Time–Temperature Dependent Brittle Fracture
of Viscoelastic Solids

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Synopsis

The Griffith formulation is used to study fracture behavior of poly(methyl methacry-late) (PMMA) as a function of strain rate and temperature over the range $4.4 \times 10^{-5} \leq \dot{\epsilon} \leq 4.4 \times 10^{-2}$ in./in./sec and $25\,°C \leq T \leq T_g$, T_g being the glass transition temperature. It is found that the transition from brittle to ductile failure occurs abruptly at a temperature T_f which is dependent on strain rate and is approximately the same as the glass transition temperature of the material. The Griffith brittle fracture criterion is found to apply below T_f for all strain rates. The brittle fracture behavior is shown to obey the time–temperature equivalence principle in the same way as the material's other viscoelastic properties, having the same shift function.

INTRODUCTION

Over the past decade an increasing number of investigations have been made to relate the ultimate strength of polymeric solids to their viscoelastic properties. Recent investigations employ either the Bueche-type quasi-microscopic formulation or a modified Griffith continuum model to report experimental findings. The Bueche formulation is based upon a molecu-lar model describing polymeric chain interaction and predicts that under constant tensile load, the time-to-break is related to test temperature by the principle of time–temperature superposition.[1-4] Further, a conse-quence of the Bueche formulation is that the temperature dependent shift function for the parameters describing the fracture behavior should be that of the material's other viscoelastic properties. At temperatures above the glass transition temperature T_g both Bueche[2] and Smith[5,6] con-vincingly demonstrated these predictions for poly(butyl methacrylate), poly(isobutylene) and GR–S gum vulcanizate.

More recently Kwei,[7] using Bueche's formulation, showed that time–temperature equivalence applies to the ultimate strength of two epoxy polymers above and below T_g. However, no attempt was made in his work to relate the shift function for fracture behavior of the polymer to that of the material's viscoelastic characterization. This is of significance

in that the data of both Buechc and Smith show departures from the theory in the vicinity of T_g.

The purpose of this paper is to report experimental findings which indicate that (a) the glass transition temperature, T_g, of a polymer may be accurately determined by simple fracture experiments, (b) the time–temperature equivalence principle applies to the brittle fracture of poly-(methyl methacrylate) (PMMA) at and below T_g, and (c) the temperature dependent shift function for parameters characteristic of the material's brittle fracture behavior is that of the material's other viscoelastic properties.

THEORY

Based upon first law energy considerations, Griffith proposed that a spontaneous increase in the length of an existing material imperfection or crack would occur if due to unit crack extension dc, the decrease in total free energy of the system dF is greater than or equal to the total energy dS required to create new surface.[8,9] Stated mathematically:

$$-dF \geq dS$$

or

$$-dF/dc \geq dS/dc \tag{1}$$

This general failure criterion is independent of the material under consideration. The differences among various approaches to the failure of viscoelastic materials lie in the method used to express and evaluate the energy derivatives. There appears to be general agreement in expressing the energy required to create new surface in the form:

$$dS = (dS/dA)dA = gdA \tag{2}$$

Where $g = (dS/dA)$ is the energy required to create a unit of new surface during fracture and A is the fracture surface. Originally, Griffith likened g to work of cohesion. This analogy has been challenged and experimentation has shown that energies associated with residual molecular distortions and reorientations on and in the vicinity of the new surface must be included in the definition of g.[10]

Evaluation of the free energy derivative usually involves approximating the magnitude of recoverable strain energy accumulated in the system up to the instant of fracture. This becomes particularly challenging for viscoelastic materials studied at temperatures above T_g. The failure of a viscoelastic material above T_g is characterized by a tearing action accompanied by large deformations and significant viscous flow. The difficulty arising from large deformations and nonlinearity in estimating the rates of dissipation energy and the release of elastic energy becomes unimportant if the specimen geometry and the loading conditions are such that the energy exchange process remains autonomous during the fracture propagation.[11] Otherwise, considerable care may be required for a reliable esti-

mate of released potential and dissipative energies during ductile fracture of viscoelastic solids.[12]

