

The mechanism of slow crack growth in polyethylene by an environmental stress cracking agent

A. L. Ward*, X. Lu, Y. Huang and N. Brown†

Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104-6272, USA

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Using single edge notch tensile specimens under plane strain conditions, the time to fail by slow crack growth was accurately measured in an ethylene–octene copolymer in Igepal and air. The primary result was the observation of a critical time for failure called the ‘Igepal transition’. Only for failure times greater than the ‘Igepal transition’ did Igepal accelerate fracture. For failure times shorter than the ‘Igepal transition’ the temperature dependence and stress dependence of the failure times in air and Igepal were the same and secondary crazes were observed in Igepal but not in air. By relaxing the local stress the secondary crazes made the failure time in Igepal longer than in air. For times longer than the ‘Igepal transition time’ the Igepal accelerated fracture. The activation energy in Igepal was reduced to 69 kJ mol^{-1} as compared to 118 kJ mol^{-1} in air and the dependence of failure time on stress was changed by the Igepal. The Igepal has two distinct effects: it enhances crazing by plasticizing the amorphous region of the bulk polymer; and it enhances fracture of the craze by plasticizing the crystalline region of the fibrils. The ‘Igepal transition time’ was related to the difference between the diffusion coefficients in the crystalline and amorphous regions.

(Keywords: crack growth; polyethylene; stress)

INTRODUCTION

Polyethylenes fail in an inert environment such as air or water by a process of slow crack growth at about room temperature. The crack starts at a craze which is initiated at a point of stress concentration. As shown by Lustiger and Corneliusen¹, the same process occurs in the commonly used environmental stress cracking agent known as Igepal CO-630 (nonylphenoxypolyethanol). The Igepal not only enhances the formation of crazes but it also reduces the time to initiate crack growth. Recently, Ward *et al.*² measured the time to failure of 22 polyethylenes in air and Igepal at 50°C. It was observed that the acceleration in failure time by the Igepal did not occur unless the time to failure was $> \sim 10^3$ min. One purpose of this investigation was to study the delay time before the Igepal became effective.

Early work by Hittmair and Ullman³ investigated the effects of Igepal concentration, temperature, stress and morphology on the environmental stress cracking (ESC) process. Limitations exist on the interpretation of their results because their fracture conditions, whether plane stress or plane strain, were not defined, and they did not control the stress intensity in their specimens. They also required 10 duplicate tests to obtain a significant result. Lu and Brown^{4–6} have developed an accurate test for measuring many variables such as stress, notch depth, mode of loading, temperature, morphology and molecular structure on the process of slow crack growth in

polyethylenes. This experimental method of Lu and Brown was used to determine the effect of Igepal on slow crack growth in polyethylene. This paper quantitatively compares the effects of stress and temperature on slow crack growth in air and Igepal. The polyethylene that was chosen has been extensively investigated in air and it represents the slow crack behaviour of a typical resin that is used in a critical application such as the distribution of natural gas.

EXPERIMENTAL

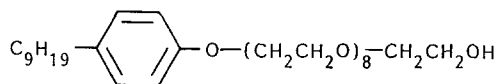
The resin is an ethylene–octene copolymer with a density of 0.9465 g cm^{-3} . The resin was compression moulded in a closed die under carefully controlled conditions and slowly cooled in the press overnight. The details of the moulding process are described elsewhere⁴. The moulded plaques were 10 mm thick. The geometry of the test specimen is shown in *Figure 1*. Each specimen was notched to a depth of 3.50 mm with a fresh razor blade by pressing it into the specimen at a rate of $50 \mu\text{m min}^{-1}$. The specimen was designed so that the fracture occurred under practically pure plane strain conditions. The slow crack growth process that was investigated is the same as the process that occurs when a polyethylene gas pipe fails in service after a long period of time.

The specimens were loaded in simple tension under a range of temperatures and stresses. The temperatures were controlled to within $\pm 0.5^\circ\text{C}$. Specimens were enclosed within a thin rubber sack containing a 10% solution of Igepal CO-630 (GAF Corp.). The chemical

* Present address: Department of Polymer, Metals and Dental Technology, Manchester Polytechnic, John Dalton Building, Chester Street, Manchester M1 5GG, UK

† To whom correspondence should be addressed

structure is:



Pre-soaking in Igepal for 1 h–2 weeks before loading had no effect on the time to failure. Hittmair and Ullman³ found that pre-soaking for 1 week did not change the failure time. In this investigation all samples were pre-soaked for 1 h.

