.

The curves in Fig. 8 indicate the importance of a realistic nonlinear consideration for describing the behavior of a medium during loading. This consideration can be used to identify points of instability and fracture for a specific model through a parameter: the fraction of integrity f, which represents a measure of the integrity of the material under stress.

On the basis of these comparisons, it seems reasonably clear that the nonlinear statistical absolute reaction rate the-

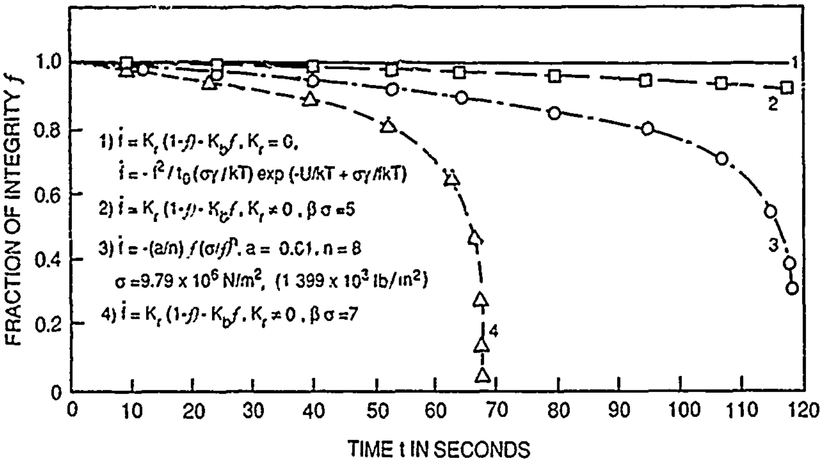

FIG. 8. Variation of the fraction of integrity f vs time t for polymers.

ory does provide a good basis for describing a fairly realistic nonlinear time-dependent fracture strength behavior of a medium under stress while the empirical linear relationship gives only partial information. Following this successful statistical consideration, the interrelation between the macroscopic fracture strength and the microscopic behaviors has been formulated.[26] The microbehavior in the vicinity of a point is expressible in terms of a spherical function which has been expanded into a series of symmetric tensorial terms. By taking into account the individual values of the directional fraction of integrity, the time-to-break and the most probable direction of fracture within any volume element in a solid or possibly a composite system may be predicted.

In addition, the temperature variation of a solid prior to its failure inception can be predicted under an increasing state of stressing At the moment of macrofracture, the governing conditions of a solid may be deduced from (2) that

$$\dot{f} = -\omega_b \exp[(-U/RT+\beta t)]f, \tag{20}$$

when the applied stress σ is directly proportional to time t and the bonding reformation process becomes unimportant. Then differentiation of (20) with respect to time will yield

$$\frac{U}{RT^2}\dot{T} = \frac{\ddot{f}}{\dot{f}} - \frac{\dot{f}}{f} - \beta. \tag{21}$$

This indicates that when

$$\ddot{f}/f - \dot{f}/f > \beta, \tag{22}$$

the temperature will increase at fracture and will decrease when

$$\ddot{f}/f - \dot{f}/f < \beta. \tag{23}$$

These complex phenomena have been observed experimentally for temperature increases at failure. Some results on these will be reported elsewhere in the future.

ACKNOWLEDGMENT

The authors wish to express their appreciation for the partial support by an AFOSR Grant in completing this work.

[1] K. F. Ha and Z. Z. An, J. Appl. Phys. 55, 94 (1984).
[2] C. C. Hsiao, J. Appl. Phys. 30, 1942 (1959).
[3] C. C. Hsiao, ASME Damage Mech. Composites AD 12, 25 (1987).
[4] G M Bartenev, Rep Acad. Sci USSR 9, 53 (1953) (in Russian).
[5] S N Zhurkov, Bull. Acad. Sci. USSR 11, 78 (1957) (in Russian).
[6] S. N. Zhurkov and T. P. Sanfirova, Sov. Phys.-Solid State 21, 933 (1960).
[7] C. C. Hsiao, Nature 186, 535 (1960).
[8] S N Zhurkov, B. Ya Levin, and E. E. Tomashevevskii, Sov. Phys.-Solid State 22, 1853 (1961).
[9] B. Ya Pines, Sov. Phys.-Solid State 11, 238 (1959).
[10] G. M. Bartenev and V. E. Gul, J. All-Union Chem. Soc. 6, 394 (1961) (in Russian).
[11] H. Kolsky, *Fracture* (Wiley, New York, 1959), 281.
[12] S N Zhurkov and B. N. Narzulayev, J Tech. Phys. USSR 3, 1677 (1953) (in Russian).
[13] S. N. Zhurkov and T. P. Sanfirova, Rep. Acad. Sci. USSR 101, 237 (1955) (in Russian).
[14] G. M. Bartenev, B. I. Panshin, I. B. Razumovskaya, and G. N. Fingenow, Bull. Acad. Sci. USSR Mech. Mach. Des. 6, 176 (1960).
[15] F Bueche, J Appl Phys. 26, 1133 (1955), 28, 784 (1957).
[16] I I Perepechko, Chap. 8, *The Strength of Polymers in an Introduction to Polymer Physics* (Mir, Moscow, 1981), Chap. 8, p. 237.
[17] B. D. Colman, J. Appl. Phys. 27, 862 (1956).
[18] B. D. Colman, A. G. Knox, and W. F. McDevit, Text. Res. J. 28, 393 (1958).
[19] C. C. Hsiao, Phys. Today 19, 49 (1966).
[20] S. N. Zhurkov, Int. J. Fract. Mech. 1, 311 (1965)
[21] A. S Krausz and H. Eyring, *Deformation Kinetics* (Wiley Interscience, New York, 1975), pp. 343, 349.
[22] H. H. Kausch von Schmeling, S. R. Moghe, and C. C. Hsiao, J. Appl. Phys. 38, 201 (1967).
[23] C C. Hsiao, S. R. Moghe, and H. H. Kausch von Schmeling, J. Appl. Phys. 39, 3857 (1968).
[24] V. S. Kuksenko and V. P. Tamuzs, *Fracture Micromechanics of Polymer Materials* (Nijhoff, The Hague, 1981), p. 167.
[25] DYSYS, Dynamic System Simulation, Copyright 1979, Massachusetts Institute of Technology Joint Computer Facility, Cambridge, MA (1979).
[26] M. S. Mun and C. C. Hsiao, J. Appl. Phys. 60, 2656 (1986).

