The effect of orientation on slow crack growth in high-density polyethylene

Z. Zhou and N. Brown*
Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA
(Received 28 June 1993; revised 7 October 1993)

High density polyethylene (HDPE) was drawn at 80°C with draw ratios from 1 to 3.5. The resistance to slow crack growth was measured on notched tensile specimens under plane strain conditions and over a range of temperatures. The notches were made parallel or perpendicular to the direction of orientation. The failure times for crack growth perpendicular to the orientation direction varied exponentially with the draw ratio, and for crack growth parallel to the orientation direction the time of failure decreased to zero for a draw ratio of about 1.5. The activation energy was 110 kJ mol^{-1} and was independent of the draw ratio.

(Keywords: high-density polyethylene; slow crack growth; molecular orientation)

INTRODUCTION

The degree of molecular orientation has a profound effect on the mechanical behaviour of all polymers. The orientation effect is based on the relative amounts of the covalent and Van der Waals bonds, which offer the resistance to the applied stress. An extensive amount of literature exists on the effects of orientation on the mechanical properties such as the elastic modulus, yield point, ductility, fracture stress, impact energy and creep. There are relatively few reports on the property of time-dependent slow crack growth. Lu *et al.*[1] have measured the effect of molecular orientation on slow crack growth (SCG) in extruded polyethylene (PE) gas pipes. They measured the resistance to SCG parallel and perpendicular to the extrusion direction. As expected, the cracks grew more slowly in a direction perpendicular to the extrusion direction. They defined the anisotropy factor for SCG as the ratio of the times to failure in directions parallel and perpendicular to the extrusion direction. They measured the degree of orientation by a shrinkage method. They correlated the anisotropy ratio with the degree of shrinkage. In order to understand better the relationship between the degree of orientation and SCG, it is desirable to obtain a more quantitative relationship between the degree of orientation and SCG. In this investigation SCG was measured in specimens that were oriented to specific draw ratios. The resistance to SCG was measured parallel and perpendicular to the draw direction. It was found that the resistance to SCG perpendicular to the draw direction varied exponentially with the draw ratio, and the resistance parallel to the draw direction decreased to a low value after a very small change in draw ratio. The activation energy for SCG was essentially independent of the draw ratio.

*To whom correspondence should be addressed

0032-3861/94/09/1948–04

EXPERIMENTAL

The material was a linear homopolymer of PE: density = 0.976; $M_w = 98\,000$ and melt index = 0.70 g/10 min when tested by ASTM D1238 Condition E. The material was compression moulded into 10 mm thick plaques and slowly cooled at a rate of less than 0.5°C min^{-1}. Dumbbell-shaped specimens were machined from the plaque and a grid was drawn on the surface. The specimen was drawn at 80°C at a strain rate of 10^{-3} s^{-1}. The drawn plaque is shown in *Figure 1*, where the local extension ratios of the plaque varied from 1 to 3.5. Specimens 20 mm long, 6 mm wide and 4 mm thick were machined from the drawn plaque. The tensile axis of the specimen was either parallel or perpendicular to the draw direction. Each specimen was identified with respect to its draw ratio and its position on the grid. The specimens were notched to depths of 1.40 or 0.60 mm with the length of the notch being 6 mm in order to enhance the amount of plane-strain fracture.

The specimens were subjected to a constant stress of 5.5 or 4 MPa, based on the unnotched area. Temperatures were 42, 50 or 60 ± 0.5°C. The crack opening displacement (COD) at the root of the notch was measured with an optical microscope and a filar eyepiece, and the time for complete failure was measured. The scatter in the time for failure is within ±15%. For each draw ratio two to four measurements of the failure time were made.

RESULTS

The density *versus* draw ratio is shown in *Figure 2*. The decrease in density from 0.9765 to 0.9665 as the draw ratio increased from 1 to 3.5 is equivalent to an increase in porosity of 1%.

Figure 3 shows the curves of COD *versus* time for the various draw ratios with the notch perpendicular to the

