Failure Criteria for Polymeric Solids

L. NICOLAIS* and A. T. DIBENEDETTO, *Materials Research Laboratory, Washington University, St. Louis, Missouri 63130*

Synopsis

A theory for predicting the stress–strain characteristics of polymeric solids is developed in terms of a description of microdefect formation. The process of irreversible change in these solids is assumed to be a combination of nucleation of submicroscopic defects at stress inhomogeneities and their subsequent growth to macroscopic dimensions. Straining results in the generation of crazes and cracks which can lead to catastrophic failure through either a general yielding of the material or by brittle fracture. It is assumed that nucleation of submicroscopic defects is an activated process and that defect growth is one-dimensional and linear. The total strain is expressed as the sum of an elastic recoverable strain and a nonlinear, nonrecoverable strain, and expressions are obtained for the stress as a function of time, temperature, and loading history. The criterion for yielding is defined in terms of a gross volume change associated with cavitation within crazes. The sum of the normal Poisson expansion plus this additional volume change leads to a deflection of the stress–strain curve. The criterion for brittle failure is defined in terms of a critical defect size. If the defects grow to their critical size before the stress–strain curve reaches a maximum, brittle failure occurs. The parameters of the resulting model are calculated for polyphenylene oxide polymer based on constant rate of loading experiments, and then the general creep behavior, including the time required under constant load for cold flow, is predicted. Experimental data are shown to agree with these predictions.

INTRODUCTION

At temperatures well below the primary glass transition, most organic polymers exhibit either brittle or ductile failure, depending upon the load and temperature history imposed on the material. When ductile, these polymers are tough and resistant to impact, and when brittle, they are not. Polyblending with finely dispersed rubber particles sometimes results in large increases in toughness, while polyblending with coarse, rigid particles sometimes results in increased brittleness.

The difficulty in describing the stress–strain behavior is complicated by many factors, of which the formation and growth of defects during loading is perhaps the most important. It is well known that the presence of stress inhomogeneities and/or finely dispersed second phases can induce crazes, cold flow, and a multitude of interacting cracks. It is the purpose of this paper to offer a rational theory to describe the stress–strain behavior of glassy polymeric solids.

* On leave from the Laboratorio di Ricerca su Tecnologia dei Polimeri e Reologia del C.N.R. Napoli, Italy.

THEORY

The process of irreversible change in a polymeric solid is assumed to be a combination of nucleation of submicroscopic defects at stress inhomogeneities and their subsequent growth to macroscopic dimensions. These defects might be either true cracks, in which case continued straining of the material results in the generation of a volume change in the solid,[1] or they might be crazes, in which case continued straining of the material results in the generation of a structured region analogous to that of a porous sponge in which the cell walls are highly drawn.[2] These porous regions may be thought of as aggregates of microscopic cavities within the material, which concentrate stress in a manner similar to a true crack. In any case, they lead to catastrophic failure through either a general yielding of the material or a brittle fracture.[3,4]

In developing any theory of failure, it is necessary to set criteria for both types of failure and then predict which will occur first under a given set of loading conditions.

In this paper, we deal specifically with amorphous polymeric solids which tend to craze under the influence of an external load. It has been observed that under a unidirectional tensile load, crazes will nucleate and grow perpendicular to the direction of loading. Under certain conditions, they tend to overlap and coalesce to form a nearly continuous zone of crazed material which ultimately leads to a general cold drawing, or macroscopic yielding, of the solid. This condition can be observed experimentally by the development of necking and optical birefringence in the solid, or, less precisely by the appearance of an apparent maximum in the engineering stress–strain curve. Under certain conditions, these crazes can grow to a greater length than can be tolerated by the material, and the craze rapidly changes to a macroscopic crack which propagates catastrophically, causing failure in a brittle manner.

It is assumed that the nucleation of craze sites is an activated process. Based on the work of Zhurkov et al.,[5] one can empirically justify the following form for the initial nucleation rate:

$$\frac{dN}{dt} = N_0 \left(\exp - \frac{\Delta E_N}{RT} \right) \sinh \left(\frac{(n-1)\sigma}{\sigma^*} \right) \tag{1}$$

where N_0 is a constant, ΔE_N is an activation energy, and $\sigma^*/(n-1)$ is a characteristic stress constant. For very long-term loading, Zhurkov's data show that it is necessary to account for an exponential decrease in the nucleation rate using a decay factor $\exp -t/[\lambda(\sigma,T)]$. However, eq. (1) is satisfactory for short-term stress–strain behavior.

