JOURNAL OF MATERIALS SCIENCE 25 (1990) 29–34

The ductile–brittle transition in a polyethylene copolymer

XICI LU*, NORMAN BROWN
Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6272, USA

The ductile–brittle transition of an ethylene–hexene copolymer was measured from 80 to 24° C. The basic curves of stress against time to failure could all be unified in terms of a single equation based on normalizing the stress relative to the transition stress between the ductile and brittle regions and using a single thermal activation parameter. This unity is based on the observations which show that the ductile and brittle failure processes are both associated with a shear process. The unifying equation is

$$\left(\frac{\sigma}{\sigma_c}\right)^n = \left(\frac{t_R}{t_f}\right) \exp\left[85\,500/R\left(\frac{1}{T} - \frac{1}{T_R}\right)\right]$$

where σ_c is the minimum stress for ductile failure at an arbitrary temperature, T_R; t_R is the time to failure at an arbitrary reference temperature T_R; n equals 34 and 3.3 for the ductile and brittle regions, respectively and R is in $\mathrm{J\,mol^{-1}\,K^{-1}}$.

1. Introduction

In the neighbourhood of room temperature and above, polyethylene undergoes a ductile–brittle transition where at high stresses it fails in a ductile manner and at low stresses the failure is brittle. Brown, Donofrio and Lu [1] analysed this transition quantitatively and Brown and Lu [2] investigated the morphological aspects of the transition. In the ductile region the failure is associated with macroscopic yielding where the time to failure is determined by the creep rate. In the brittle region the failure is associated with the slow growth of a crack which emanates from a defect in the specimen. Both failure mechanisms occur together. At high stresses the creep rate dominates and at low stresses the rate of crack growth dominates. There is a transition region where the time to failure increases as the stress decreases. This anomalous transition region occurs because the creep strain which blunts the defect reduces the stress concentration so that crack growth is impeded. Brown and Lu [2] have nicely correlated the blunting with the changes in morphology in the neighbourhood of the notch.

The brittle mode of failure is associated with the following events: (1) immediately after loading the specimen, a craze forms at the root of the notch whose size is well approximated by the Dugdale theory, (2) the craze grows slowly, (3) fracture initiates by rupturing the fibrils near the base of the craze, (4) the crack then grows at an accelerated rate and (5) finally, when the remaining ligament reaches critical size, ultimate failure occurs by yielding of the ligament.

The ductile–brittle transition was investigated in a tough PE resin used for gas pipes. A unity between the ductile and brittle failure modes was discovered. By normalizing the stress with respect to the critical stress adjoining the brittle and ductile regions, it was found that the temperature dependence of the time to failure was the same for the ductile and brittle regions. These results are useful for predicting the very long failure times at room temperature in terms of the experimental results at elevated temperatures.

2. Experimental details

The polyethylene is an ethylene–hexene copolymer with 4.5 butyl branches per 1000 C. $M_n = 15000$ and $M_w = 170000$. The density is 0.938 and the yield point at room temperature is 21.5 MPa. The specimens were made from 10 mm thick compression moulded plaque which was slowly cooled overnight in the press. The geometry of the single-edge notched tensile specimen is shown in Fig. 1. The notch depth was 3.50 ± 0.01 mm. The 1 mm side grooves not only eliminated most of the plane stress fracture but also decreased the failure times. Each notch was made with a razor blade which was pressed in at a speed of $50\,\mu\mathrm{m\,min^{-1}}$.

The craze and crack growth processes were observed by measuring the crack opening displacements at the surface and at the tip of the notch and at the base of the craze with an optical microscope (Fig. 2).

The creep curves were observed on an unnotched dumb-bell shaped tensile specimen with a 15 mm gauge length and a 4 mm × 4 mm cross-section. The creep strain was measured with the microscope on two scratches 1 mm apart.

*Visiting Scientist from the University of Science and Technology of China, Hefei, Anhui, Peoples Republic of China.

0022–2461/90 $03.00 + .12

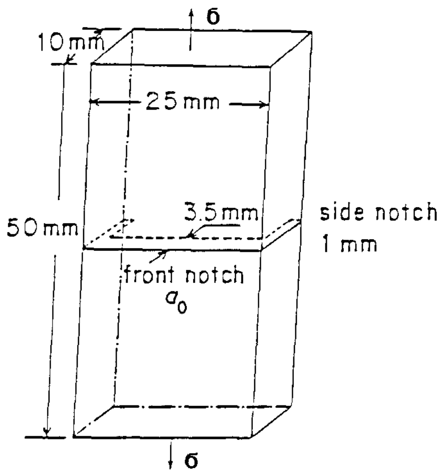

Figure 1 Geometry of specimen.