K4.

TEMPERATURE VARIATION DURING POLYMER FAILURE

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Using the statistical absolute reaction rate theory for thermally activated fracture processes an attempt is made to investigate the temperature gradient during polymer failure. By considering the broken and intact bonds in a polymeric system, the fundamental mechanisms of failure initiation and propagation are analyzed through the application of a quantity $f(t)$ describing the fraction of integrity of a material system as a measure of the bond breaking and connecting at time t under stress. As a result the variation of temperature at fracture is formulated and examined.

By considering different broken and intact bonding densities, the net rate of change of the fraction of integrity f can be established as follows [1,2]

$$\dot{f} = K_r[1-f(t)] - K_b f(t) \tag{1}$$

$$K_r = \omega_r \exp[-U/RT(t) - \rho\psi(t)] \tag{2}$$

$$K_b = \omega_b \exp[-U/RT(t) + \beta\psi(t)] \tag{3}$$

where K_r and K_b are r[illegible]vely the rate of connecting of the broken and breaking of the intact bonds, ω_r and ω_b are the frequencie[illegible] motion of the broken and intact bonds, U is the activation energy, and R is the universal gas constant. T(t) is the absolute temperature and ρ and β are respectively positive, definite constants modifying the longitudinal stress $\psi(t)$ per bond at time t.

In a random molecular system, the dominating bonds are those oriented in the direction of stressing. For simplicity, consider a fully oriented system which is thought to well represent the kinetic behavior of either a brittle or ductile polymer system.

The stress along each individual bond in a system under a simple stress $\sigma(t)$ is:

$$\psi(t) = \sigma(t)/f(t) \tag{4}$$

In the case of monotonically increasing stress as a linear function of time,

$$\beta\psi(t) = \beta_o t \tag{5}$$

and ρ becomes increasingly unimportant, thus the governing equation for the rate of change of the fraction of integrity becomes:

$$\dot{f} = -\omega_b f \exp[-U/RT(t)] \exp(\beta_o t) \tag{6}$$

By differentiation with respect to time, the acceleration of the fraction of integrity can be obtained:

$$\ddot{f} = \omega_b f[U\dot{T}/RT^2(t) + \beta_o + \dot{f}/f(t)] \exp[-U/RT(t)] \exp(\beta_o t) \tag{7}$$

Using (6), it becomes evident that

$$U\dot{T}/RT^2(t) = \ddot{f}/\dot{f} - \dot{f}/f - \beta_o \tag{8}$$

Here β_o is likely to be positive, since $\beta, \psi(t)$ and t are all positive, therefore when

$$\ddot{f}/\dot{f} - \dot{f}/f < \beta_o,\ \dot{T} < 0 \text{ is negative} \tag{9}$$

the temperature must decrease. However, when

$$\ddot{f}/\dot{f} - \dot{f}/f > \beta_o \qquad 10)$$

the temperature of the system must increase, i.e.

$$\dot{T} > 0 \text{ is non-negative.} \tag{11}$$

This is especially true when $f \rightarrow 0$ at fracture. Fig. 1 shows the temperature rise at the lower right edge of a brittle polystyrene specimen stressed vertically just prior to the occurrence of fracture. Similarly, for polycarbonate which is somewhat ductile under tensile load, an increase in temperature was also observed at fracture (Fig. 2) in a region on the right center edge of a circular hole after a large plastic deformation had taken place.