Once craze sites have been nucleated, their growth can be represented by a one dimensional, linear growth process.[6] It is assumed that the growth rate dG/dt is given by

$$\frac{dG}{dt} = G_0 \left(\exp - \frac{\Delta E_G}{RT} \right) \sinh \frac{\sigma}{\sigma^*} \tag{2}$$

where G_0 is a constant, ΔE_G is an activation energy, and σ^* is a characteristic stress constant.

The isothermal rate of formation of microcavities within the crazed volume, $(dV_f/dt)_T$, can then be obtained from the product of nucleation and growth rates as

$$\left(\frac{dV_f}{dt}\right)_T = \beta_0 N(t) \frac{dG}{dt} = B(T) \sinh \frac{\sigma}{\sigma^*} \int_0^t \sinh \frac{(n-1)\sigma}{\sigma^*} dt \qquad (3)$$

where

$$B(T) = \beta_0 N_0 G_0 \exp - \frac{(\Delta E_N + \Delta E_G)}{RT} \qquad (4)$$

and β_0 is a porosity factor for the craze and is assumed to be constant.

In the glassy state, one can neglect pure viscous flow, and, following the suggestion of DiBenedetto and Trachte,[7] the total strain can be expressed as the sum of two terms, a linear elastic (and recoverable) strain and a non-linear (and irrecoverable) strain. The elastic strain is equated to the initial elasticity of the material σ/E_S, and the irrecoverable strain is equated to the strain caused by the additional volume created by the microcavities in the crazed regions:

$$\epsilon = \epsilon_S + \epsilon_P = \frac{\sigma}{E_S} + \frac{V_f(t)}{(1-2\mu)} \qquad (5)$$

where σ is the stress, E_S is the initial elastic modulus, μ is the Poisson ratio, and $V_f(t)$ is the microvoid volume obtained from integration of eq. (3).

Equation (5) gives the relationship between stress, strain, temperature, and time. In order to fix a point of failure for the material, failure criteria must be established. From Table I and also from data on other polymers[7] it has been found experimentally that the irrecoverable strain ϵ_P at the yield point is independent of strain rate and a linear function of temperature:

$$V_f(t_y) = b(T_m - T) \qquad (6)$$

where b is a constant and T_m is the maximum temperature at which craze sites can nucleate. The form of eq. (6) is the same as that obtained from the development of free-volume theories,[7,8] but in this paper the volume V_f is merely the microvoid volume within the crazes, and the constants b and T_m are measurable parameters.

It is also assumed that the criterion for brittle failure is determined by a critical flaw length $l_C^*(T,\rho_C)$ that is primarily a function of temperature and flaw density.

Thus, whether the material yields before brittle fracture depends upon whether the formation of crazes develops sufficient microvoid volume $V_f(t_y)$ before reaching a critical flaw size l_C^*. Which criterion is reached first depends upon the relative rates of nucleation and growth. The stress–strain behavior under some well-defined loading conditions will be considered next.

TABLE I
The Irrecoverable Strain at Yield, $\epsilon_P = V_f(T_y)/(1 - 2\mu)$, as a Function of Temperature and Strain Rate

T, °C	$\dot{\epsilon} =$ ϵ_P, (in./in.) $\times 10^2$								
	2.62×10^{-3a}	5.24×10^{-3}	1.31×10^{-2}	2.62×10^{-2}	5.24×10^{-2}	1.31×10^{-1}	2.62×10^{-1}	5.24×10^{-1}	1.31
34	2.12	2.00	2.20	2.20	2.28	2.28		2.30	2.38
52		2.08		2.18		2.12		2.12	
63	1.78	1.80	1.75	1.91	1.90	2.00	1.95	2.00	2.08
81		1.65		1.80		1.72		1.75	
100		1.40	1.43	1.57	1.53	1.55	1.68	1.68	1.60
115		1.35		1.40		1.35		1.52	
130	1.30	1.10		1.18	1.20	1.22	1.35	1.25	
140		1.18		1.15		1.13		1.22	

ᵃ $\dot{\epsilon}$ in units of in./in.-min.