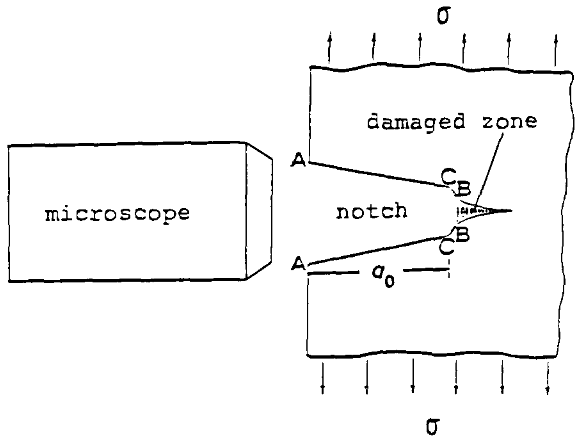

Figure 2 Experimental measurement of notch opening.

3. Results

Fig. 3 shows stress plotted against time to failure at 80, 70, 60, 50, 42, and 24° C. The stress is based on the unnotched area. In the ductile region $t_f \sim \sigma^{-34}$ and in the brittle region $t_f \sim \sigma^{-3.3}$. The behaviour in the transition region is anomalous where t_f increases as σ increases. In the ductile region the notch becomes very blunt and the failure occurs by the yielding of the ligament. In the brittle region the failure occurs by slow crack growth which initiates at a craze which forms at the root of the notch.

Fig. 4 compares the ductile failure of notched and unnotched specimens. In both cases $t_f \sim \sigma^{-34}$. The failure time in the notched specimen was based on the ultimate fracture of the ligament after general yielding occurred in the ligament. Failure time in the unnotched specimen was related to the initiation of a neck that is associated with the yield point. The small difference between the ductile failure curves of the notched and unnotched specimen is related to their difference in geometry and is not associated with a difference in the failure mechanism which is caused by creep. Creep curves of the unnotched specimens are shown in Fig. 5 at 80° C for various stresses. Necking failure occurs when the curves begin to accelerate. The critical strain to failure was about 70% at 80° C. As the temperature decreases the creep strain at yielding decreases. At room temperature the strain at yielding is about 12%.

Fig. 6 shows the typical behaviour in the brittle region. AA is the notch opening at the surface of the specimen. CC is the notch opening at the root of the notch and BB is the thickness of the fibrilla structure of the craze. The fact that BB and CC are very nearly equal indicates that the notch is sharp as a result of the small amount of creep that occurs at the bottom of the notch. When the specimen was initially loaded, a craze with a thickness of about 50 μm was formed as shown in Fig. 7a. The craze grew in thickness to about 150 μm after about 3×10^4 min. Figs 7b to d show the increase in size of the craze. Fracture initiated after 3×10^4 min as indicated in Fig. 6 at point c. Fig. 7e shows the craze shortly after fracture occurred and Fig. 7f shows the growing crack with its craze leading the way. In Fig. 6 the slow crack growth process proceeds from point d to g. After the point g in Fig. 6 the remaining ligament rapidly creeps and the final failure process occurs by the ductile fracture of the remaining ligament. The fact that the AA and CC curves are nearly parallel indicates that the angle of the craze remains constant during most of the fracture process.

Fig. 8 contains micrographs of the fracture of the fibrils in the craze. Each fibril behaves like a tensile specimen which undergoes necking and eventually fractures by a process of shear thinning as described by Bahttacharya and Brown [3]. On a microscopic scale the failure process in the brittle region is similar