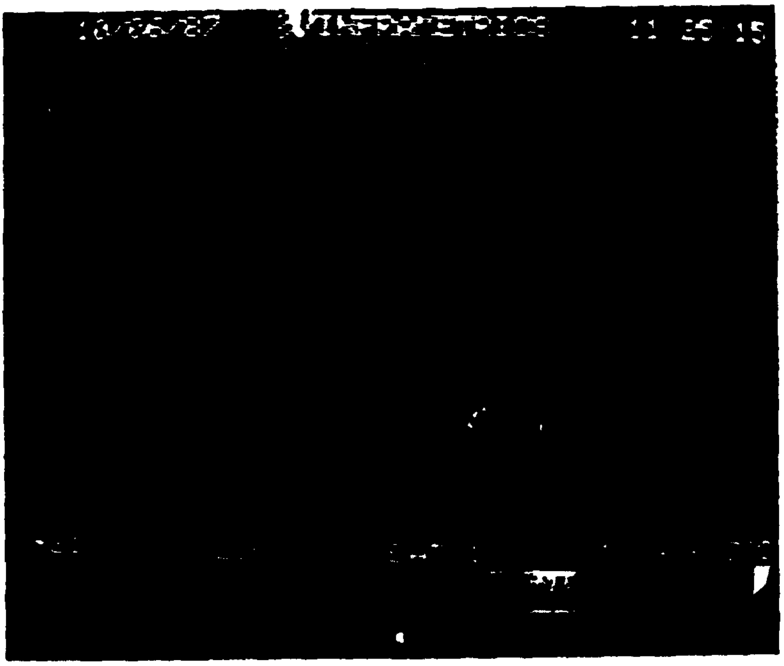

Fig. 1. Temperature Gradient at Fracture of Polystyrene

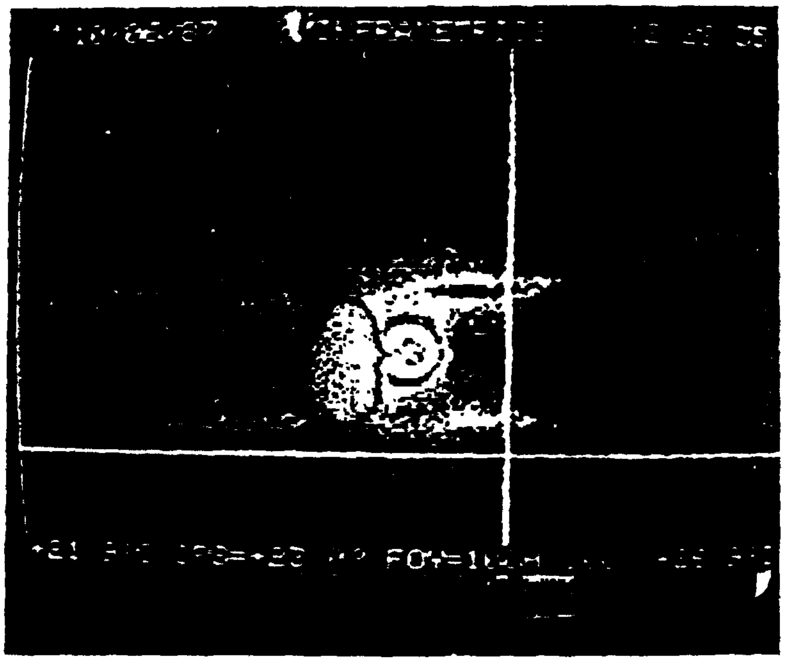

Fig. 2. Temperature Gradient at Fracture for Polycarbonate

It is interesting to note that the initial increase in temperature for the polystyrene specimen (lower right edge in Fig. 1) just before the catastrophic fracture is no more than 2°C, whereas for the polycarbonate specimen a 5° C temperature rise is shown on the right central periphery of the deformed circle (Fig. 2).

References.
1. O. M. Ettouney and C. C. Hsiao, J. Appl. Phys. (1988) in press
2. A. S. Krausz and H. Eyring, Deformation Kinetics, Wiley Interscience, New York, London, Sydney, Toronto, C[illegible]

V. 5.

A NEW GENERALIZED DAMAGE CRITERION FOR POLYMERS

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Since the dawn of human culture the problem of the strength of solids has been experienced and utilized empirically. Probably, not until the past 500 years has the problem of strength and deformation of solid bodies been investigated quantitatively. The phenomena of yielding and strength have been carefully considered during the past 100 years. It is only during the last twenty years that special attention has been given to the study of craze initiation criteria of polymers by Sternstein and Ongchin (1969), Gent (1970), Bowden and Oxborough (1973) and Argon et al. (1973). More recently S. S. Chern and C. C. Hsiao (1985) have developed a generalized time-dependent theory of craze initation for viscoelastic materials. Since the mechanical damage behavior is intimately associated with deformation and yield as well as crazing and fracture, a generalized damage criterion is described to account for the initiation of yield, craze and fracture of polymeric systems in a unique theory.

The damage mechanism of polymers under stress may be associated closely with microcavitation and molecular orientation. From the microstructural viewpoint stressing may be visualized as a source of instable process which causes the field of homogeneous deformation to develop into localized flow characteristics. Thus the creation of microcavities under hydrostatic tension and the micromolecular slippage form highly oriented molecular domains occur in regions of crazes. This bifurcation creates free volume and sharp flow which are provided by the existence of the deviatoric stress tensor S. In terms of stress tensor components σ_{ij} the magnitude of the deviatoric stress is expressible as follows:

$$S = \{\frac{1}{6}[(\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2 + 6(\sigma_{12}^2 + \sigma_{23}^2 + \sigma_{31}^2)]\}^{1/2} \quad (1)$$

At any locale when the magnitude of the deviatoric stress reaches a critical value S_c (i.e. $S \geq S_c$), flow will develop. Here S_c is seen as the intrinsic flow resistance associated with the damage including the non-uniform and non-gradual behavior of yielding, crazing and fracturing.

The intrinsic flow resistance is dependent upon the intermolecular forces and in turn the interatomic spacings. The average intermolecular distance may be related closely with the specific free volume characterizing this distance. Hence

$$S_c = \Phi(V) \quad (2)$$

where V is the free volume. That is the critical deviatoric stress is a function Φ of the dominating specific free volume V among others.

Therefore it may be adequate to establish a generalized criterion for damage intiation when

$$S \geq \Phi(V) \quad (3)$$

where the function Φ is to be determined for initial yielding, crazing or fracturing.

A general expression for Φ may be obtained by series expansion with respect to V:

$$\Phi(V) = \sum_{n=-\infty}^{\infty} C_n V^n \quad (4)$$

where C_n are material parameters dependent upon the microstructural conformation of the medium. For example when $C_n = C_o$ = constant, $V^n = V^o = 1$, the above theory subject to certain restrictions gives the well known von Mises theory of yielding--the distortional strain energy criterion. This indicates that the criterion is not affected by volume variation. When n is not zero, volume is permitted to change, therefore crazing and fracturing criteria can be formulated. All the criteria put forward earlier are reducible as special cases from the following time dependent generalized damage criterion:

earlier are reducible as special cases from the following time dependent generalized damage criterion [1].

$$S(x_k, T, t) \geq \sum_{n=-\infty}^{\infty} C_n \left[3\alpha_0 \theta(T) + \int_{-\infty}^{t} J_2(\xi - \eta)\, \dot{\sigma}_{ii}(x_k, \tau)\, d\tau\right]^n \qquad (5)$$