Creep

In a creep experiment, the stress is constant at σ_0. The integration of eq. (3) and substitution of $V_f(t)$ into eq. (5) gives

$$\epsilon_t = \frac{\sigma_0}{E_S} + \frac{B(T)}{2(1 - 2\mu)} \left(\sinh \frac{n\sigma_0}{\sigma^*} \right) t^2. \tag{7}$$

The first term on the right side of eq. (7) represents the recoverable elastic deformation and the second term, the irrecoverable deformation associated with microvoid formation. The use of eq. (6) for the yield criterion leads to the following expression for the time to yield t_y (i.e., the time required to initiate cold drawing):

$$t_y = \left\{ \frac{2b(T_m - T)}{B(T) \sinh \dfrac{n\sigma_0}{\sigma^*}} \right\}^{1/2}. \tag{8}$$

Integration of eq. (2) gives the defect size at the yield point $G(t_y)$ as

$$G(t_y) = G_0 \left(\exp - \frac{\Delta E_G}{RT} \right) \left(\sinh \frac{\sigma_0}{\sigma^*} \right). \tag{9}$$

If $G(t_y) > l_c^*$, brittle failure occurs before cold drawing.

Constant Loading Rate

In this case, the stress is a linear function of time, $\sigma = E_S r_0 t$, and the rate of loading $\dot{\sigma}$ is constant and equal to $E_S r_0$. The integration of eq. (3) gives

$$V_t = \frac{B(T)\sigma^{*2}}{(n - 1)\dot{\sigma}^2}$$

$$\times \left[\frac{\cosh \dfrac{n\sigma}{\sigma^*}}{2n} + \frac{\cosh \dfrac{(2 - n)\sigma}{\sigma^*}}{2(2 - n)} - \cosh \frac{\sigma}{\sigma^*} - \frac{1}{n(2 - n)} + 1 \right]. \tag{10}$$

From experimental observation it is found that $n > 1$ and $\sigma_y/\sigma^* >>> 1$, so that for all practical purposes over most of the stress–strain curve, eq. (10) reduces to

$$V_f \doteq \frac{B(T)\sigma^{*2}}{4\dot{\sigma}^2 n(n - 1)} \exp \frac{n\sigma}{\sigma^*}. \tag{11}$$

Substitution of eq. (11) into eq. (5) gives

$$\epsilon_t(\sigma) \doteq \frac{\sigma}{E_S} + \frac{B(T) \, \sigma^{*2} \left(\exp \dfrac{n\sigma}{\sigma^*} \right)}{4\dot{\sigma}^2 n(n - 1)(1 - 2\mu)}. \tag{12}$$

Since the criterion for yielding is $V_f(\sigma_y) = b(T_m - T)$, the yield stress can be obtained from eq. (11) as

$$\exp \frac{n\sigma_y}{\sigma^*} = \left[\frac{4b \ (T_m - T)n(n - 1)}{B(T)\sigma^{*2}} \right] \dot{\sigma}^2. \tag{13}$$

The sensitivity of yield stress to loading rate is given by

$$\frac{d\sigma_y}{d \ln \dot{\sigma}} = \frac{2\sigma^*}{n} \tag{14}$$

which predicts that yield stress is a linear function of the log of the rate of loading. The temperature dependence of yield stress is given by

$$\frac{d\sigma_y}{dT} = -\frac{\sigma^*}{n} \left[\frac{(\Delta E_N - \Delta E_G)}{RT^2} + \frac{1}{(T_m - T)} \right], \tag{15}$$

which shows that the temperature dependence of yield stress is controlled primarily by the difference in activation energies between the nucleation and growth processes.

The defect size at the yield point can be obtained from integration of eq. (2):

$$G(\sigma_y) = G_0 \exp - \frac{\Delta E_G}{RT} \left[\frac{2^{2-n}(b)(T_m - T)n(n - 1)}{B(T)\sigma^{*2-n}} \right]^{1/n} \dot{\sigma}^{(2-n)/n}. \tag{16}$$