All data points consist of an average of at least two duplicate tests. If the times to failure for the duplicate tests did not agree within $\pm 15\%$ of the average value, the test was repeated. In this investigation and in prior investigations² it has been demonstrated that the average scatter in the times to failure between two duplicate tests is $< \pm 15\%$ for both the air and Igepal environments. This degree of precision is much better than the results that have been published by other laboratories. The

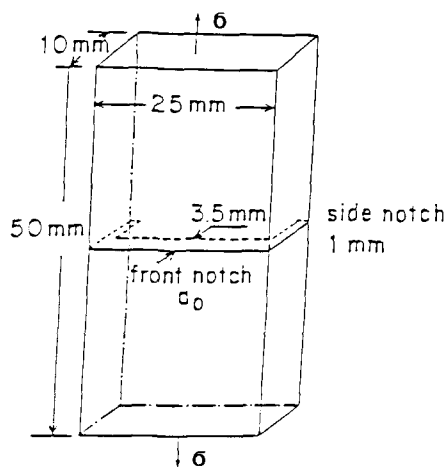


Figure 1 Specimen geometry

accuracy of the values of the failure times depends primarily on how accurately the temperature can be controlled since a 1°C change in temperature will change the time to failure by $\sim 16\%$.

RESULTS

Stress dependence

The reported stress is the load divided by the unnotched cross-section area. Figure 2a shows stress versus time to failure at various temperatures in Igepal. It is to be noted that for each temperature the curves have two slopes. As will be demonstrated below, brittle fracture occurs throughout this stress range and the transition in slope is not the conventional ductile–brittle transition that is characteristic of polyethylene at higher stresses. We will call this transition in slope the ‘Igepal transition’. For failure times shorter than the ‘Igepal transition’ the slope of the curve at each temperature is identical to the slope in air as shown in Figure 2b.

Each straight line portion of the data can be described by

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

where t_f is the time to failure and σ is the stress. In air (Figure 2b) there are two regions, ductile and brittle, as shown by the data at 60°C . In the high stress ductile region $n=28$. In the brittle region n varies with temperature going from 4.6 to 7.6 as the temperature decreases from 80 to 30°C .

In Igepal (Figure 2a), for times shorter than the ‘Igepal transition’, the slopes are the same as in air at the corresponding temperature. For times longer than the ‘Igepal transition’ n decreases to a value of ~ 1.8 and varies slightly with temperature.

The change in n with stress is shown in Figure 2c in air and Igepal at 60°C . In the high stress ductile region there is no difference between air and Igepal with $n = 28$.