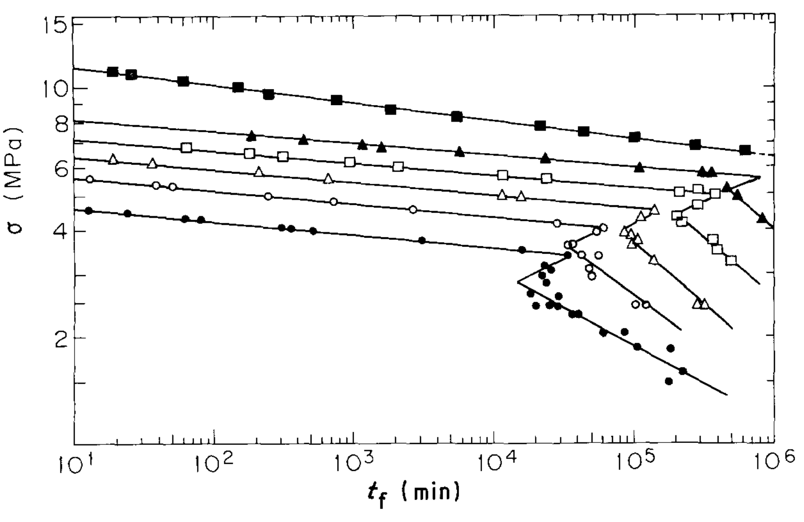

Figure 3 Stress plotted against time to failure at different temperatures (■ RT, ▲ 42° C, □ 50° C, △ 60° C, ○ 70° C, ● 80° C).

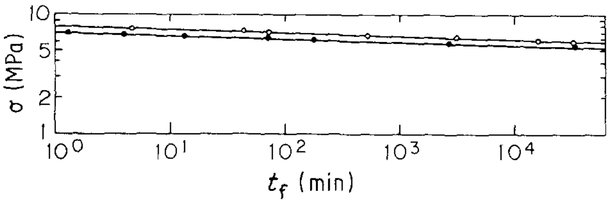

Figure 4 Stress plotted against time to failure for notched (○) and unnotched (●) specimens in ductile regions at 80° C.

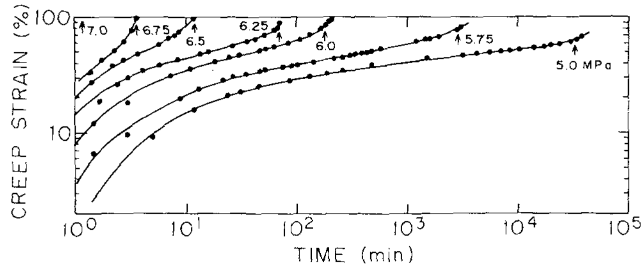

Figure 5 Creep curves of unnotched specimens at 80° C for various stresses.

to macroscopic shear failure that occurs in the ductile region. Whereas the average applied stress governs the ductile failure, the localized stress field at the root of the notch governs failure in the so-called brittle region.

An important aspect of the ductile–brittle transition is the stress that adjoins the ductile to the brittle region. This critical stress which is the minimum stress in the ductile region we call σ_c; it can be obtained from Fig. 3. The curves of crack opening displacement for these critical stresses are of special importance and are shown in Fig. 9 for the temperatures ranging from 24 to 80° C. These curves are essentially linear up to the time when the initial fracture of the fibrils occurs (i.e., crack initiation). At crack initiation, the values of the COD based on an extrapolation of the linear region to the time of crack initiation is essentially constant at 1450 μm between 24 and 70° C. Plots of σ_c and σ_y against temperature are shown in Fig. 10. σ_c is related to σ_y because both the ductile and brittle failure processes involve shear and σ_y is the basic measure of the shear strength in the material.

The temperature dependence of the time to failure for the ductile region for a constant stress is shown in Fig. 11. The plots of log t_f against $1/T$ vary with stress with slopes of 270 kJ mol^{-1} to 172 kJ mol^{-1} as the stress varies from 5 to 7 MPa. The temperature dependence of the time to failure in the brittle region is 116 kJ mol^{-1} and is independent of stress.

4. Discussion

The temperature dependence of the time to failure in the ductile region depends on the temperature dependence of the creep rate, of the amount of strain to produce yielding and of the yield point. The creep rate is a thermally activated process governed by an activation energy. The yield strain changes with temperature and is related to the amount of strain that the amorphous and crystalline regions can sustain before the lamella structure becomes unstable. The effect of the stress is relative to the yield point of the material at that temperature and thus the temperature dependence of the yield point contributes to the overall temperature dependence of the time to failure. It was found that the temperature dependence of the time to failure in the ductile region was unified by normalizing the stress relative to σ_c rather than σ_y. Fig. 12 shows the result where for a constant value of σ/σ_c

$$t_{fD} = t_{oD} \exp(Q/RT) \qquad (1)$$

where $Q = 85$ kJ mol^{-1} and was independent of σ/σ_c and t_{oD} depends on σ/σ_c.