Constant Strain Rate

The major difficulty in analyzing constant strain rate data is that the rate of formation of microvoid volume is defined as an integral of stress over time, eq. (3), and since the stress–strain curve is nonlinear, the dependence of stress on time is not known. One can, however, define the stress–strain relation as $\sigma = E_S(\sigma)(r_0 t)$, where $E_S(\sigma)$ is a stress dependent modulus and r_0 is the rate of straining. From observations of experimental stress–strain curves, a reasonable expression for the time dependence of the stress to nearly the yield point is

$$\frac{d\sigma}{dt} \doteq E_{S0}r_0 \exp - \frac{\delta\sigma}{\sigma^*} \tag{17}$$

where δ is a constant of the order of 0.01 to 0.1. The use of eq. (17) in eq. (3) leads to

$$V_f \doteq \frac{B(T)\sigma^{*2} \exp \dfrac{(n + 2\delta) \ \sigma}{\sigma^*}}{4 \ E_{S0}^2 r_0^2 (n + \delta - 1)(n - 2\delta)} \tag{18}$$

and

$$\frac{d\sigma_y}{d \ln r_0} \doteq \frac{2\sigma^*}{n + 2\delta}. \tag{19}$$

As long as the stress–strain curve is nearly linear, constant rate of loading and constant rate of straining result in nearly the same behavior, with the yield stress being slightly less dependent on strain rate than on stress rate.

EXPERIMENTAL RESULTS

The material studied was General Electric's Grade 631-111 polyphenylene oxide with a glass transition temperature $T_g = 210°C$, a Poisson's ratio of 0.35, and the following structural formula:

$$\left[\begin{array}{c} CH_3 \\ \text{—} \langle \bigcirc \rangle \text{—O—} \\ CH_3 \end{array} \right]_n$$
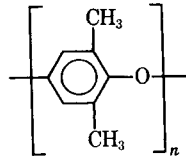
Test specimens were compression molded at 285°C, followed by a slow cooling to room temperature. All samples were annealed below T_g to minimize molding stresses. Standard ASTM tensile tests were carried out on a mod-
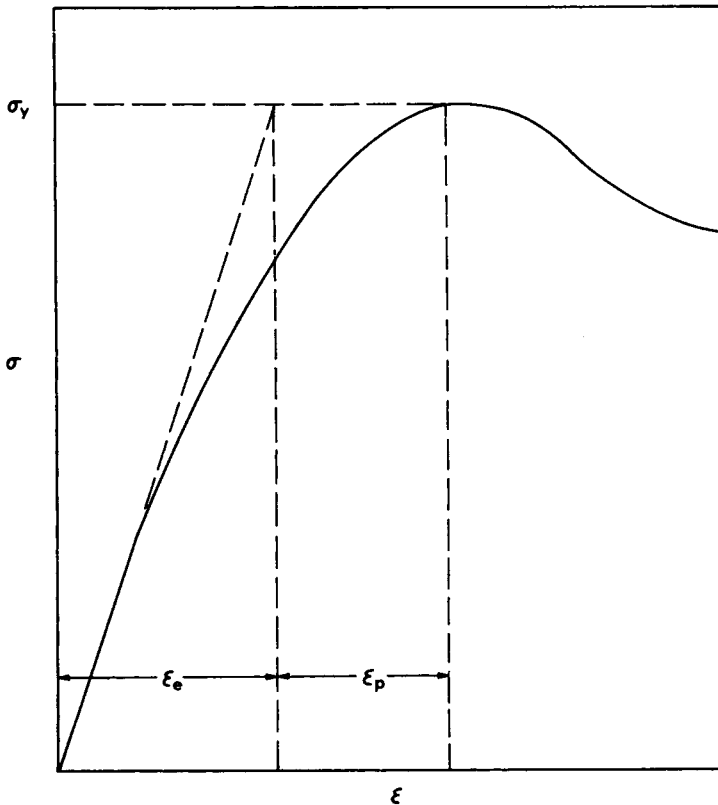
Fig. 1. Typical engineering stress–strain curve for PPO.
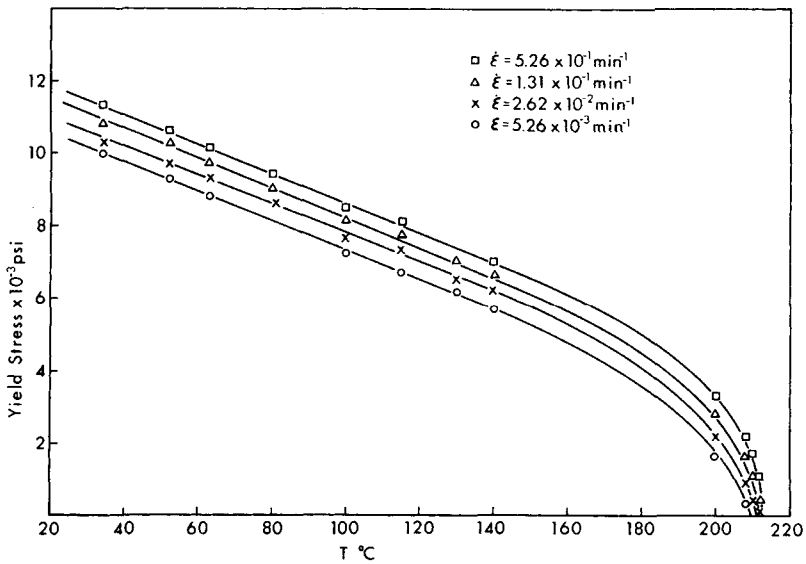
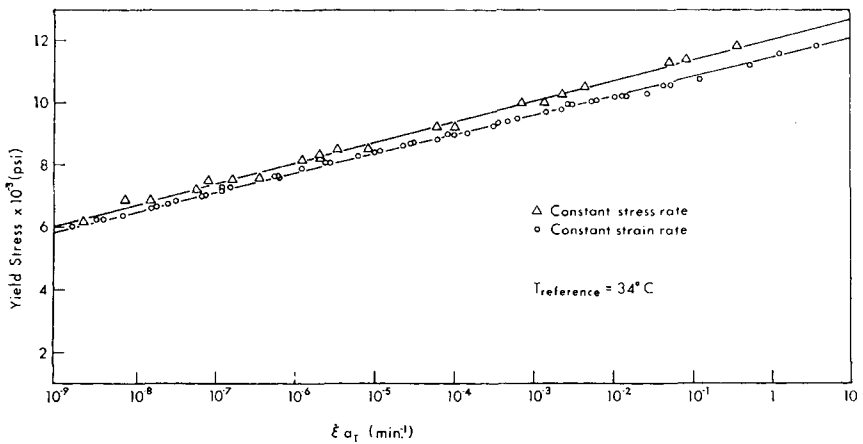Fig. 2. Effect of strain rate on yield stress.