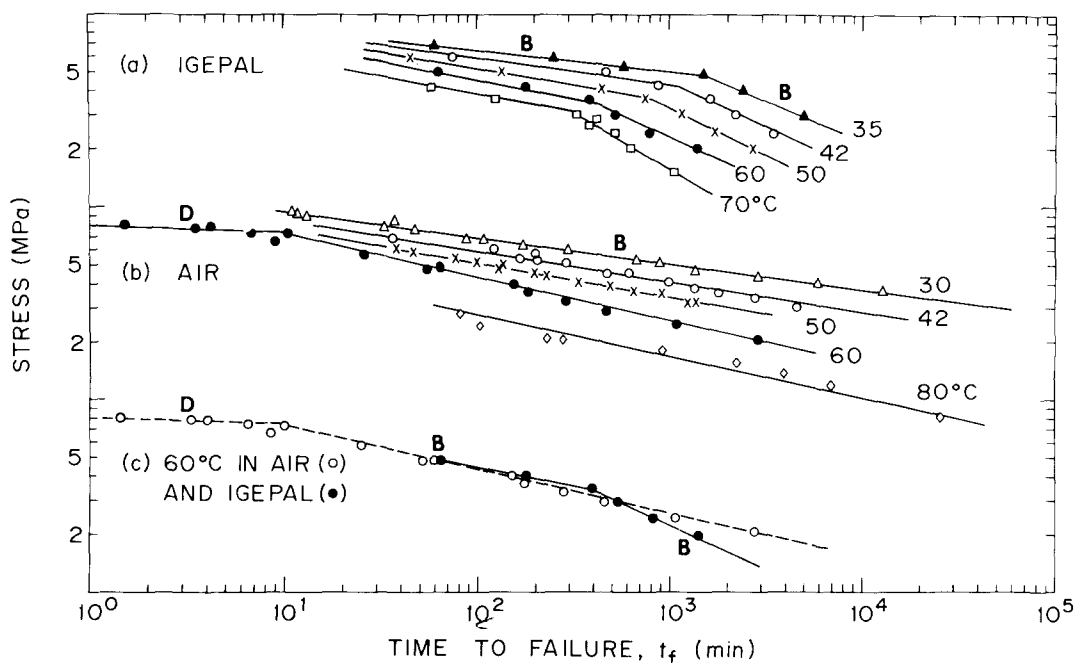


Figure 2 Stress versus time to failure at various temperatures; (a), (b) and (c) have a common y axis. D designates a ductile region and B designates a brittle region. (a) In Igepal, (b) in air, (c) in air and Igepal at 60°C

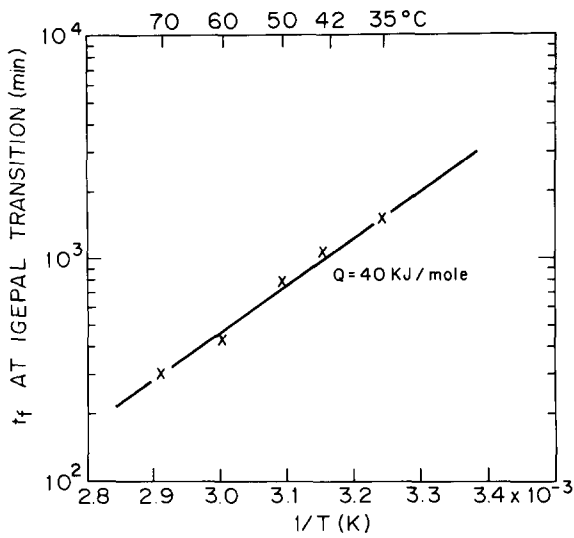


Figure 3 Time of failure at the 'Igepal transition' versus temperature

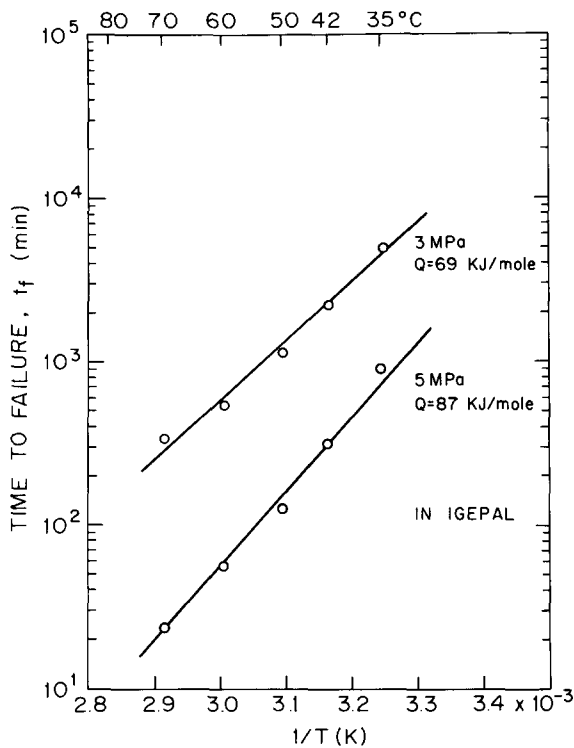


Figure 4 Time to failure versus the reciprocal of temperature in Igepal at 3 MPa after and 5 MPa prior to the 'Igepal transition'

Then there is a brittle region where the behaviour in air and Igepal is nearly the same and $n = 4.6$. Finally, the Igepal becomes effective at the 'Igepal transition' below which $n = 1.8$. The failure time at the 'Igepal transition' increases as the temperature decreases (Figure 2a). The stress at the 'Igepal transition' also increases as the temperature decreases.

