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Abnormal slow crack growth in polyethylene

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The normal slow crack growth behaviour of polyethylenes consists of a ductile–brittle transition where the transition to brittle fracture occurs below a critical stress and after a critical time. The curves of stress vs. failure time depend on temperature, but all curves can be shifted vertically and horizontally by well established shift functions. It has been observed that there are some polyethylenes whose stress vs. time to failure curves do not shift in the normal way and in some cases the time for brittle fracture does not change with temperature. SEM micrographs do not reveal any difference between the fibrillated fractured surfaces from the normal and abnormal specimens. Whereas the normal slow crack growth behaviour has been attributed to the disentanglement of the molecules by sliding without chain scission, it is proposed that the abnormal fracture behaviour may involve a disentanglement mechanism that consists of a combination of chain sliding and scission. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The long time behaviour of polyethylene (PE) structures has been extensively investigated because PE is a very important structural material being used in pipes, fittings, tanks, and jacketing for electrical cables. Under a constant load, PE exhibits two general modes of failure: (1) ductile failure by homogeneous deformation, and (2) brittle failure which initiates at a point of stress concentration and the crack is proceeded by a craze. This general behaviour has been observed in thousands of tests on pipes during the past 30 years, where the ductile failure occurs at high stress and below a critical stress, which depends on the temperature, brittle failure occurs. It was found that under certain conditions, some polyethylenes violated the usual time dependent fracture behaviour with respect to the effect of temperature and the quantitative relationship between stress and the failure time.

The normal time dependent failure behaviour of polyethylenes is shown in *Figures 1*[1] and *2*[2], where the stress, σ, is plotted against the time to failure, t_f, at various temperatures. *Figure 1* is for an unnotched gas pipe under a hydrostatic pressure and *Figure 2* is for a notched tensile specimen from a compression moulded commercial resin. Each curve consists of a region of ductile failure at high stresses and a brittle region at lower stresses.

The slope of each region is given by

$$t_f \alpha \sigma^{-n} \tag{1}$$

where typical values of n for ductile failure range from about 20–27, and for the brittle region, 2.5–4.5. Generally, the transition stress is about one-half the yield point at the particular temperature. The region of

ductile failure is characterized by macroscopic shear flow of the ligament. The region of brittle fracture occurs by the slow crack growth (SCG) of a craze. The jog which occurs in the transition region is caused by a blunting of the notch by localized shear flow.

The entire curve at a temperature, T_1, can be shifted to another temperature, T_2, by a horizontal and vertical shift as pointed out by Popelar et al.[3]. The following shift functions based on detailed experiments by Lu and Brown[2,4] are modifications of those presented by Popelar et al.

$$t_f(T_1) = t_f(T_2)\, e^{Q_1/R(1/T_1 - 1/T_2)} \tag{2}$$

$$\sigma(T_1) = \sigma(T_2)\, e^{Q_2/R(1/T_1 - 1/T_2)} \tag{3}$$

Popelar et al. have shown that Q_1 and Q_2 are about the same for all polyethylenes that exhibit the normal behaviour shown in *Figures 1* and *2*, where $Q_1 = 100\,000\,\text{J mol}^{-1}$ and $Q_2 = 10\,500\,\text{J mol}^{-1}$.

Thousands of PE resins have been extensively tested in industry in the form of a pipe under hydrostatic pressure during the past 30 years. All results that have been reported obey equations (1)–(3). Gas pipes resins which are validated for use in industry are tested at elevated temperatures and the room temperature behaviour is obtained by extrapolation using equations such as equations (2) and (3). For example, the time to produce brittle failure at 20°C is about 250 times that at 80°C.

We have discovered that there are some PE resins that do not obey equations (2) and (3). In fact, SCG brittle fracture has been observed in less time at 3°C than at 80°C. Also, the n values in equation (1) for the brittle region have been found which are much greater than 5.