Fig. 3. Effect of temperature on yield stress.

ified Instron testing machine which could be controlled for both constant load and constant rate of loading as well as constant rate of deformation. Tests were conducted at temperatures ranging from 34°C to 210°C and at strain rates ranging from 0.00526 to 0.525 in./in.-min.

A typical stress–strain curve is shown in Figure 1. The yield point was assumed to be the maximum in the curve. If failure occurred before this maximum, it was defined as brittle failure. The elastic strain was measured from the initial elastic modulus, and the irrecoverable deformation was associated with the nonlinear portion of the stress–strain curve. A
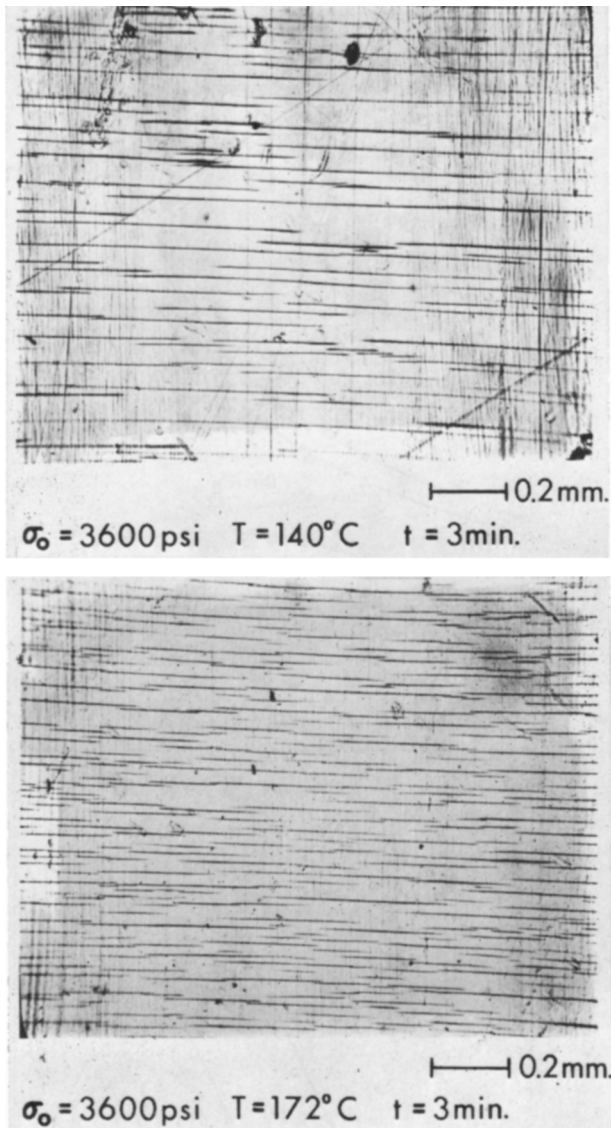
Fig. 4. Illustration of the appearances of crazes.