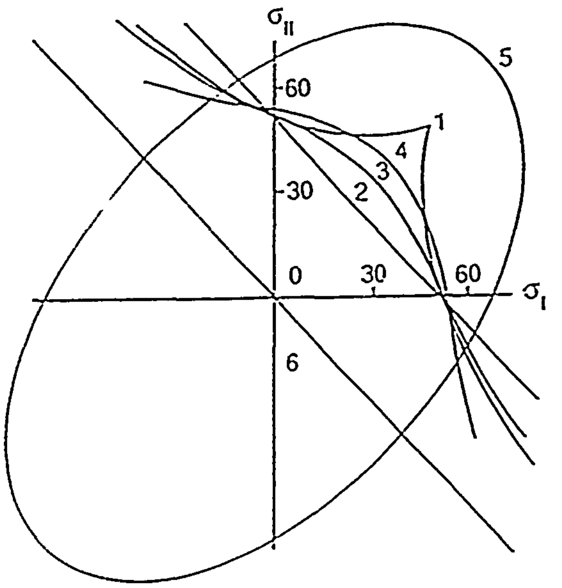
where the symbols designate quantities as below:

S	magnitude of the deviatoric stress tensor S,
x_k	coordinates in current frame of reference ($k = 1, 2$ or 3),
T	absolute temperature,
t	real time,
C_n	expansion material coefficients,
n	integers ($-\infty < n < \infty$),
α_0	constant linear thermal coefficient of expansion,
$\theta(T)$	temperature function,
$J_2(\xi - \eta)$	bulk creep compliance function, with

$\xi = t\phi(T)$ and $\eta = \tau\phi(T)$ as shift times defined by the "temperature-time shift" function ϕ for "thermorheologically simple" viscoelastic media,

and $\dot{\sigma}_{ii}$ derivative of the isotropic stress tensor with respect to time τ.

This three dimensional generalized damage criterion is reducible to any of the other criteria by introducing appropriate values for C_n. In the two dimensional situation for craze initiation this new criterion is represented by line 3 as shown in Fig. 1. This reduces to each of the other curves from 1 to 5 when appropriate values of C_n and n are introduced.



σ_I and σ_{II} designate principal stresses in MPa

Biaxial locus for criterion of craze initiation in polymers by:

1. Sternstein and Ongchin, $n = -1, 0$
2. Mohr-Coulomb (Gent, Bowden and Oxborough), $n = 0, 1$
3. New Criterion,
4. Argon, et al., $n = -1$
5. Distortion strain energy, $n = 0, 1;\ C_1 = 0$
6. 45° reference line

Fig. 1 2D Biaxial Locus for Criteria of Craze Initiation in Polymer Matrix

This generalized 3D Damage Criterion is also applicable to fracture including fatigue failure for combined cyclic stress for fiber reinforced composites [2].

References

1 C. C. Hsiao, Damage Mechanics in Composites AD12, [illegible] ASME (1987)

2 C. C. Hsiao and Y. S. Cheng, "A General Damage Criterion for Solids" proc. ICF7. International Conference on Fracture, Houston, TX, March (1989).

VI. 1.

A NEW DAMAGE CRITERION FOR COMPOSITES

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A new general damage theory for anisotropic viscoelastic composite material systems has been constructed. The theory is expressed in terms of the stress tensor function and the microstructural intrinsic damage resistance. Deformational damages such as localized sharp flow and molecular orientation, cavitation, and time-dependent volume variation including temperature effects are considered. The bifurcations and instabilities associated with the average molecular distances resulted from unbonded atomic forces and intermolecular attractions create the dominating free volume variations among others. Using series expansion the damage resistance is given in terms of internal and external energies. As a result a new general anisotropic damage criterion is obtained.

A composite material may consist of many phases of reinforcement such as whiskers, particles, or fibers which are bonded together by interphase matrices. The strength and failure behavior is critically important in analysis and design. Damages such as yielding, crazing, and fracturing of the composites are natural consequences of deformation under stress and are considered the result of the variation of the energy density in the media. From the microstructural viewpoint stressing may be visualized as a source of instable process which causes the homogeneous deformation to develop into localized bifurcation. This in turn creates distortional and dilatational changes. In general at any locale when the magnitude of the total energy density $\mathcal{E}$

reaches a critical value $\mathcal{E}_c$ damage will develop. That is when the following condition is met, damage will occur.

$$\mathcal{E} > \mathcal{E}_c \,. \tag{1}$$

Here $\mathcal{E}_c$ is seen as the intrinsic damage resistance to yielding, crazing, and/or fracturing.

The intrinsic damage resistance is dependent upon the intermolecular forces and in turn the interatomic spacings. The average intermolecular distance may be closely associated with the specific free volume Δv characterizing the distance. Hence the damage resistance can be approximated by a function of the specific free volume Δv which is a dimensionless quantity identifying the variation of the volume of the media:

$$\mathcal{E}_c = \Phi(\Delta v) \,. \tag{2}$$

A general expression for Φ may be obtained by series expansion with respect to Δv [1]

$$\Phi(\Delta v) = \sum_{n=-\infty}^{\infty} a_n (\Delta v)^n \tag{3}$$

where a_n are material parameters dependent upon the microstructural conformation of the medium.