EXPERIMENTAL

The resins in this paper are commercial copolymers: one

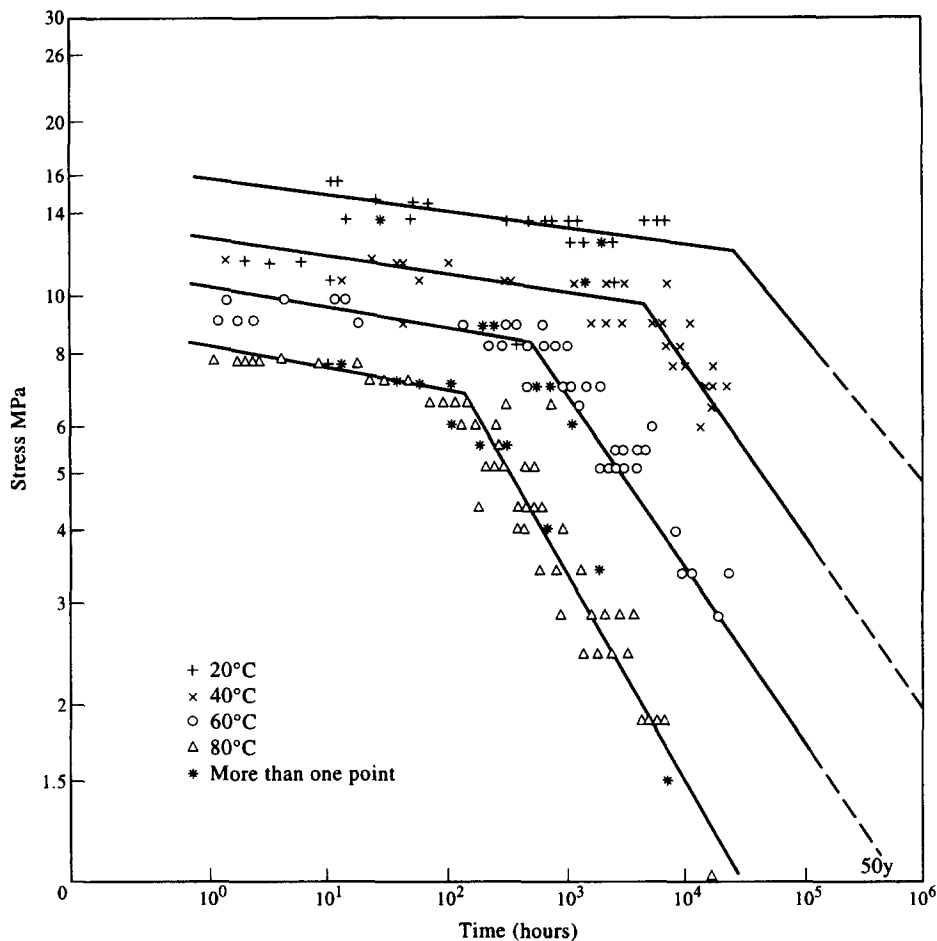* To whom correspondence should be addressed

Figure 1 Log hoop stress vs. log time to failure at various temperatures for a pipe under hydrostatic pressure. Normal behaviour
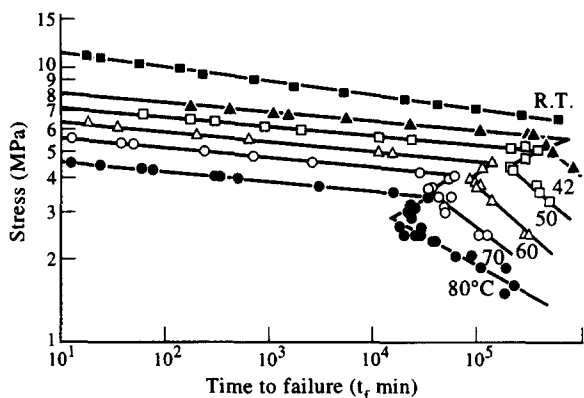

Figure 2 Tensile stress vs. time to failure with a 3.5 mm notch at various temperatures. Test method ASTM F1473 with ethylene–hexene copolymer. Normal behaviour
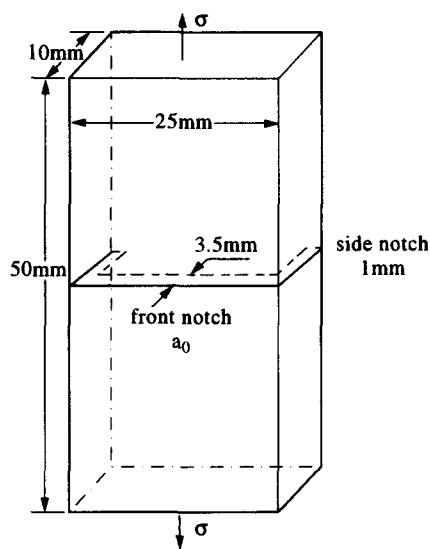