In the low energy or brittle fracture of a large plate with a central through crack of length $2c$ and subjected to a uniform stress σ_∞ relatively large distances away from and perpendicular to the direction of the crack, the rate of free energy may be expressed as [9]

$$\frac{dF}{dc} = -\frac{2\pi c\sigma_\infty^2}{E}\alpha \tag{3}$$

where E is the modulus of elasticity, and $\alpha = 1 - \nu^2$ if c is small relative to plate thickness (plane strain) and $\alpha = 1$ if c is large relative to plate thickness (plane stress), ν being the Poisson's ratio. Equations (1)–(3) combine to define the critical uniaxial boundary stress for an elastic sheet containing an initial crack as:

$$\sqrt{c}\sigma_{\infty c} = [2Eg/\pi\alpha]^{1/2} \tag{4}$$

Berry[13] used eq. (4) by assuming $\alpha = 1 - \nu^2 = $ constant to study the brittle fracture of PMMA over the range -190 to $50°C$. Specifically, by recording the peak load at which intentionally cracked samples of PMMA fractured at various extension rates, Berry deduced the apparent temperature dependence of g. His justification for using eq. (4) is based upon the fact that viscous effects are likely to be inconsequential over the temperature range studied. Hence, elastic theory may well serve as a good approximation to brittle viscoelastic fracture. For the same reasons, it is apparent that the range of applicability of eq. (4) is bounded by the brittle–ductile transition temperature of the material, which is expected to be dependent on the strain rate and below which the deformations are small and the response of the material is brittle.

EXPERIMENTS

The material used is commercially known as Plexiglas II-UVA. The viscoelastic characterization of the material was compared to that published by McLoughlin and Tobolsky[14] and was found to be in good agreement. The glass transition temperature of the material is quoted as $108°C$.

Test blanks, 9 in. long by 5 in. wide were cut at random orientation from sheet stock of nominal thickness 0.125 in. A through slot, 0.375 in. long by 0.010 in. wide was machined into the center of each blank. The blanks were individually sealed in polyethylene bags along with a quantity of silica gel and allowed to dry for 30 days at $37°C$. Immediately before testing, a blank was removed from the bag, fitted with clamps, and a natural crack was made at both ends of the slot. The natural crack was wedged open by inserting a razor blade into the slot and gently tapping. A crack of length 0.125 in. could be formed with less than 0.008 in. penetration of the razor blade. After forming the cracks, the specimen was fitted with circular vacuum cups to insure that the natural crack was shielded
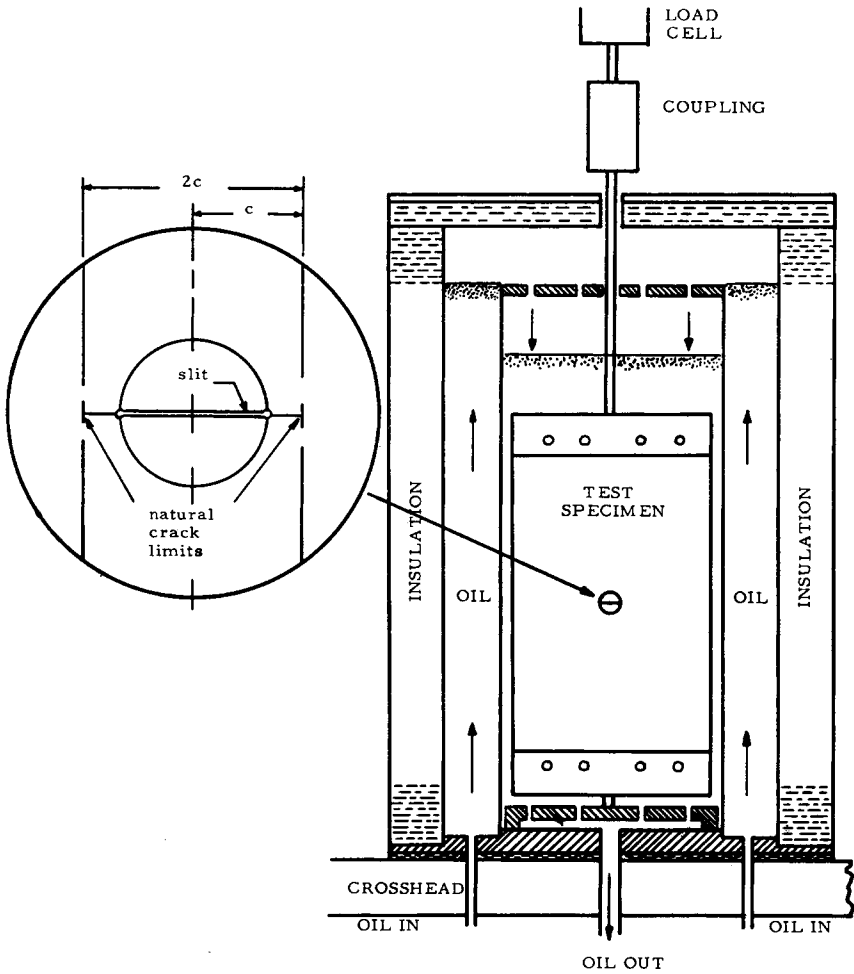
Fig. 1. Schematic of experimental apparatus.