The same normalization of the stress was used for the brittle region as shown in Fig. 13 where

$$t_{fB} = t_{oB} \exp(Q/RT)$$

where $Q = 86$ kJ mol^{-1}. These results indicate that by normalizing the stress relative to σ_c the same temperature parameter held for time to failure in the ductile and brittle regions. As a result all the curves in Fig. 3 were unified by plotting the normalized stress σ/σ_c against $t_f \exp(85\,500/RT)$. The curves were reduced to a single curve where the temperatures were normalized to 24° C as shown in Fig. 14. In the ductile region

$$t_{fD} = 9.3 \times 10^6 (\sigma/\sigma_c)^{-34} \text{ min}$$

and in the brittle region

$$t_{fB} = 2.2 \times 10^6 (\sigma/\sigma_c)^{-3.3} \text{ min}$$

At $\sigma/\sigma_c = 1$; $t_{fD}/t_{fB} = 9.3/2.2 = 4.2$ which represents the extent of the anomalous transition region. This simple unification of all the curves in Fig. 3 was a surprise. It demonstrates a unity between the ductile and brittle failure processes which probably is based on the fact that a shear mechanism is involved in both regions. Clements and Sherby [4] found a similar unification procedure in their investigation of the creep behaviour of PE under compression. Their data showed two distinct stress regimes for the dependence of the creep rate on stress. When they normalized the applied stress with respect to the stress that adjoined the two regimes, they were able to unify all their data in a manner similar to our discovery.

The curves in Figs 3 and 14 are for single edge

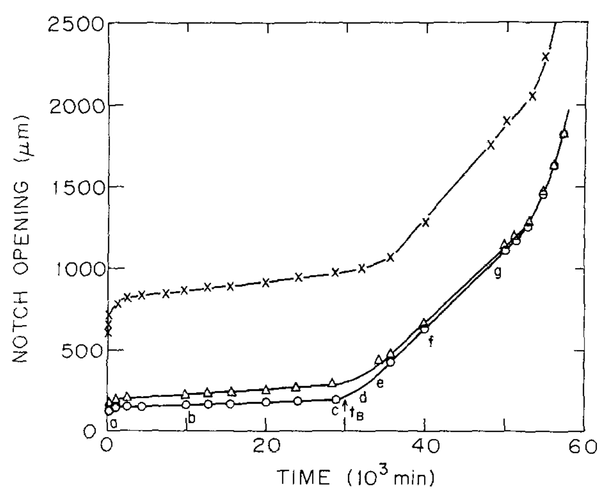

Figure 6 Notch opening AA (×), at surface, CC (△) at root of notch and BB (○) at base of craze in brittle region at 80° C.