Figure 3 Specimen geometry for test method ASTM1473

ethylene–hexene with a density of $0.946 \, g \, cm^{-3}$ and the other two are ethylene–octene with densities of 0.943 and $0.939 \, g \, cm^{-3}$. The test method is a notch tensile test in accordance with ASTM F1473. The resins were compression moulded and slow cooled at a rate of $0.5°C \, min^{-1}$ in the form of 10 mm thick plaques. The specimen geometry is shown in *Figure 3*. The specimen width of 25 mm and the side grooves insured that the brittle fracture occurred under plane strain conditions. All stresses are calculated on the basis of the unnotched cross-section area. Temperatures were controlled within $\pm 0.5°C$. The notches were made by very slowly pressing a razor blade into the specimen. Generally, the reproducibility of the failure times is within $\pm 15\%$ for duplicate tests.
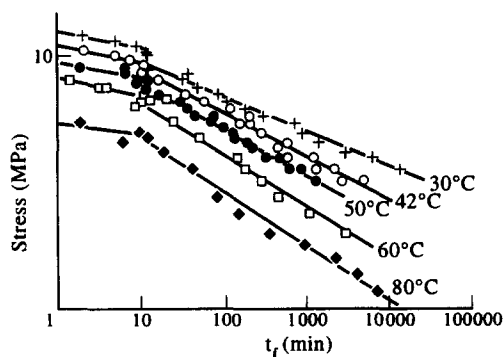

Figure 4 Same as *Figure 2* except ethylene–octene copolymer. Abnormal behaviour
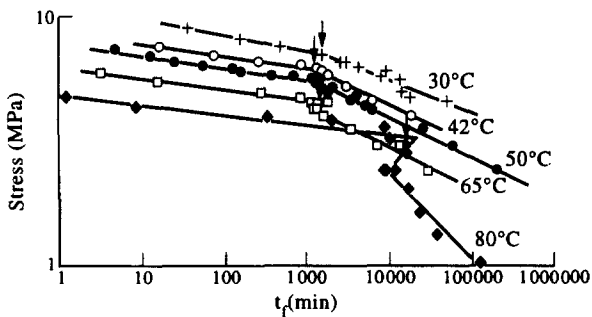
Figure 5 Same as *Figure 4* except another ethylene–octene copolymer. Abnormal behaviour
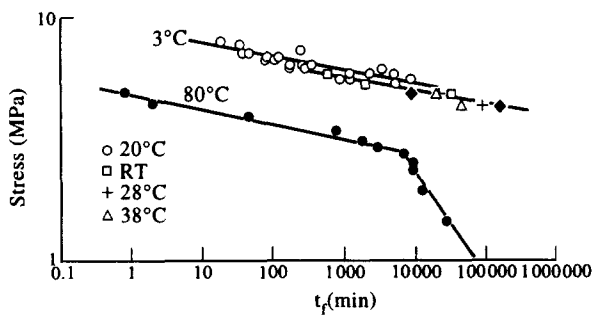

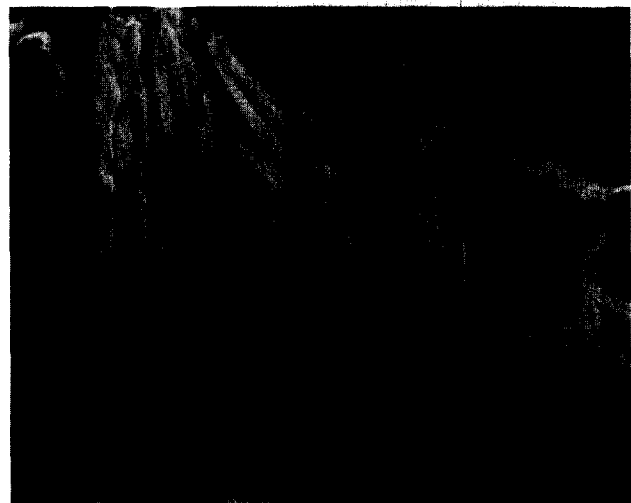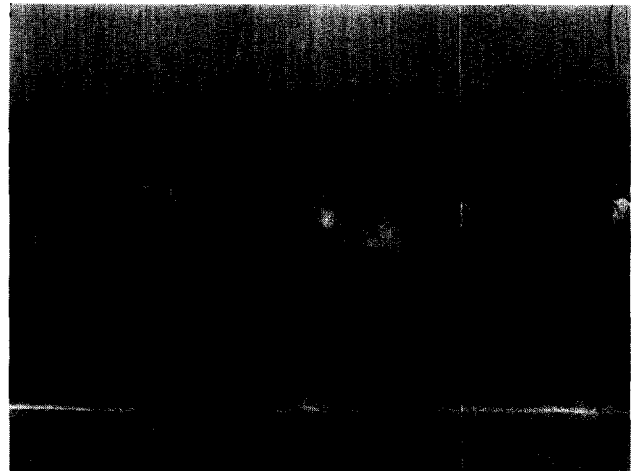**Figure 6** Same as *Figure 4* except ethylene–hexene copolymer. Abnormal behaviour