Since most composite systems may be regarded as viscoelastic, the volume variation is expressible by summing the principal strains $\varepsilon_I(x,t)$, $\varepsilon_{II}(x,t)$ and $\varepsilon_{III}(x,t)$ or $\varepsilon_{ii}(x,t)$ the normal components of the strain tensor where x represents the spatial coordinates and t is time:

$$\Delta v(x,t) = \varepsilon_{I}(x,t) + \varepsilon_{II}(x,t) + \varepsilon_{III}(x,t) = \varepsilon_{ii} = \varepsilon_{11}(x,t) + \varepsilon_{22}(x,t) + \varepsilon_{33}(x,t)\,. \tag{4}$$

From anisotropic linear viscoelasticity, $\varepsilon_{ii}(x,t)$ can be written as the sum of thermal expansion volume and dilatational change as follows:

$$\Delta v(x,t) = \int_{-\infty}^{t} J_{iikl}(\xi-\eta)\,\frac{\partial}{\partial\tau}\sigma_{kl}(x,\tau)\,d\tau + \alpha_{ii}\theta(T) \tag{5}$$

with $\xi=t\phi(T)$ and $\eta=\tau\phi(T)$ as defined by the temperature-time shift principle for thermorheologically simple viscoelastic materials. Using (5), the time-, temperature-dependent damage theory can be rewritten as

$$\mathcal{E}(x,T,t) \geq \sum_{n=-\infty}^{\infty} a_n\Big[\,\alpha_{ii}\theta(T) + \int_{-\infty}^{t} J_{iikl}(\xi-\eta)\,\frac{\partial}{\partial\tau}\sigma_{kl}(x,\tau)\,d\tau\Big]^{n}\,. \tag{6}$$

where the symbols are reviewed as follows:

$\mathcal{E}$	is the specific energy per unit volume,
x	are the spatial coordinates,
T	is the absolute temperature,
t	is real time,
α_{ii}	is the summation of the thermal coefficients of expansion,
$\theta(T)$	is the thermal function,
$J_{ijkl}(\xi-\eta)$	is the time-dependent anisotropic compliance function with $\xi=t\phi(T)$ and $\eta=\tau\phi(T)$ as the temperature-time shift functions for thermorheologically simple viscoelastic materials,
$\phi(T)$	is the temperature function,
σ_{kl}	is the stress tensor,
τ	is a dummy time variable, and
$\dot{\sigma}_{kl}$	is the time derivative of the stress tensor σ_{kl} with respect to τ.

Since a material system can be loaded under a complex state of stressing, multiaxial conditions must be taken into consideration. The available input associated with the deformation up to damage may be divided into two parts. One part is the internal strength that the system possesses and the other part is the energy introduced into the system by stressing. The total energy may be considered as proportional to the product of a tensor β_{ij} and the stress tensor σ_{ij} as given below:

$$\mathcal{E} \sim \beta_{ij}\sigma_{ij} \tag{7}$$

where β_{ij} are the tensor coefficients which are related to functions of the internal and external energies. That is

$$\beta_{ij} = b_{ij} + b_{ijkl}\sigma_{kl} \tag{8}$$

where b_{ij} represent the internal tensor coefficients of the second rank and b_{ijkl} are the anisotropic tensor coefficients of the fourth rank.

The total energy then introduced in the material system at any time t, temperature T, and position x becomes:

$$\mathcal{E}(x,T,t) = b_{ij}\sigma_{ij}(x,T,t) + b_{ijkl}\sigma_{kl}\sigma_{ij}(x,T,t)\,. \tag{9}$$

The first term on the right hand side of (9) represents the potential energy of the system. The energy introduced by complex loading conditions is represented by the second term.

Combining (9) and (6), a new damage criterion for composites can be written as follows:

$$b_{ij}\sigma_{ij} + b_{ijkl}\sigma_{kl}\sigma_{ij} \geq \sum_{n=-\infty}^{\infty} a_n\left[\alpha_{ii}\theta(T) + \int_{-\infty}^{t} J_{iikl}(\xi-\eta)\,\frac{\partial}{\partial t}\sigma_{kl}(x,T,t)\,dt\right]^n \qquad (10)$$

At this stage when $a_0 \neq 0$, and $a_n = 0$ ($n \neq 0$), the above equation reduces to Tsai-Wu's tensor theory [2] and in turn to Tsai-Hill's theory [3,4] for anisotropic composite systems.

The development of their strength theories was originated from the distortional energy theory for yielding of solids. However, it is generally accepted that distortion cannot be separated from dilation in anisotropic composite systems. But based upon the structure of their theories there is no provision for considering the dilatational change of the material system. On the other hand the present theory does provide the possibilities of dealing with both distortion and dilatation. Detailed information will be published elsewhere in the future.

The validity of the present theory can also be seen by considering the strength theories of isotropic material systems [5]. By simplification and reduction of (10) it is also found that the general theory is applicable to not only static but also dynamic loads.

References

1. S.S. Chern and C.C. Hsiao, "A generalized time-dependent theory on craze initiation in viscoelastic media," *J. Appl. Phys.* 57, 1823 (1985).

2. S.W. Tsai and E.M. Wu, "A General Theory of Strength for Anisotropic Materials," *J. Composite Materials* 5, 58 (1971).

3. R. Hill, *The Mathematical Theory of Plasticity.* Clarendon Press, Oxford. (1953)

4. S.W. Tsai, “Strength Theories of Filamentary Structures” in *Fundamental Aspects of Fiber Reinforced Plastic Composites,* (R.T. Schwartz and H.S. Schwartz, eds.), Wiley (Interscience), New York, 3 (1968).

5. C.C. Hsiao and Y.S. Cheng, “A General Damage Criterion for Solids,” to appear in *Proc 7th Int. Conf. on Fracture* (1989).

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VI. 2.

Kinetic Strength of Solids

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ABSTRACT

The kinetic strength of a solid has been analyzed empirically and theoretically. It is found that the statistical reaction rate theory can explain satisfactorily the nonlinear behavior between fracture strength and time while the linear empirical relationship is limited in its scope.