from contamination during subsequent heating. Sufficient vacuum was pulled to allow the cups to remain in contact with the specimen until fracture.

A temperature-controlled oil bath, containing medium weight mineral oil, was securely attached to the moving crosshead of an Instron tensile tester. After bringing the oil bath to temperature, a test specimen complete with vacuum cups was totally immersed. One end was fastened to the base of the bath, the other to a load cell. The test configuration is illustrated schematically in Figure 1.

Having experimentally determined the thermal response time of the specimen–vacuum cup assembly, 30 min was allowed to attain thermal equilibrium. With a preselected crosshead displacement rate, the specimen was strained at constant rate and the load–time curve to fracture was

recorded. Temperature, crack length, and displacement rate were primary experimental variables. Time-to-fracture and peak fracture load were primary data.

As used in subsequent discussion, the critical fracture stress $\sigma_{\infty c}$ is defined as the fracture load divided by the cross section of the sample at its boundary. Each sample was measured prior to testing. Strain rate $\dot{\epsilon}$ is defined as crosshead displacement rate divided by the original distance between clamps, approximately 7.5 in.

RESULTS AND DISCUSSION

Fracture around the Glass Transition Temperature

Initially, a series of experiments was performed to determine the applicability of eq. (4) in the vicinity of T_g. By holding temperature, strain rate, and crack-tip environment constant, time-to-break and the principal variables affecting the crack-tip surface chemistry were considered experimental constants. Hence, the time–temperature dependent relaxation modulus E and the time, temperature, and environment sensitive fracture energy parameter g would be fixed at the instant of fracture. This premise could be confirmed by determining experimentally if the product $\sqrt{c}\sigma_{\infty c}$ remained constant if only crack length was varied.

With crack length the variable, Figure 2 shows the results of fracture tests conducted at 92.5°C at six separate strain rates, over the range 4.4 $\times$
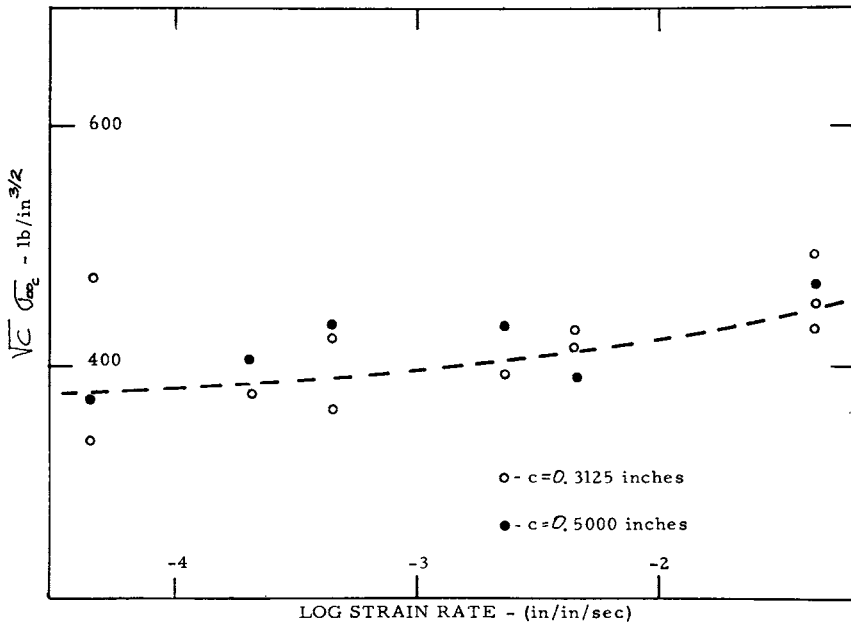