summary of the yield stress data at constant loading rate and constant deformation rate over a range of temperatures is given in Figure 2. Time–temperature superpositioning at a reference temperature of 34°C[9] was used to condense the data, and the required shift factor a_T is given by

$$\log_{10} a_T = \frac{8750}{T} - 28.0$$

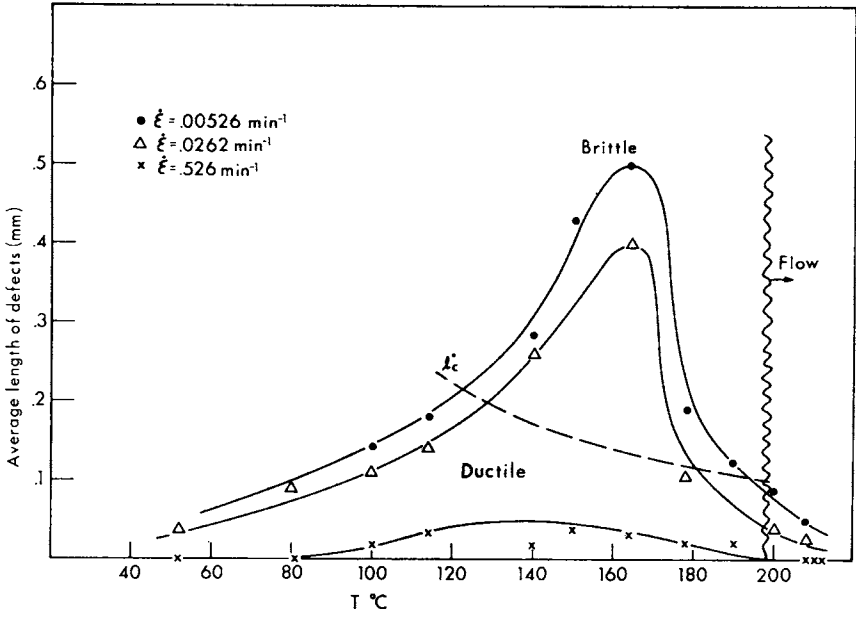where T is the temperature in degrees Kelvin.

Fig. 5. Effect of temperature and strain rate on average defect size.
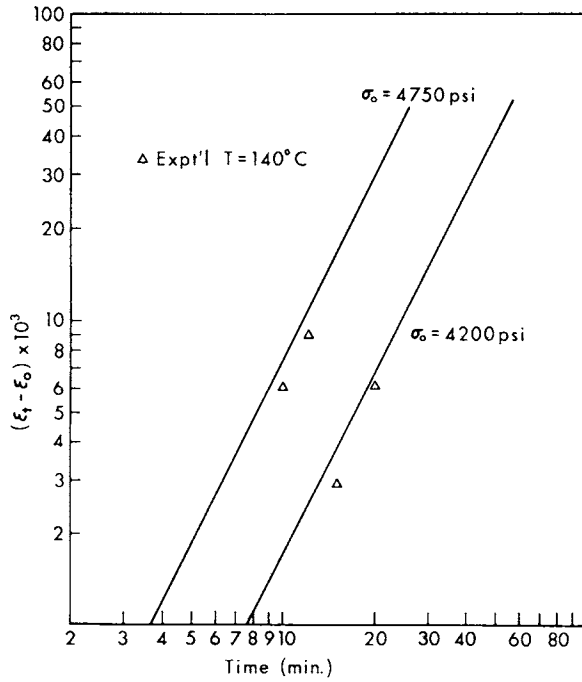

Fig. 6. Nonrecoverable deformation in creep as a function of time.