Figure 8 Same as *Figure 7* except exhibited abnormal behaviour at 38°C under 4.5 MPa
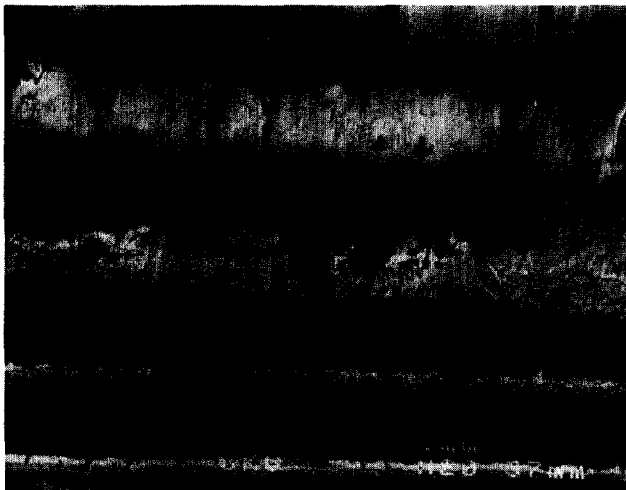

Figure 7 Fractured surface of ethylene–hexene copolymer which exhibited normal behaviour at 80°C under 2.4 MPa

RESULTS

Figure 4 shows log stress, σ, vs. log failure time, t_f, for a compression moulded and slow cooled specimen of an ethylene–octene copolymer over the temperature range of 30–80°C. The discontinuities correspond to the time for the ductile to brittle transition. Note that the times for the ductile–brittle transition are independent of temperature. This behaviour is abnormal relative to the normal behaviour shown in *Figures 1* and *2* and described by equation (2). However, the stress at the transition does increase with decrease in temperature in accordance with equation (3) with a Q_2 value of about 13 700 J mol^{-1} which is slightly higher than the normal value of 10 900 J mol^{-1} from *Figure 2*. The slopes of the curves in *Figure 4* in the ductile and brittle region are about the same as for the normal behaviour in *Figure 2*. In the case of this polymer, the important deviation from normal behaviour is the fact that the time for the ductile to brittle transition was the same from 30°C to 80°C.

Figure 5 shows log σ vs. log t_f for another commercial ethylene–octene copolymer. The times for the ductile–brittle transition are indicated by the arrows. The abnormal behaviour manifests itself by the fact that the times for the ductile–brittle transition are the same from 65°C to 30°C and that these times are less than that at 80°C.