Fig. 2. Variation of $\sqrt{c}\sigma_{\infty c}$ with crack size: (O) $c = 0.3125$ in.; (●) $c = 0.5000$ in. Crack-tip environment, air; temperature, 92.5°C.
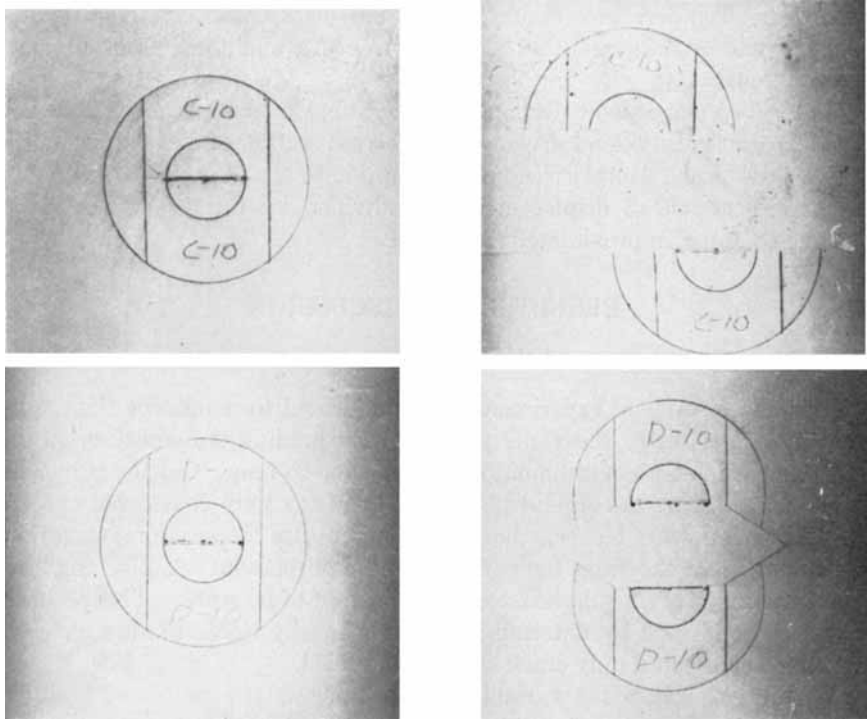
Fig. 3. Failure across the transition zone.   Strain rate = 0.011 in./in./sec.

10^{-5} to 4.4×10^{-2} (in./in./sec).   Within the data scatter encountered during this study, there appears to be no perceptible trend differentiating $\sqrt{c}\,\sigma_{\infty_c}$ as a function of crack length when time-to-break, temperature, and crack-tip environment are held constant.   The dotted line representing the variation of $\sqrt{c}\,\sigma_{\infty_c}$ with strain rate will be discussed in subsequent paragraphs.

A second observation made in the course of these tests is shown in Figure 3.   With strain rate, crack size, and environment held constant, an abrupt change in the character of failure occurred as a function of temperature alone.

The brittle mode was characterized by sudden, rapid, catastrophic fracture.   Up to the instant of fracture no changes in the geometry of the crack or sample were observed.   Subsequent calculation indicated gross strain in the order of 0.5% had occurred.   By contrast, the ductile mode showed a slow, deliberate tearing of the sample in the presence of very large deformations.

Figure 4 shows the failure transition zone as a function of temperature and log strain rate for both conditioned and unconditioned PMMA.   The data points define the limits to which the respective failure modes could be dependably reproduced.   Conditioned material is that subjected to the drying procedure previously described.   Unconditioned refers to material

allowed to freely absorb water vapor from the atmosphere for a period of at least 30 days prior to testing. In all cases the specimens were geometrically identical and the natural cracks were made immediately before testing.