KEYWORDS

Strength of solid bodies, Kinetic strength, Fracture strength, Time dependent strength, Reaction rate theory

The time dependent kinetic strength of solids has been studied for over half of a century. In general, two levels of approach have been employed. One is submicroscopic atomic consideration and the other may be referred to as supermacroscopic continuum investigations. The latter is mostly phenomenological which results in numerous empirical relationships. One of the most extensive investigations is that done by Zhurkov (1965). Under a state of constant stress creep condition more than 50 different kinds of solids including metallic and nonmetallic, amorphous and crystalline, oriented and unoriented systems were recorded the stress dependent of the time-to-break data. Even data on the temperature variations were tested and analyzed. It was found that the logarithm of time-to-break and the applied uniaxial tension were linearly related as

$$t_b = t_o \exp[(U - \gamma\sigma)/kT] \qquad (1)$$

where t_b is time-to-break,
t_o is a constant,
U is a constant which may be related to the activation energy of the solid,
γ is a positive definite constant,
σ is the applied constant stress,
k is Boltzmann constant and
T is the absolute temperature.

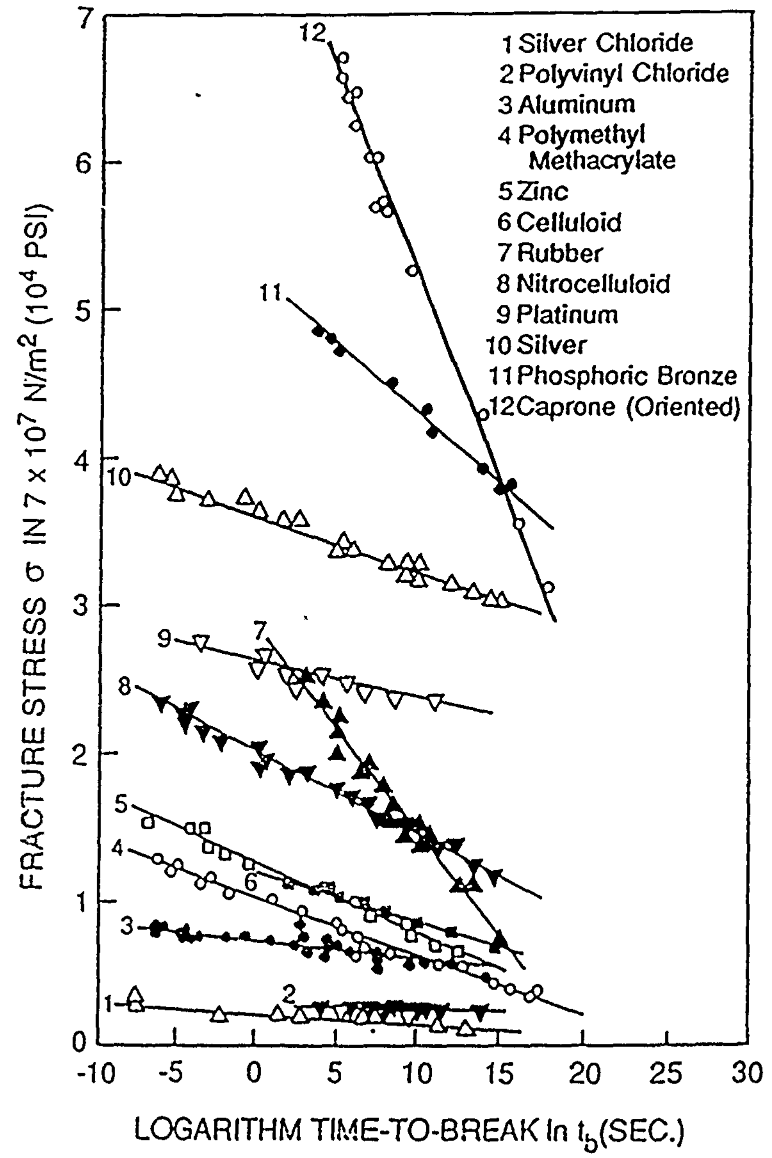

Fig. 1. Time-dependent fracture strength for solids, (after Zhurkov).

This result has been very useful as it was found to be reasonably consistent within a meso-stress range. Figure 1 shows the results of a variety of solids. It is seen that the time dependent fracture strength is indeed linearly related between the logarithm of time-to-break and the stress at fracture.

However, in reality, there is deviation from this empirical linearity when either super high stresses or relatively low stresses beyond the meso-stress range is encountered.

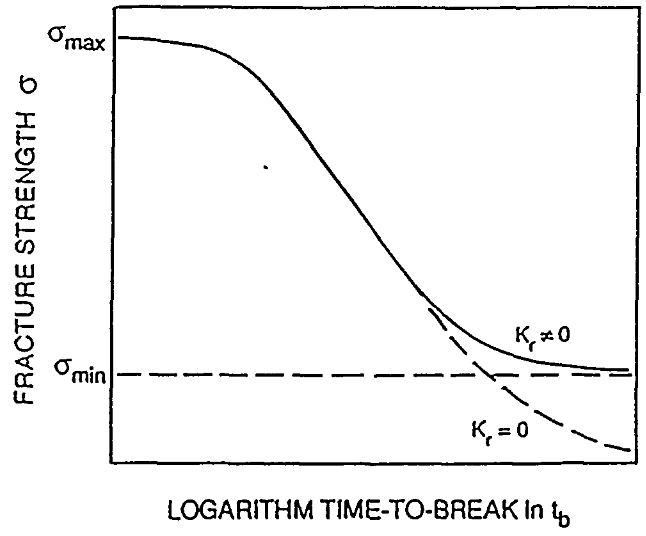

Fig. 3. Time-dependent strength of solids under simple tension.