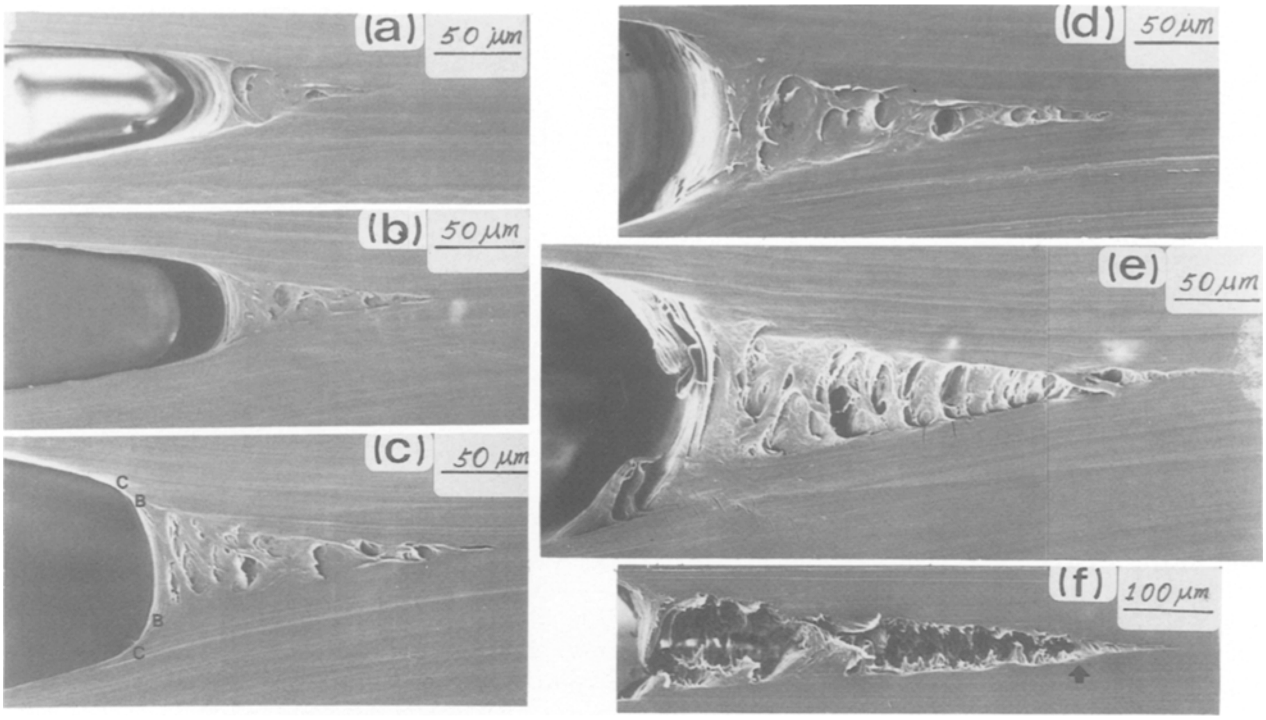

Figure 7 The damage zone at different loading times, a to f. (See text.)

tension specimens with a 3.5 mm deep notch. The ductile region is governed by stress and temperature, but the brittle region is essentially governed by the stress intensity and temperature as shown by Lu and Brown [5]. Thus, the ductile region is essentially independent of notch depth if the stress is based on the notched area. The brittle region at a given temperature should consist of series of parallel curves which are shifted in accordance with the notch depth, but it is more fundamental to plot stress intensity, K, against t_f in the brittle region. Lu and Brown [5] showed that for this copolymer K varied approximately as $t_f^{-1/4}$. As an example of the effect of notch depth on t_f, Fig. 14 predicts that the minimum time for brittle failure at