Figure 6 shows the abnormal behaviour for a commercial ethylene–hexene copolymer. The 80°C
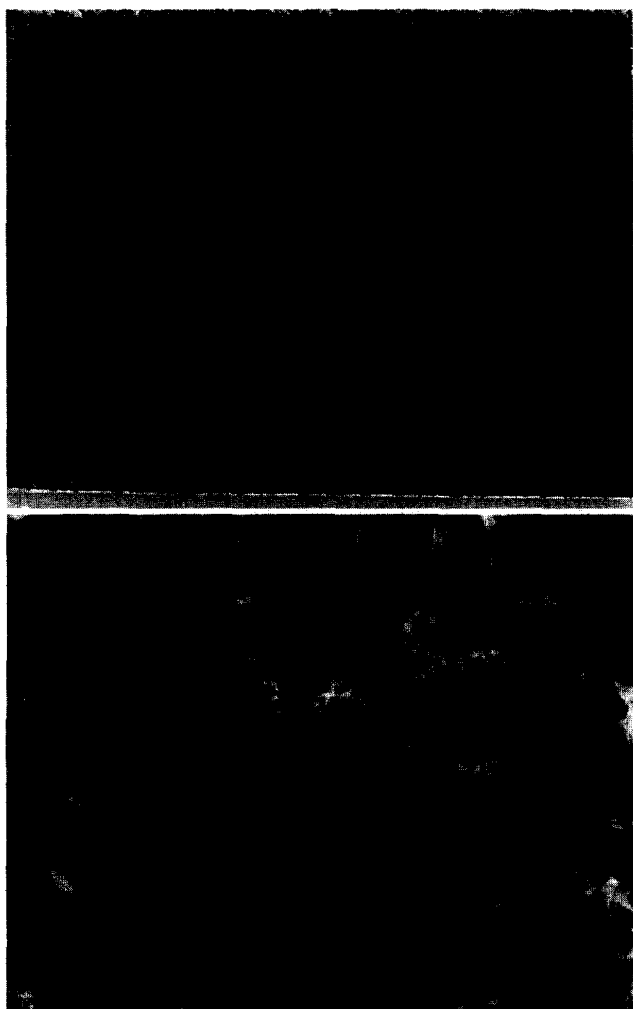
Figure 9 Same as *Figure 8* at 3°C under 5.5 MPa

Figure 10 Same as *Figure 8* at 3°C under 8 MPa

curve shows the normal behaviour in that the slopes in the ductile and brittle regions correspond to n [equation (1)] = 18 and 2.4 respectively. However, between 3 and 38°C, all the data are brittle and no ductile–brittle transformation was observed. All stresses for a given t_f did not change with temperature. Also, the n in equation (1) for this brittle behaviour is 18, which is much greater than the n values for the normal brittle behaviour.

The fractured surfaces were observe with the SEM. *Figure 7* shows the fractured surface of the normal behaviour exhibited at 80°C in *Figure 6*, by the ethylene–hexene resin. This fibrilla fracture is characteristic of all slow crack growth fractures in PE. *Figures 8, 9* and *10* are examples of fracture from specimens that exhibited abnormal behaviour in *Figure 6* at 38°C and 3°C. These fibrilla fractures have the same general characteristics as those in the normal specimen in *Figure 7*. *Figure 11* is a micrograph of another ethylene–octene resin that exhibited the abnormal fracture at 30°C and 7 MPa stress (*Figure 5*). Its fibrilla structure is the same as that exhibited by a normal fracture.

In all the micrographs, the general trend is for the fibrilla structure to become finer the lower the temperature and the lower the stress. This general trend has been observed in all fractured surfaces whether the fracture was normal or abnormal.

DISCUSSION

The most general feature of abnormal time-dependent fracture in polyethylene is that the σ vs. t_f curves do not exhibit the time–temperature shift described by equation (2). In some case such as *Figure 5*, the time for the ductile–brittle transition temperature is shorter at temperatures below 80°C than at 80°C. This behaviour is contrary to the usual rate-process phenomenon where the rate of the reaction decreases as the temperature decreases.

At the level of resolution of the SEM, there is no difference between the fibrilla fractures of the normal and abnormal specimens. However, there must be a difference in the fracture mechanism at the sub-microscopic level. The previous theories suggested that the slow crack growth involved a disentanglement process without chain scission. The details of the disentanglement are not known at the molecular level, but the activation energy of the normal fracture process, which is about $100 \, \text{kJ} \, \text{mol}^{-1}$, is not sensitive to the molecular structure. Thus, a homopolymer, which will fail 10^4 times faster than a copolymer, has about the same activation energy.