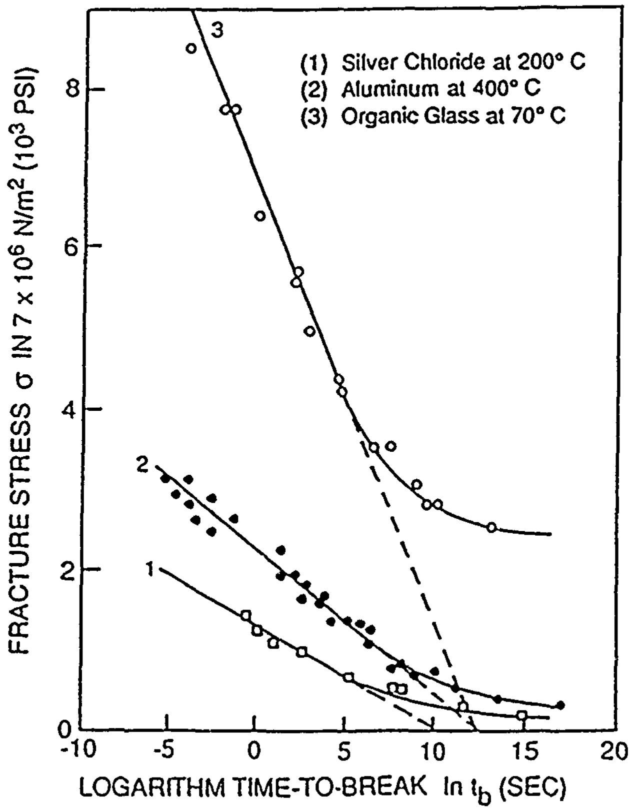

Fig. 4. Fracture stress vs. logarithm time

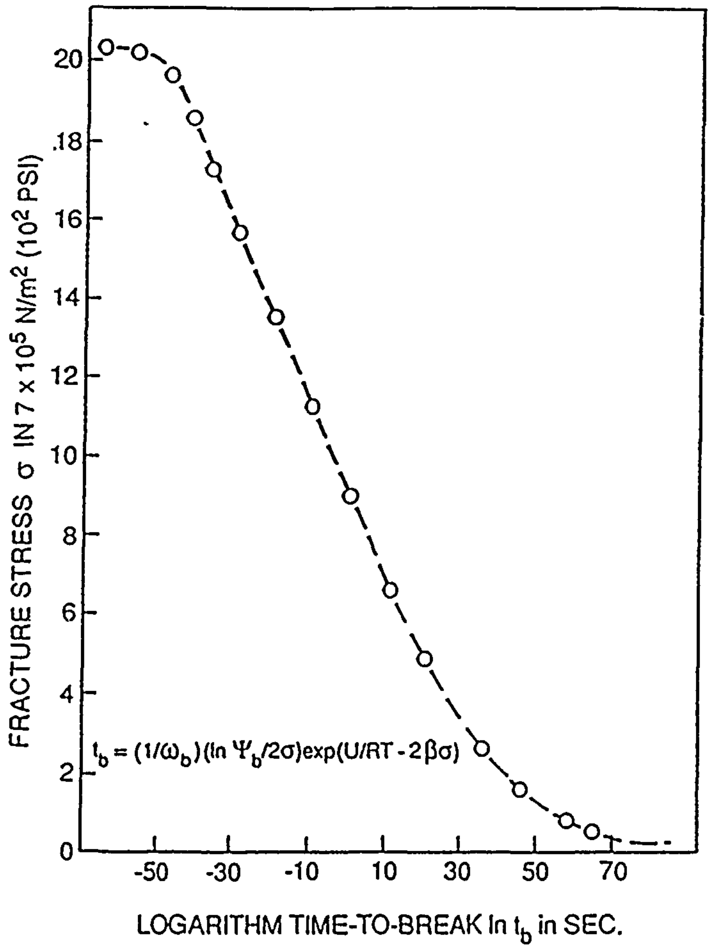

Fig. 2. Fracture stress vs. time-to-break.

$$t_b = (1/\omega_b)(\ln\psi_b/2\sigma)\exp(U/RT - 2\beta\sigma)\,. \qquad (8)$$

Using proper values (Ettouney and Hsiao, 1988) for the various quantities, (8) is plotted in Fig. 2. As can be seen, not only the mesostress range is satisfied, as the central section shows the linear relations between the logarithm of time-to-break and the fracture stress but also the nonlinear portions for both the high and low stresses beyond the linear region. From the expression (8), it is seen that K_r has been assumed zero; otherwise, the low stress region would move up as shown in Fig. 3 with $K_r \neq 0$.

All these tell us that using equation (2), the nonlinear relationships between high and low levels of the fracture stress and the logarithm of time-to-break can be matched. Indeed, this can be illustrated in Fig. 4 in which the data points for solids tested at elevated temperatures when low stress values become dominating were obtained earlier by Zhurkov and the curves were computed to show the possible representation at all stress levels.

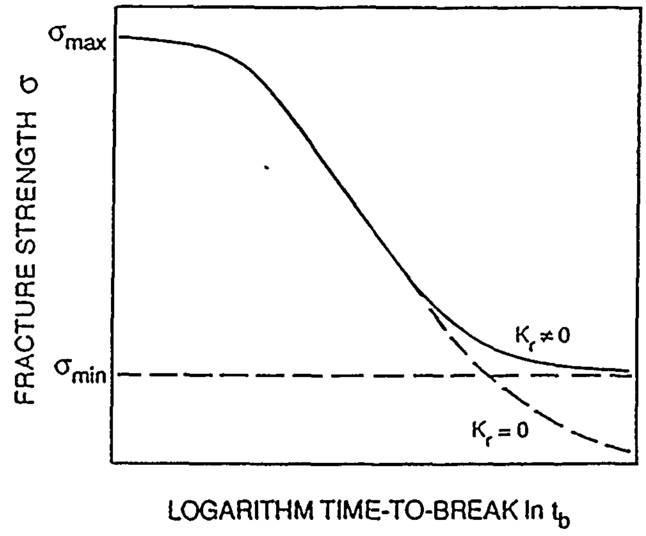

Fig. 3. Time-dependent strength of solids under simple tension.