It is of interest to qualitatively compare, as a function of water content and testing rate, the temperature of brittle–ductile failure transition T_f to the glass transition temperature T_g. It has been well documented that values of T_g determined by dilatometer or mechanical indentor tests are sensitive to test time or rate.[15,16] In general, short test times or high test rates result in higher reported values of T_g.[16] Both curves in Figure 4 show increasing values of T_f with increasing rate, i.e., shorter times to fracture. Also, an increase in plasticizer content of a polymer has the effect of depressing T_g. Water is an effective plasticizer of PMMA.[14] Figure 4 shows that at low strain rates the brittle–ductile transition temperature T_f for unconditioned material is smaller than for the dried material. As strain rate is increased, the influence of plasticizer content diminishes and the curves for the unconditioned and conditioned materials converge. In a study of the response of PMMA to cyclic loading below T_g, Yamamoto and Wada[17] reported that the effect of water as a plasticizer diminished with increasing frequency. Their explanation was that at high loading rates, water molecules tended to congest chain motion and cause abnormal stiffening.

Due to the remarkable qualitative similarities described above, as well as the quantitative correlation between the quoted value of glass transition temperature $T_g = 108°C$ and the measured values of the brittle–ductile transition temperature T_f at high strain rates, it is conjectured that these two quantities are representative of essentially the same characteristic behavior of the material. Also since T_f may easily be determined within $\mp 1°C$, it is felt that the fracture experiment described in this paper may provide a relatively simple method of determining the approximate value of T_g as well as its dependence on strain rate and temperature.

Fracture below Transition Temperature

The Griffith criterion as expressed by eq. (4) is not applicable to the fracture of viscoelastic materials above the brittle–ductile transition temperature T_f where material undergoes large deformations. However, as stated earlier, the energy balance equation, eq. (1), is still valid above T_f and can be used quite effectively if the energy exchange process remains autonomous as the crack propagates. Thus, it was used for example, by Rivlin and Thomas[11] in analyzing the tearing failure of elastomers. Again as previously indicated, for both above and below the transition temperature, the energy balance may be expressed in terms of a specific fracture energy g which is considered to be a characteristic parameter of the material. The question we are concerned with here is the behavior of this parameter. In a general way it was indicated by Greensmith et al.[18] that the time–temperature equivalence principle is applicable to
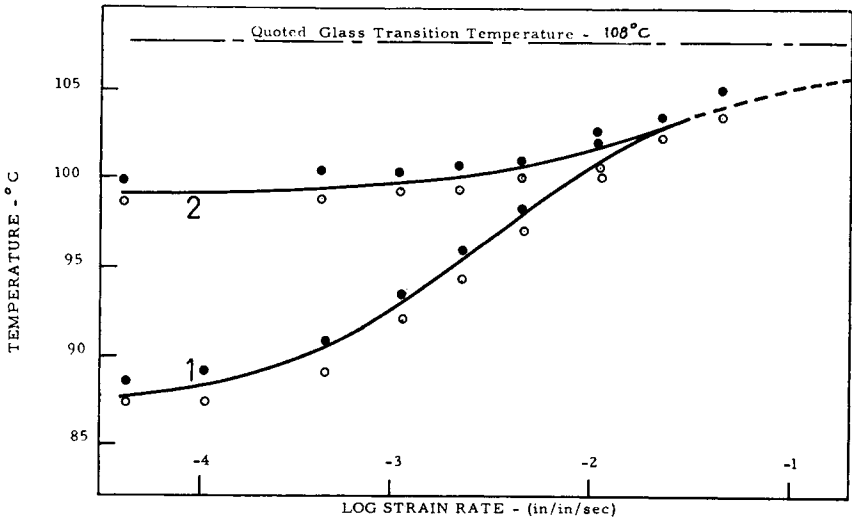
Fig. 4. Failure transition zone for (*1*) unconditioned and (*2*) conditioned material; (●) ductile; (○) brittle.

the failure of viscoelastic solids above the transition temperature—implying that g may be subject to the same principle.