It is important to understand the physical basis for the normal behaviour represented by equations (2) and (3) and *Figure 2*. The vertical shift in stress is determined by the fact that the strength as represented by the yield point increases as the temperature decreases. The horizontal shift in time means that for a given equivalent stress, i.e. stress relative to the yield point, the rate of molecular motion responsible for fracture decreases exponentially as the temperature decreases. In the case of the abnormal behaviours shown in *Figures 4* and *5*, the stress for a
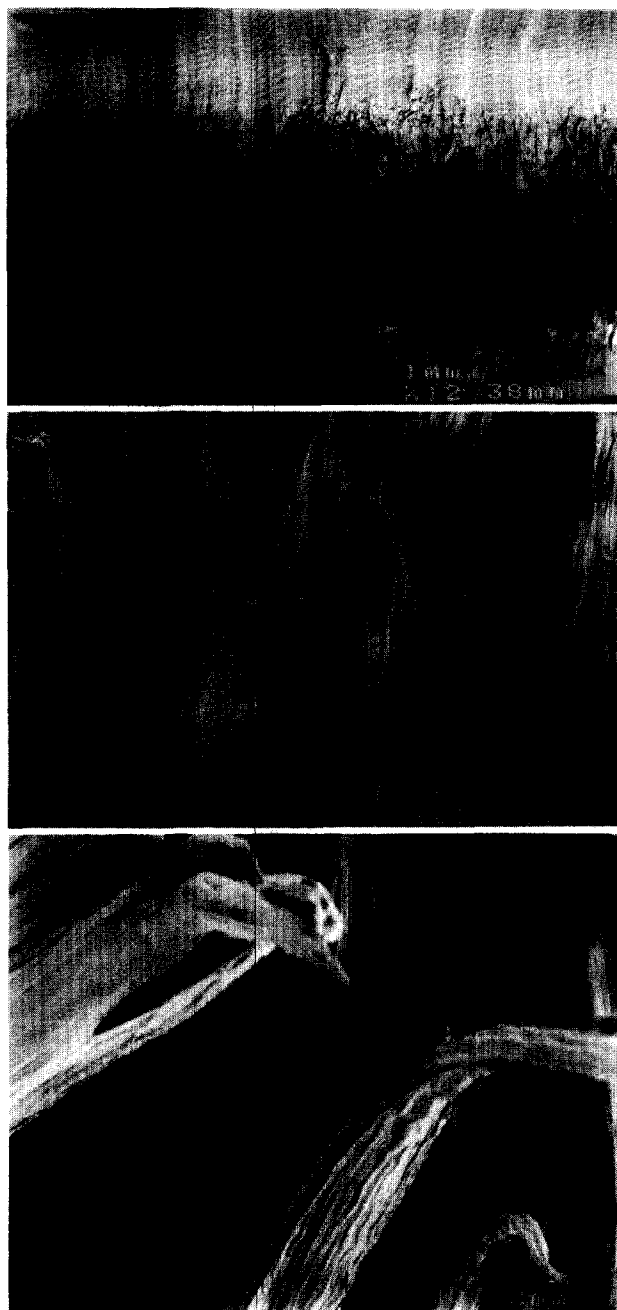
In the case of the abnormal behaviour in *Figure 6* between 3°C and 38°C, there is neither a shift in stress nor in failure time with temperature. The failure time is simply a function of the stress independent of temperature. At extremely low temperatures, it may be expected that the failure would be instantaneous and simply depend on the stress, but this abnormal behaviour is still time dependent.

The abnormal behaviour suggests that a certain number of bonds need to be broken before failure occurs, but the rate of bond-breaking is a constant that depends on the stress but not on the temperature. It is suggested that the failure mechanism is a complex combination of two fracture processes involving the breaking of both covalent and Van der Waals bonds. At the present time, there are not enough data to be more specific about the mechanism. However, some preliminary data suggest that the morphology of the polymer as well as the molecular structure in conjunction with the stress intensity and temperature determine whether or not abnormal fracture will occur in a particular resin.

CONCLUSION

The stress vs. time to failure curves of some polyethylenes do not exhibit the well established shift with temperature. In one case the time for the ductile to brittle transition did not change with temperature but this time was less at lower temperatures than at 80°C. It was observed that the slope of the stress vs. time to failure curve for brittle failure was substantially different than the slope for brittle behaviour that is normally associated with polyethylene. The abnormal behaviour does not follow a consistent pattern.

ACKNOWLEDGEMENTS

Figure 11 Fractured surface of ethylene–octene copolymer that exhibited abnormal behaviour at 30°C under 7 MPa

given failure time does indeed increase as the temperature is lowered in agreement with equation (3); however, for the same equivalent stress, there are times for the ductile–brittle transition which do not change with temperature.

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