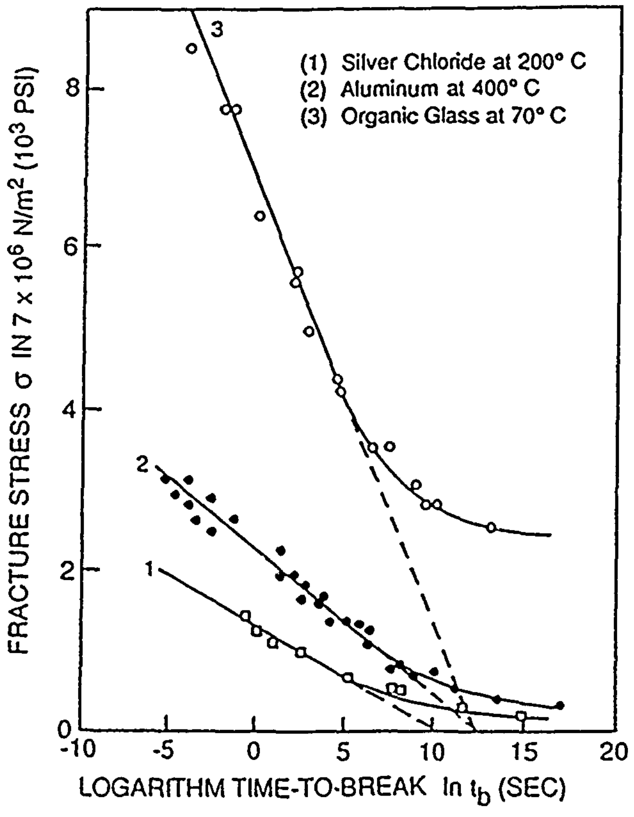

Fig. 4. Fracture stress vs. logarithm time

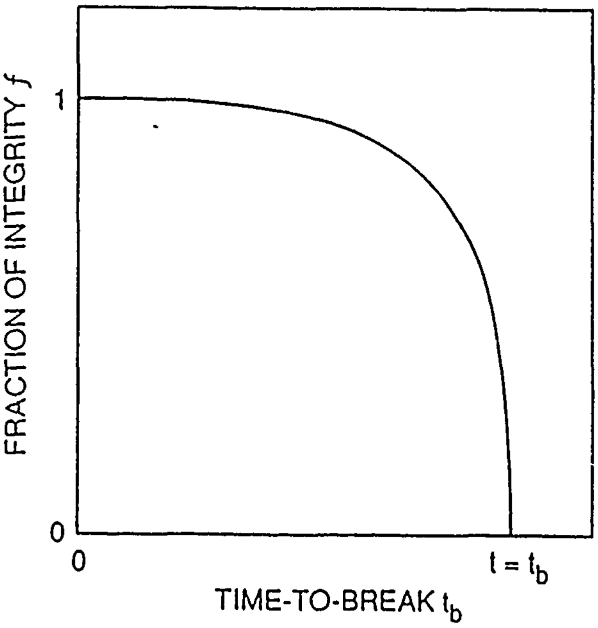

Fig. 5. Qualitative representation of fraction of integrity f versus time t.

It would be interesting to compare the high kinetic strengths with experimental values. Up to now little or no data have been found yet. However, it is felt that expression (2) should predict the kinetic strength behavior adequately. If this is accepted then the time-to-break t_b vs. f, the fraction of integrity, for a solid will be related as shown in Fig. 5.

It should be pointed out that this report seems to give the appearance of the extension of the classical one-dimensional Zhurkov model, however, it is fundamentally different from it. As stated at the beginning of this write-up that Zhurkov's model was and is an empirical relationship whereas the present model is based upon the submicroscopic atomic as well as molecular considerations. It is also quite apart from Hoff's (1953) or Kachanov's (1958) models. Using atomistic approach the current model should not be looked upon as a one-dimensional model as it is easily extended to a three-dimensional situation by introducing molecular orientation mechanism as a result of deformation (Mun and Hsiao, 1986). This mesomechanics approach is considered to be very sound as it makes the connection between microstructure, micromechanics, and macromechanics. Therefore the kinetic strength is given in terms of the basic atomic and molecular quantities, thereby the mechanical properties can be deduced for solids exhibiting creep, diffusion, or dislocation glide and so on as the time, temperature, molecular motion, and elementary bonding stresses, etc. have been incorporated into the model in the first place (Hsiao and Moghe, 1971; Hsiao, 1971).

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References

Ettouney, O.M. and C.C. Hsiao (1988). Time dependent fracture strength of solid bodies. *J. Appl. Phys.* to appear in the November issue.

Hoff, N.J. (1953). The necking and rupture of rods subjected to constant tensile loads. *J. Appl. Mech.* 20, No. 1, 105.

Hsiao, C.C. (1964). Molecular orientation–dependent fracture strength. *Fracture processes in Polymeric Solids,* Chap. IVC, p. 529.

Hsiao, C.C. and S.R. Moghe (1971). Characterization of random microstructrual systems. *Proc. Int. Conf. in Structure, Solid Mechanics, and Engineering Design in Civil Engineering Materials, Part I.* (Southampton, England). p. 95. John Wiley, London.

Kachanov, L.M. (1958). On the time of fracture under creep conditions. *Izv. AN SSSR. Otd. teckn nauk.,* No. 8, 26.

Kachanov, L.M. (1974). *Principles of Fracture Mechanics.* Moscow. Nauka, Moscow.

Krausz, A.S. and H. Eyring. (1975). *Deformation Kinetics.* Chap 4.4 Fracture. John Wiley, New York, p. 349.

Mun, M.S. and C.C. Hsiao. (1986). Time dependent fracture strength of oriented polymers. *J. Appl. Phys.* 60, 2655.

Zhurkov, S.N. (1965). Kinetic concept of the strength of solids. *Int. J. Frac. Mech.,* 1, 311.