To examine the validity of the time–temperature equivalence principle concerning the fracture behavior of viscoelastic solids below the transition temperature a second series of experiments was conducted. For the simple geometry considered here, the measured quantity is the critical stress intensity factor $\alpha_{\infty c}\sqrt{c}$, which represents the resistance of the solid to fracture. It should be noted that the Griffith formulation gives no direct evidence that $\sigma_{\infty c}\sqrt{c}$ should follow the equivalence principle. Although the right side of eq. (4) contains the relaxation modulus, it is difficult enough to define the fracture energy parameter g, let alone to suggest that its behavior with time, temperature, and environment should be so regular as to result in an identifiable time–temperature equivalence for $\sqrt{c}\sigma_{\infty c}$. Nevertheless, this is suggested by the Bueche theory. The experimental results are shown in Figure 5, where it is seen that for a crack-tip environment of air slightly below atmospheric pressure individual constant temperature plots of $\sqrt{c}\sigma_{\infty c}$ versus log $\dot\epsilon$ can be shifted to form a continuous master curve. The resulting log shift function, referenced to 40°C, is nearly identical to the relaxation modulus log shift function as reported by McLoughlin and Tobolsky.[14] Due to the personal judgements involved in performing the shifting process, as well as the extent of data scatter, the following procedure was used to construct the master curve and hence determine the shift function. First, a least-squares fit was made of the $\sqrt{c}\sigma_{\infty c}$ data, which was then shifted to construct a master curve and determine the shift function. The resulting master is essentially the curve shown in Figure 5. The shift function determined for the quantity $\sigma_{\infty c}\sqrt{c}$
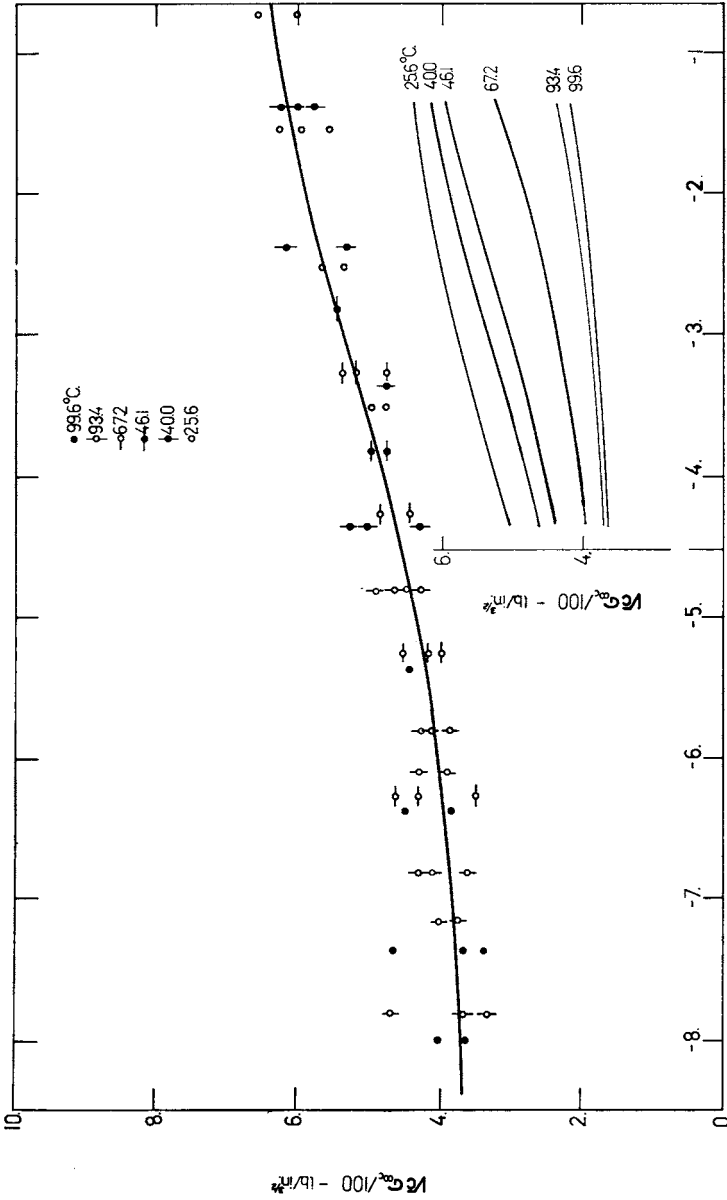
LOG STRAIN RATE   (in/in/sec)