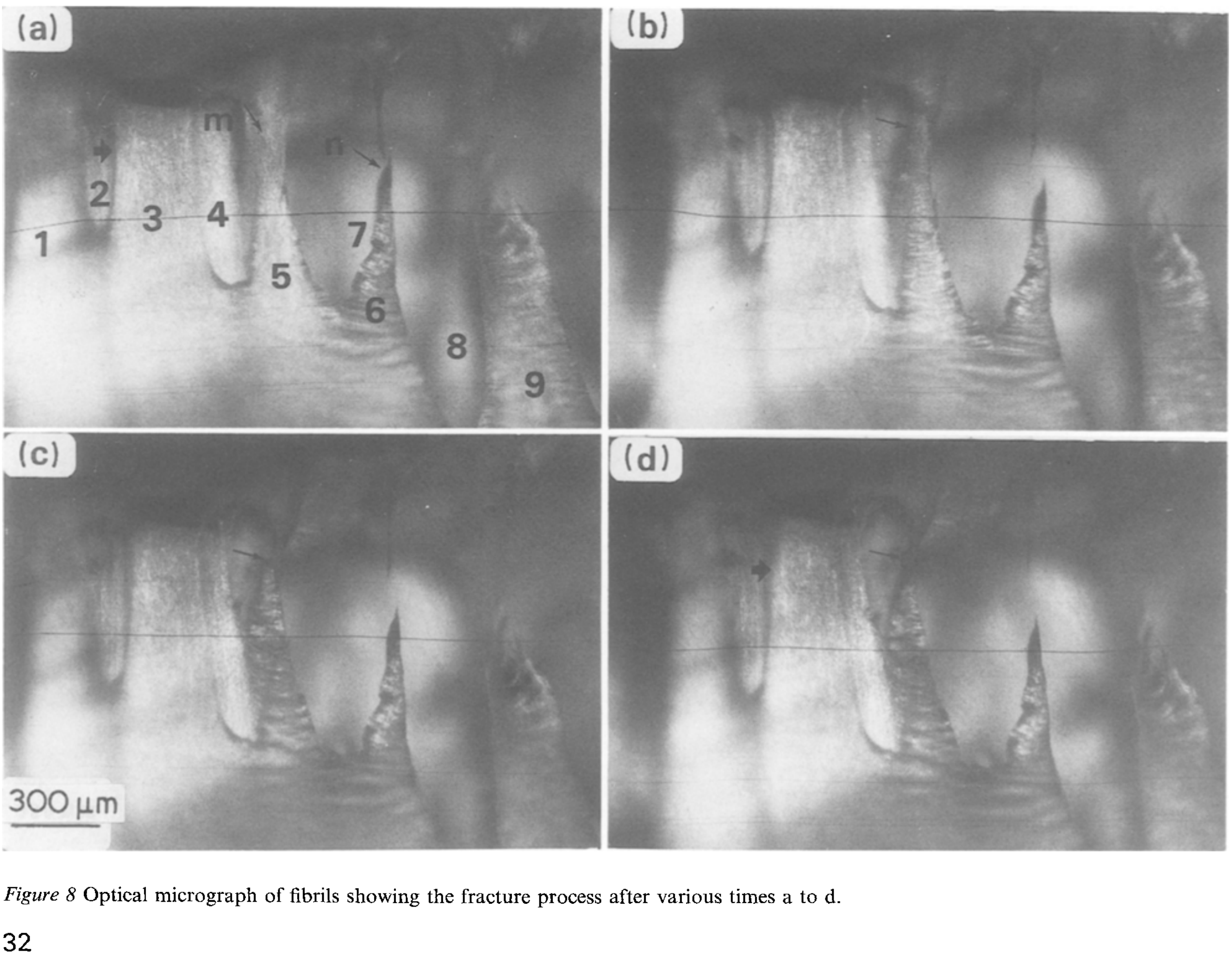

Figure 8 Optical micrograph of fibrils showing the fracture process after various times a to d.

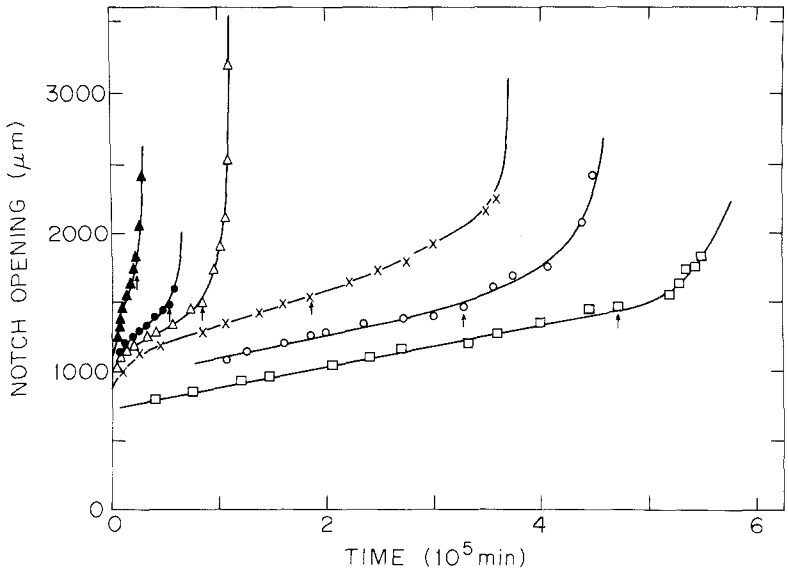

Figure 9 Notch opening, CC, plotted against time at the critical stress σ_c which adjoins the brittle and ductile regions at various temperatures. (▲ 80° C, ● 70° C, △ 60° C, × 50° C, ○ 42° C, □ 24° C) Arrows indicate when fracture initiates.

24° C is about 4 years for a 3.5 mm notch. The corresponding time for a 0.35 mm notch is about 10^3 times greater.

It is useful to predict the time for failure at low temperatures and stress from data obtained in the laboratory for relatively short time experiments at higher temperatures and stresses. Accordingly, it seems necessary to determine σ_c as a function of temperature and the stress exponents in the ductile and brittle region and the thermal activation parameter, Q. The stress exponents are rather independent of temperature especially for 70° C and below, and thus can be determined from relatively short time experiments. If σ_c is measured as a function of temperature, then the curve can be extrapolated to a lower temperature of interest. Once σ_c is obtained, the ductile curve can be drawn according to its stress exponent. The brittle curve is almost determined except for the offset associated with the transition region. The offset is about a factor of 4 for all temperatures.

A method of prediction of failure in the brittle region that is now being proposed by an ASTM committee is based on the equation

$$t_f = A\,\sigma^{-n} \exp\left(Q/RT\right)$$

where A, n, and Q are assumed to be independent of T and the purpose is only to predict failure in the brittle region at low stresses. At least three data points are required, two at the same stress and different temperatures and two at the same temperature and different stresses, but all data points must be in the brittle region in order to determine A, n and Q. However, the above equation does not give the maximum stress at which brittle behaviour occurs at a particular temperature. Our method of prediction requires more data points but is more complete. The most revealing information about the slow crack growth resistance for different polyethylenes is shown by the curves of σ_c against T and σ_c against t_f. The greater t_f at σ_c and at the temperature of service, the better the polyethylene.