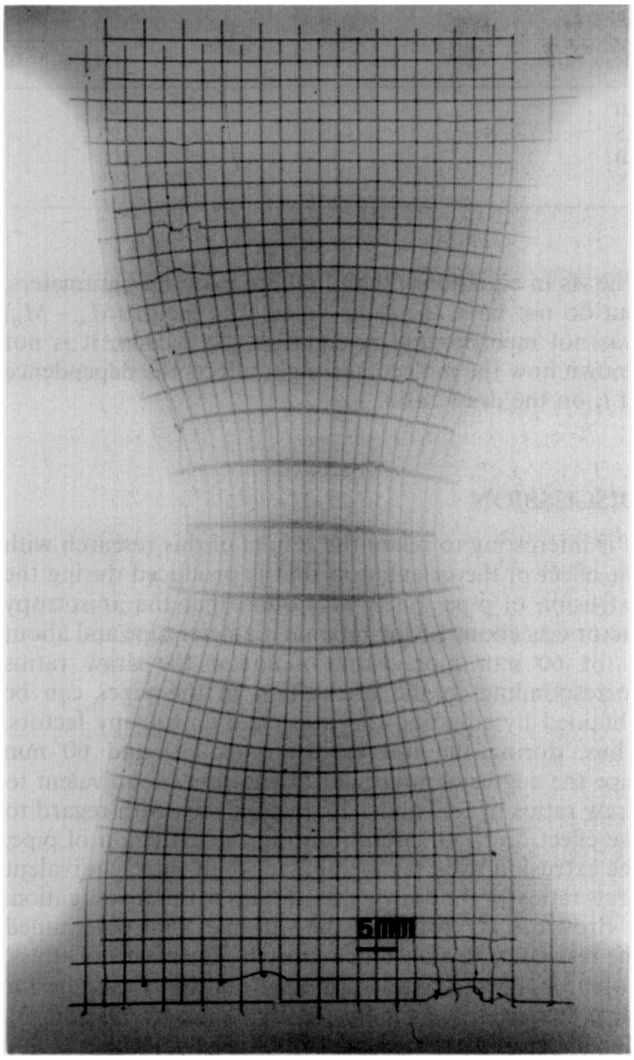

Figure 1 Compression-moulded plaque after drawing at 80°C at a strain rate of 10^{-3} s^{-1}

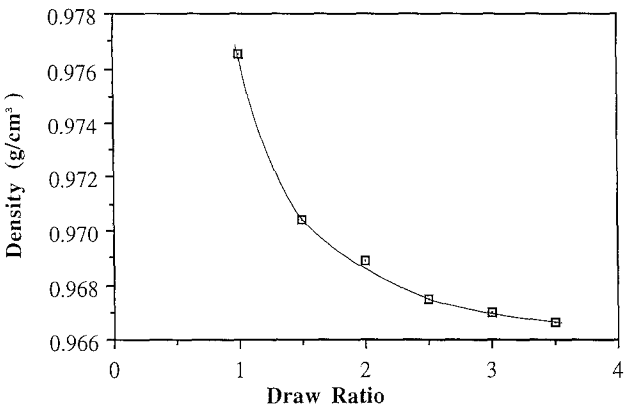

Figure 2 Density *versus* draw ratio

draw direction. The time when the curves begin to accelerate corresponds to the initiation of fracture in the craze, which is produced during the loading of the specimen. The time to initiate fracture is generally related to the time for complete failure.

Figure 4 shows time to failure at 42°C, 5.5 MPa and 1.40 mm notch depth *versus* draw ratio. For specimens with the notch perpendicular to the draw direction, the relationship between time to failure, t_f, and draw ratio, λ, is:

$$t_f = 1.1e^{4\lambda} \text{ (min)} \tag{1}$$

For specimens with the notch parallel to the draw direction, t_f decreases from 60 min to less than 1 min when the draw ratio is about 2.

In order to increase the failure time for a notch parallel to the draw direction, the stress was reduced from 5.5 MPa to 4 MPa and the notch depth was decreased from 1.40 mm to 0.60 mm. The variation in t_f with draw ratio under these conditions is shown in *Figure 5* at 50

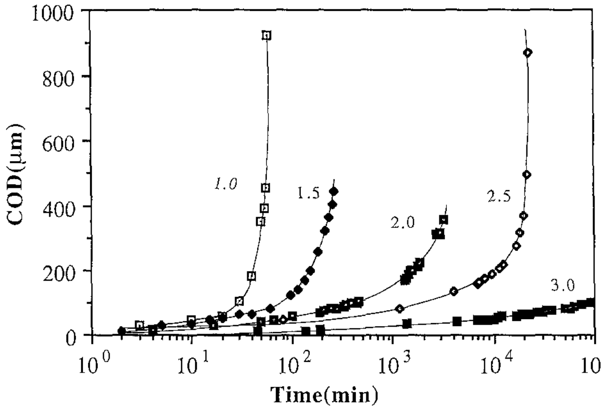

Figure 3 Crack opening displacement at root of notch *versus* time at 42°C, 5.5 MPa and notch depth of 1.40 mm for various draw ratios. Notch is perpendicular to draw direction (DD)