Fig. 5. 40°C master curve for $\sqrt{c}\sigma_{\infty c}$ vs. log strain rate: ($\bullet$) 99.6°C; (ϕ) 93.4°C; ($\circ$-) 67.2°C; (-$\bullet$-) 46.1°C; ($\dot{\bullet}$) 40.0°C; ($\circ$) 25.6°C.
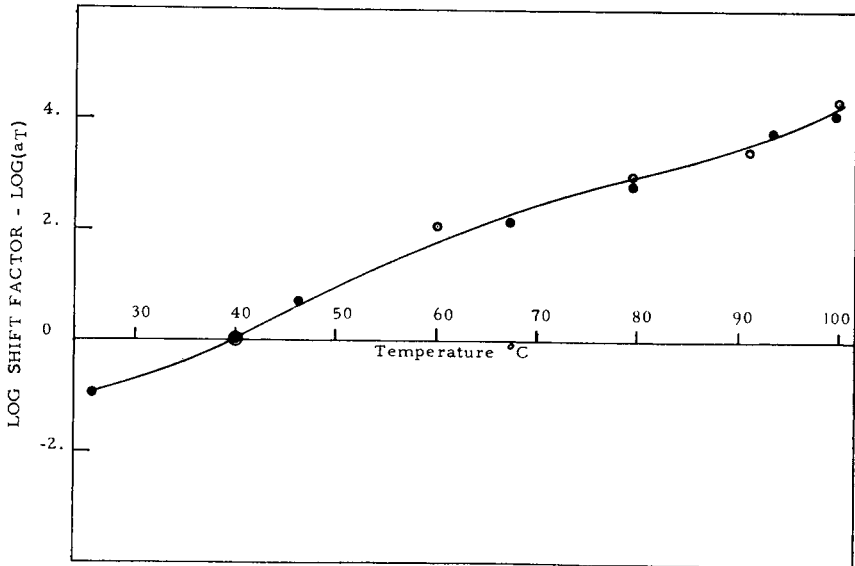
Fig. 6. Plot of log shift function for $E(t)$ and $\sqrt{c}\sigma_{\infty c}$ vs. temperature: (●) from $\sqrt{c}\sigma_{\infty c}$ data; (○) from determination of relaxation modulus by McLoughlin and Tobolsky.[14]

and that obtained by McLoughlin and Tobolsky for the viscoelastic properties of the material are shown in Figure 6. The dimensions of strain rate being t^{-1}, the log strain rate shift factors have been multiplied by -1 for the comparison. It should be noted that the master curve and associated shift function were determined from the experimental data and are independent of the author's choice of the material's viscoelastic characterization. Having used the same material and similar experimental methods, it is of interest to compare the values of $\sqrt{c}\sigma_{\infty c}$ determined in this study to those reported by Berry.[19] For experiments at room temperature and prevailing atmospheric pressure, Berry's data shows the variation:

$$600 \geq \sqrt{c}\sigma_{\infty c} \geq 450 \text{ lb./in.}^{3/2}$$

for tests conducted at strain rates:

$$8 \times 10^{-3} \leq \dot{\epsilon} \leq 8 \times 10^{-4} \text{ in./in./sec}$$

Over the same range of strain rate, the master curve when shifted to 25°C predicts:

$$600 \geq \sqrt{c}\sigma_{\infty c} \geq 560 \text{ lb./in.}^{3/2}$$

With time–temperature equivalence established for $\sqrt{c}\sigma_{\infty c}$, it remained to be deduced whether the fracture energy g is a constant or a time–temperature dependent parameter. Berry,[13] while not including time or rate effects in his analysis, reported that the fracture energy appeared to approach a constant value of 2.0×10^{-5} ergs/cm² (1.18 lb./in.²) between 0° and 50°C. He compares this value favorably to that of 4.9×10^{-5}
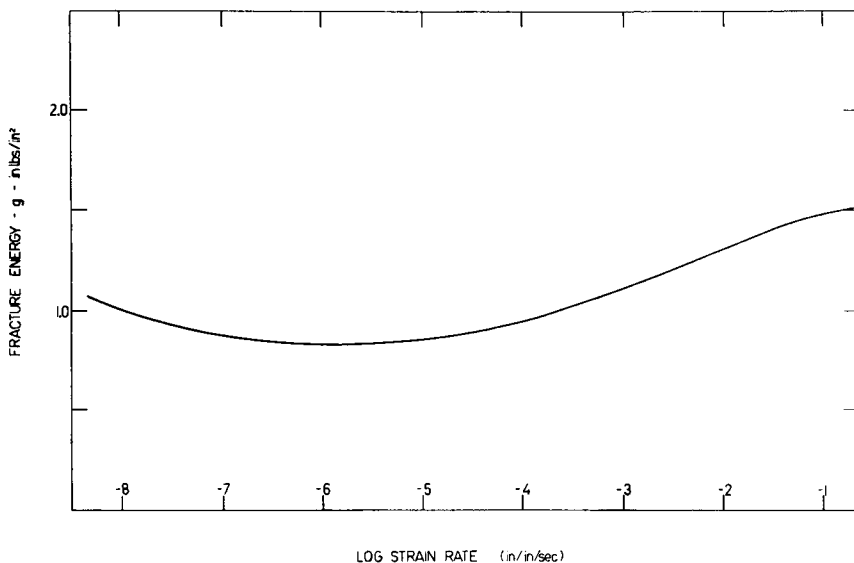
LOG STRAIN RATE   (in/in/sec)

Fig. 7. 40°C master curve for fracture energy vs. log strain rate.

ergs/cm² reported by Benbow and Roesler[20] for PMMA studied at room temperature.

If g is indeed a constant, then eq. (4) predicts that $\sqrt{c}\sigma_{\infty c}$ should behave as $\sqrt{E}$. Since only the time base is involved in the shifting process, $\sqrt{E}$ possesses the same shift function as E. Alternatively, if g is a time–temperature dependent parameter, it must possess the same shift function as the relaxation modulus to produce the behavior determined for $\sqrt{c}\sigma_{\infty c}$.

Using the relations:

$$E(\log t) = E_{T_0}(\log t + \log a_T)$$

(5)

$$\sqrt{c}\sigma_{\infty c}(\log \dot{\epsilon}) = (\sqrt{c}\sigma_{\infty c})_{T_0}(\log \dot{\epsilon} + \log a_T)$$

to represent the relaxation modulus and $\sqrt{c}\sigma_{\infty c}$, respectively, the time–temperature behavior of g, shown in Figure 7, was deduced in the following way.

For a given test temperature, the value of $\log a_T$ was selected from Figure 6 where a_T is the shift factor. Using the actual time-to-fracture at a corresponding strain rate, eqs. (5) were used to determine the values of $\sqrt{c}\sigma_{\infty c}$ and E at the instant of fracture. The values of $\sqrt{c}\sigma_{\infty c}$ and E were obtained from Figure 5 and the McLoughlin and Tobolsky[14] characterization of PMMA, respectively. Values of the fracture energy g were computed from eq. (4) and plotted as a function of strain rate. One such plot, referenced to 40°C, is shown in Figure 7. Over the range $8 \times 10^{-4} \leq \dot{\epsilon} \leq 8 \times 10^{-3}$ in./in./sec, the curves show the variation $1.1 \leq g \leq 1.25$ in.-lb./in.². This compares favorably to the value of 1.18 in.-lb./in.² reported by Berry.

CONCLUSIONS

An abrupt transition takes place in the fracture behavior of PMMA at a temperature which is essentially the same as its glass transition temperature. The specific value of this brittle–ductile failure transition temperature is a function of rate of loading and water content of the material. The Griffith criterion for the brittle fracture of an elastic-like solid applies from low temperatures up to the failure transition temperature. At temperatures below the failure transition point, the brittle fracture of PMMA obeys the time–temperature superposition principle as predicted by the Bueche formulation with the same shift function as the material's other viscoelastic properties.

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