The effect of temperature on yield stress is shown in Figure 3. Table I shows that the irreversible strain at the yield point is a linear function of temperature and independent of loading rate. Its temperature dependence can be expressed as follows:

$$(\epsilon_P)_y = V_f(t_y)(1-2\mu) = 3.09 \times 10^{-5}(525 - T).$$

Figure 4 illustrates the appearance of the crazes for two test conditions. An average defect size was measured from such pictures, and the results are shown in Figure 5. Defect size is seen to be a complex function of strain rate and temperature. As long as the defect size was below the locus of points representing $l_C{}^*$, the failure was by yielding, while if the defect size was greater than $l_C{}^*$, the failure was brittle. It is reasonable to expect tha the critical defect size is a function of temperature, defect density, and defect size distribution, so that it is probably more realistic to imagine a narrow zone about the locus of points representing $l_C{}^*$ which divides the brittle and ductile zones.
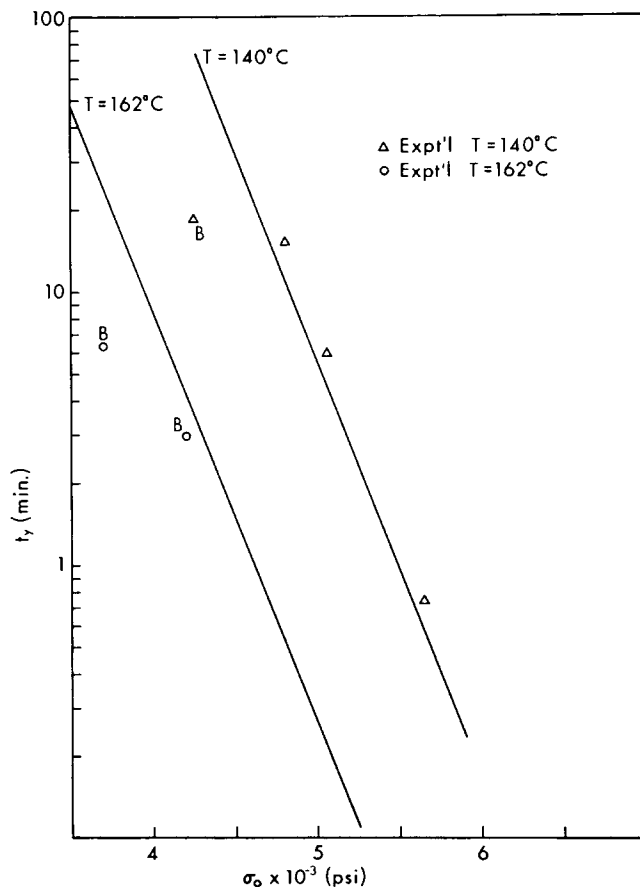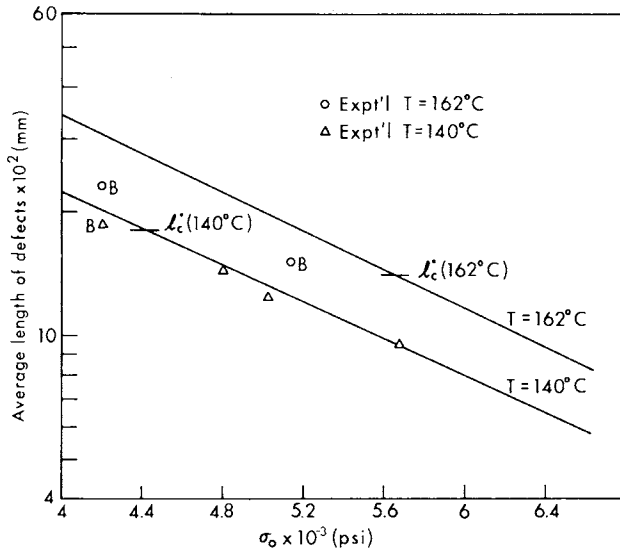

Fig. 7. Time to yield under constant load.

Fig. 8. Effect of creep stress on average defect size.