5. Summary

It was found that the curves of stress versus time to failure in the ductile and brittle regions from 80 to 24° C for a polyethylene copolymer could be unified

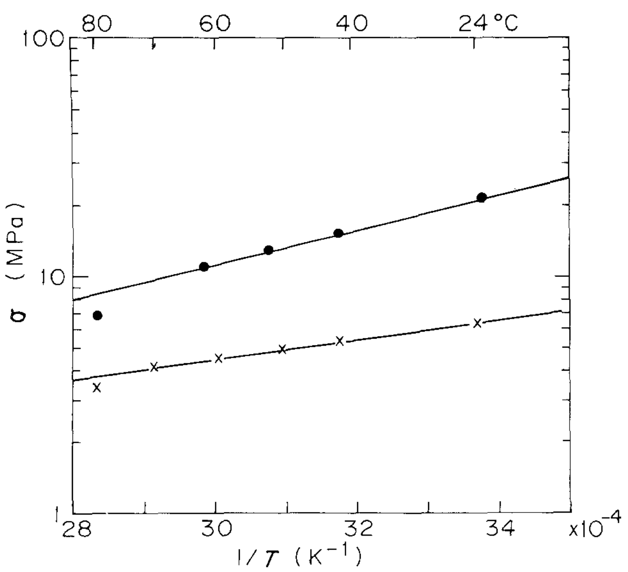

Figure 10 Temperature dependence of the yield point, σ_y (●) and σ_c (×).

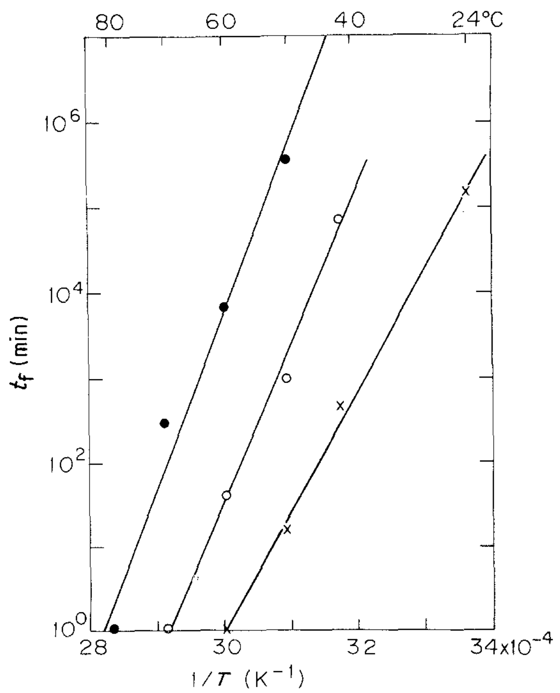

Figure 11 Time to failure in the ductile region plotted against $1/T$ at various stresses (● 5 MPa, ○ 6 MPa, × 7 MPa).

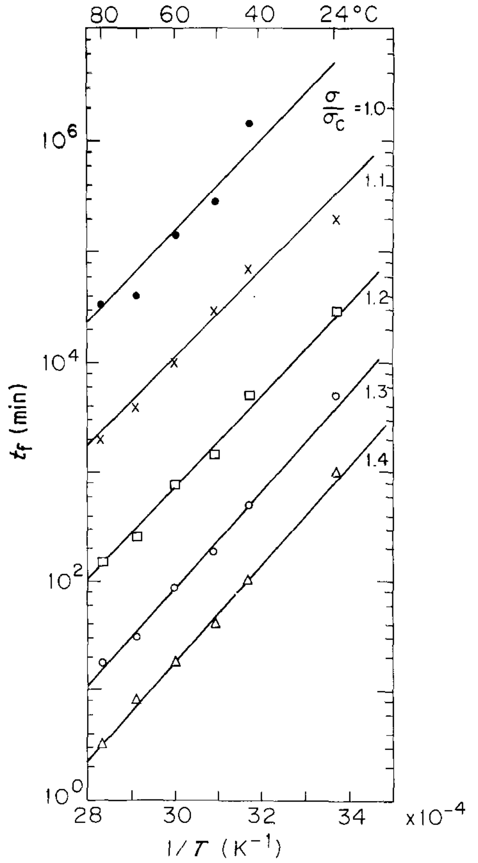

Figure 12 Time to failure plotted against $1/T$ in the ductile region for constant values of σ/σ_c (● 1, × 1.1, □ 1.2, ○ 1.3, △ 1.4).