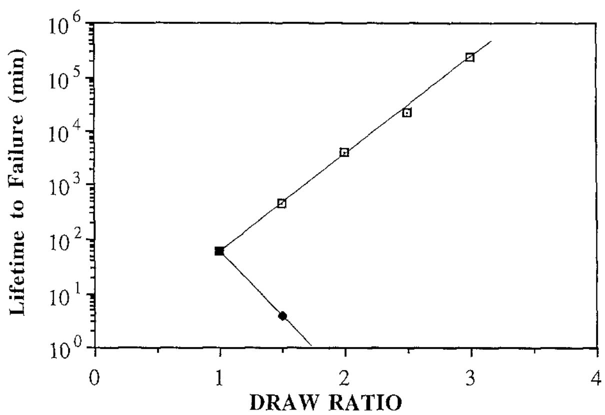

Figure 4 Time to failure *versus* draw ratio at 42°C, 5.5 MPa and notch depth of 1.40 mm: (□) notch perpendicular to DD; (■) notch parallel to DD

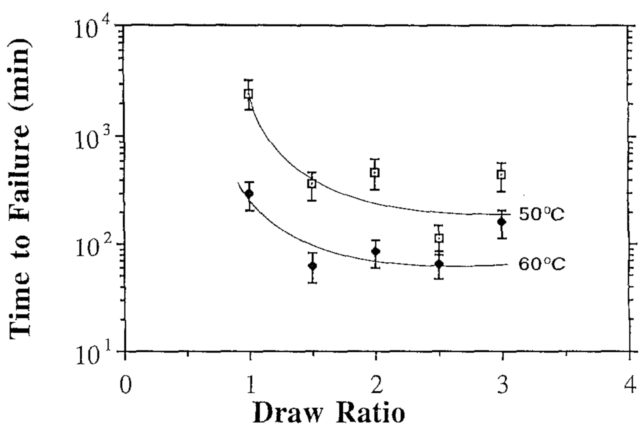

Figure 5 Time to failure *versus* draw ratio for notch parallel to DD; 4 MPa, 0.60 mm notch depth

and 60°C. *Figure 5* shows that t_f for the notch parallel to the draw direction decreases to an equilibrium value after a draw ratio of about 1.5, and this equilibrium value after a draw ratio of about 1.5 is about one-fourth t_f for the unoriented state.

The effect of temperature was investigated at 42, 50 and 60°C at 5.5 MPa and a notch depth of 1.40 mm, as shown in *Figure 6*. The change in time to failure *versus* draw ratio obeys equation (1) for all temperatures except that the pre-exponential coefficient varies with temperature. In order to determine the activation energy for the process, log t_f was plotted against $1/T$, as shown in *Figure 7*. From the slopes of these curves, the activation energies Q for the various draw ratios were obtained, as listed in *Table 1*. Within the experimental error, Q for the drawn materials is essentially constant with an average value of 110 kJ mol^{-1}. The difference in Q between the unoriented and oriented states is small and may not be significant because Huang and Brown[2] measured Q for a series of homopolymers with different molecular weights and obtained a value of 115 kJ mol^{-1}.

Huang and Brown[2] also measured the effect of stress, notch depth, temperature and molecular weight on t_f and found the following empirical equation for linear homopolymers:

$$t_f = A(M_w - M_0)\sigma^{-5}a^{-2}e^{115\,000/RT} \qquad (2)$$

where A is a material parameter, M_w is weight-average molecular weight, M_0 is a critical molecular weight of 18 000 for which $t_f = 0$, σ is stress and a is notch depth. Now equation (2) can be combined with equation (1) as follows:

$$t_f = Ae^{4\lambda}\sigma^{-5}a^{-2}e^{110\,000/RT} \qquad (3)$$

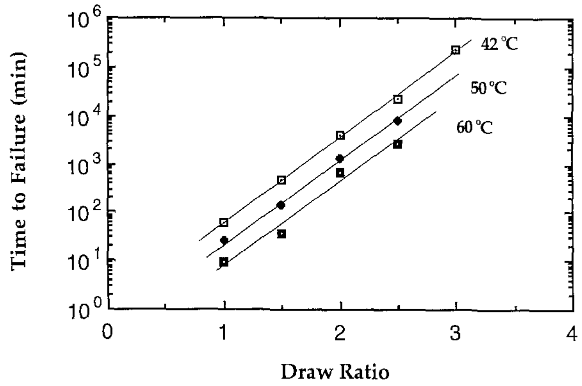

Figure 6 Time to failure *versus* draw ratio for notch perpendicular to DD at various temperatures; $\sigma = 5.5$ MPa, notch depth = 1.40 mm