From the data shown in Figures 2 to 5 and using eqs. (4) and (12) to (16), one may evaluate all of the constants required to define the stress–strain behavior of the material.   These values are listed below:

b $= 3.09 \times 10^{-5}°K^{-1}$
T_m $= 525°K$
σ^* $= 334$ psi
n $= 2.3$
ΔE_N $= 41,700$ cal/g-mole
ΔE_G $= 32,300$ cal/g-mole
$\beta_0 G_0 N_0$ $= 2 \times 10^{20} \pm 100\%$

The values for the activation energies are reasonable for the assumed processes, and the value of σ^* is very low compared to the yield stresses in the material.   Because of this latter fact, the constant $\beta_0 G_0 N_0$ is susceptible to large error.   The limits of $\pm 100\%$ in $\beta_0 G_0 N_0$ correspond to a ± 100 psi error in load measurement, or a $\pm 1°C$ in temperature control.

The primary value of such a model is to predict the mechanical behavior in other modes of loading, based on the data from constant loading rate experiments.   By using eqs. (7) to (9), one can calculate the irreversible deformation, the time to yield, and the defect size at the yield point under a constant load.   Creep recovery experiments were run in order to experimentally determine these quantities.   The theoretical curves and the experimental data are shown in Figures 6 to 8.   The irrecoverable deformation as a function of time was calculated from the second term on the right-hand side of eq. (7).   The experimental values shown on Figure 6 agreed with theory to within experimental accuracy.   Similarly, the experimental

values for time to yield agreed with those calculated from eq. (8), as shown in Figure 7. When the failure was in the brittle mode, it occurred earlier than the calculated value for yield time. These points are marked by the symbol B in Figure 7. Equation (9) is used to calculate average defect size at yield, and the theoretical curves are plotted in Figure 8. The values of l_c^* shown in Figure 8 were obtained from Figure 5. As predicted, when the defect size was above l_c^*, a brittle failure was encountered. When ductile failure was attained, the calculated values of defect size agreed with experiment.

CONCLUDING REMARKS

A theory for predicting the stress–strain characteristics of polymeric solids has been presented. The process of irreversible change is assumed to be a combination of nucleation of submicroscopic defects at stress inhomogeneities and their subsequent growth to macroscopic dimensions. The total strain is expressed as the sum of an elastic recoverable strain and a nonlinear, nonrecoverable strain, and expressions are obtained for the stress as a function of time, temperature, and loading history. The criterion for yielding is defined in terms of a gross volume change associated with cavitation within crazes. The sum of the normal Poisson expansion plus this additional volume change leads to a deflection of the stress–strain curve. The criterion for brittle failure is defined in terms of a critical defect size. If the defects grow to their critical size before the stress–strain curve reaches a maximum, brittle failure occurs.

It has been shown that the resulting model quantitatively describes the mechanical behavior of polyphenylene oxide and that, by using stress–strain data obtained at constant rate of loading, one can predict the creep behavior of the material at constant load. A description of the ductile–brittle transition has also been presented, and it has been shown that one can qualitatively define the locus of points separating the ductile from the brittle behavior.

Concerning this latter point, it is well known that brittle failure is a stochastic process and that one cannot predict with absolute certainty the time to failure. This implies that the brittle–ductile transition cannot be represented by a single locus of points, but rather the two regions are separated by a narrow transition zone within which both modes of failure are more or less equally probable. A second point is that the concept of a simple critical crack dimension for brittle failure is oversimplified, and the criterion for brittle failure must certainly be examined in terms of stress intensity factors around crazes. Both of these points are presently under study.

References

1. R. J. Farris, *Trans. Soc. Rheol.*, **12**, 303 (1968).

2. R. P. Kambour, Paper 4.1, Conference Handbook, *The Yield, Deformation and Fracture of Polymers*, March 31 to April 3, 1970, Churchill College, Cambridge, Mass., 1970.

3. K. C. Rusch, and R. H. Beck, *J. Macromol. Sci.-Phys.*, **B3**, 365 (1969).

4. S. S. Sternstein, L. Ongchin, and A. Silverman, *Appl. Polym. Symp.*, *No.* **7**, 175 (1968).

5. S. N. Zhurkov, V. S. Kuksenko, and A. I. Slutsker, *Proceedings of the Second International Conference on Fracture*, Brighton, England, April 1969, pp. 531–544.

6. J. C. Halpin and H. W. Polley, *J. Composite Mater.*, **1**, 64 (1967).

7. A. T. DiBenedetto, and K. L. Trachte, *J. Appl. Polym. Sci.*, **14**, 2249 (1970).

8. M. H. Litt and A. V. Tobolsky, *J. Macromol. Sci.*, **B1**, 433 (1967).

9. H. Leaderman, *Text. Res. J.*, **11**, 171 (1941).