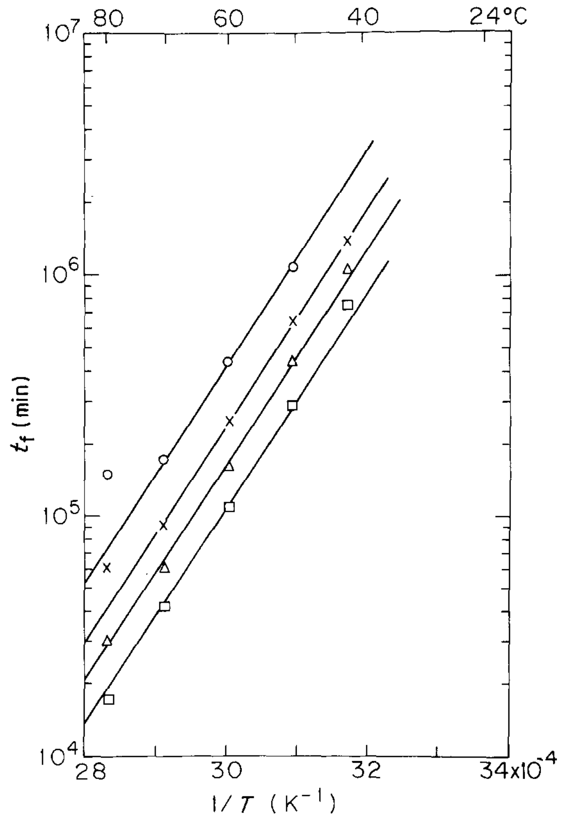

Figure 13 As Fig. 12 for the brittle region. (○ 0.5, × 0.6, △ 0.7, □ 0.8).

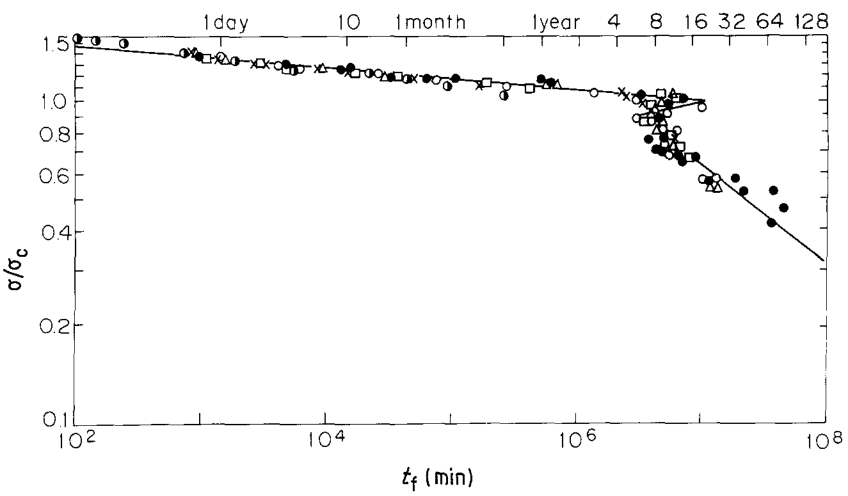

Figure 14 Master curve of σ/σ_c plotted against t_f for a reference temperature of 24° C. Test temperature room temperature (◑), 42° C (×), 50° C (□) 60° C, (△), 70° C (○) and 80° C (●).

by the following equation

$$\left(\frac{\sigma}{\sigma_c}\right)^n = \left(\frac{t_R}{t_f}\right) \exp\left[85\,000/R\left(\frac{1}{T} - \frac{1}{T_R}\right)\right]$$

where σ_c is the minimum stress for ductile failure at the temperature, T; t_R is the time to failure at T_R which is an arbitrary reference temperature; n equals 34 and 3.3 for the ductile and brittle regions respectively; R is in J mol^{-1} K^{-1}.

Acknowledgements
The research was supported by the Gas Research Institute and the Department of Energy. The central facilities of the Materials Research Laboratory at the University of Pennsylvania as supported by NSF were most helpful.

References
1. N. BROWN, J. DONOFRIO and X. LU, *Polymer* **28** (1987) 1326.
2. X. LU and N. BROWN, *J. Mater. Sci.* in press.
3. S. K. BHATTACHARYA and N. BROWN, *J. Mater. Sci.* **19** (1984) 2519.
4. L. CLEMENTS and O. D. SHERBY, Strain Rate/Temperature Behavior of High Density Polyethylene in Compression, NASA Technical Memorandum 78544, Nov. 1978.
5. X. LU and N. BROWN, Tenth Plastic Fuel Gas Pipe Symposium (American Gas Association, Arlington, VA, 1987) p. 298.

Received 27 January
and accepted 13 February 1989