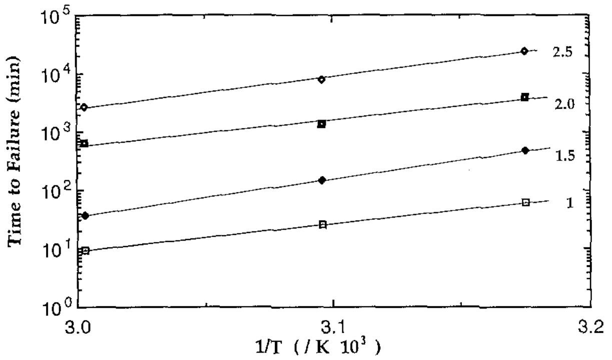

Figure 7 Time to failure *versus* $1/T$ at various draw ratios using data from *Figure 6*

Table 1

Draw ratio	Q (kJ mol^{-1})
1.0	92
1.5	125
2.0	100
2.5	105

The As in equations (2) and (3) are material parameters, but do not have the same value. The factor $(M_w - M_0)$ was not incorporated in equation (3) because it is not known how the molecular weight affects the dependence of t_f on the draw ratio.

DISCUSSION

It is interesting to relate the results of this research with the effect of the orientation that is produced during the extrusion of pipe. Lu *et al.*[1] found that the anisotropy factor was about 1.5 for 110 mm diameter pipe and about 4 for 60 mm pipe. From *Figure 4* the draw ratios corresponding to the orientation in the pipes can be obtained by equating the respective anisotropy factors. Thus, during the hot extrusion of 110 and 60 mm pipe the degree of molecular orientation is equivalent to draw ratios of 1.07 and 1.16, respectively, with regard to the effect on t_f. Of course, during the extrusion of pipe, the extrusion ratio is much higher than these equivalent draw ratios for the drawing conditions in this investigation.

Brown *et al.*[3] reviewed the variables that determined the resistance to slow crack growth. The effects of stress, notch depth and temperature were about the same for all polyethylenes, as indicated by equations (2) and (3). The material parameter may vary by as much as a factor of 10^6 depending on molecular-weight distribution, branch density, placement of the branches relative to the molecular weight and morphological variations. The current work is in agreement with the previous investigations in that the material parameter has been varied by a factor of 10^4, but the activation energy is about the same as that for all other polyethylenes.

It is of interest to discuss the mechanism by which orientation affects slow crack growth. The structure may be viewed as a network consisting of tie molecules and crystals surrounded by the amorphous region. The process of slow crack growth consists of the disentanglement of the tie molecules from the crystals. Increasing the number of tie molecules decreases the average force on each tie molecule for a given applied stress as described by Huang and Brown[4]. When the crystal–tie molecule network is oriented, the surrounding molecules in the amorphous region become aligned with the tie molecules. Consequently, the support of the aligned molecules reduces the force on the tie molecule as it becomes disengaged from the crystal. The details of disengagement are not known as it may consist of pulling tie molecules out of the crystal or of a shredding of the crystal. It is known that the strength of the crystals determines the rate of slow crack growth, as shown by the work of Lu *et al.*[5]. When the testing temperature is above the α transition temperature, corresponding to a certain thickness of the crystals, then crystals of that thickness cease to offer resistance to the disentanglement process.

It should also be realized that, even when the bulk polymer is unoriented, the disentanglement process involves the fracture of oriented fibrils in a craze. The craze is always produced during the initial loading of the specimen under plane-strain conditions. However, the degree of orientation within the fibrils of the initially unoriented material is not known. It is probably small compared to the bulk orientation that was produced in this investigation.

ACKNOWLEDGEMENTS

The work was supported by the Gas Research Institute. The use of the Central Facilities as supported by the NSF-MRL under Grant Number DMR 91-20668 was most important. Professor Xici Lu provided excellent discussions.

REFERENCES

1 Lu, X., Zhou, Z. and Brown, N. *Polym. Sci. Eng.* in press
2 Huang, Y.-L. and Brown, N. *J. Mater. Sci.* 1988, **23**, 3648
3 Brown, N., Lu, X., Huang, Y. and Qian, R. *Makromol. Chem., Macromol. Symp.* 1991, **41**, 55
4 Huang, Y. and Brown, N. *J. Polym. Sci., Polym. Phys.* 1991, **29**, 129
5 Lu, X., McGhie, A. and Brown, N. *J. Polym. Sci., Polym. Phys.* 1993, **31**, 767