It may be useful to think in terms of stress intensity, K , instead of stress. Since the notch depth is the same for all the single edge notched tensile specimens, it is only necessary to multiply the stress (MPa) by the factor 0.197 in order to obtain K ($\text{MPa m}^{1/2}$). Thus, in this investigation, the stresses in the brittle region ranged from 10 to 1 MPa; the corresponding K values ranged from 1.97 to 0.197 $\text{MPa m}^{1/2}$.

Temperature dependence

In Figure 3, the time for the 'Igepal transition' is plotted against the reciprocal of temperature $1/T$. The slope of this curve corresponds to an activation energy of 40 kJ mol^{-1} . This activation energy may be related to the time for the Igepal to effectively diffuse into the fibrils of the craze.

The temperature dependence of the time for brittle fracture in Igepal, $t_f(I)$, is shown in Figure 4. For the times prior to the 'Igepal transition' at a constant stress of 5 MPa, the plot $t_f(I)$ versus $1/T$ gives an activation energy of 87 kJ mol^{-1} and for times longer than the 'Igepal transition' at 3 MPa the activation energy is 69 kJ mol^{-1} . In Figure 5, time for brittle fracture in air, $t_f(A)$, is also plotted versus $1/T$ at the 3 and 5 MPa stress levels. At the 5 MPa stress level the activation energy is 85 kJ mol^{-1} . This is about the same value as in Igepal at the same stress level prior to the 'Igepal transition'. At the 3 MPa stress level, the activation energy is 118 kJ mol^{-1} in air which is much greater than the 69 kJ mol^{-1} activation energy in Igepal at the same stress level.

Microstructure

Scanning electron micrographs of surfaces that have been fractured in Igepal before and after the 'Igepal transition' are shown in Figure 6. The same type of fibrillar morphology that is characteristic of slow crack growth brittle fracture occurs before and after the 'Igepal transition'. This is additional proof that the change in slope of the stress versus time to failure curve at the 'Igepal transition' is not associated with the change in slope that occurs at the ductile-brittle transition at a higher stress.

Figure 7 compares the damage zones in air and Igepal before the 'Igepal transition' at 50°C and 4.2 MPa after

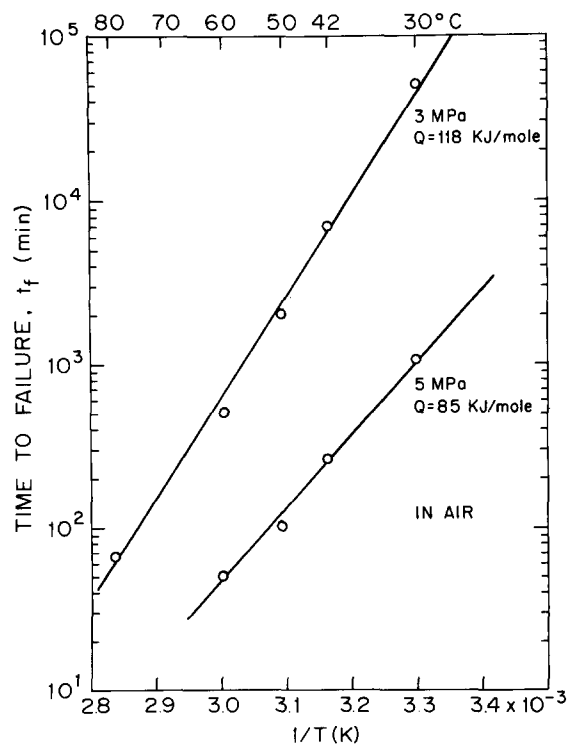


Figure 5 Time to failure versus the reciprocal of temperature in air at 3 MPa after and 5 MPa prior to the 'Igepal transition'

40 and 120 min. In both air and Igepal there is the primary craze-like damage zone in the plane of the notch. However, only in Igepal do secondary damage zones occur at an angle of about 25° to the plane of the notch. The secondary damage zones are craze-like and they emanate from the sharp corners at the bottom of the notch. Lustiger and Corneliusen¹ also observed these secondary crazes in Igepal but not in air, but did not specify the conditions under which this occurred. Figures 7a and b show that after 40 min the primary craze in Igepal is $650\ \mu\text{m}$ long and the one in air is $350\ \mu\text{m}$ long. However, after 120 min the craze has fractured in air, but not in Igepal (Figures 7d and c). Finally, complete fracture occurred in Igepal after 400 min but took only

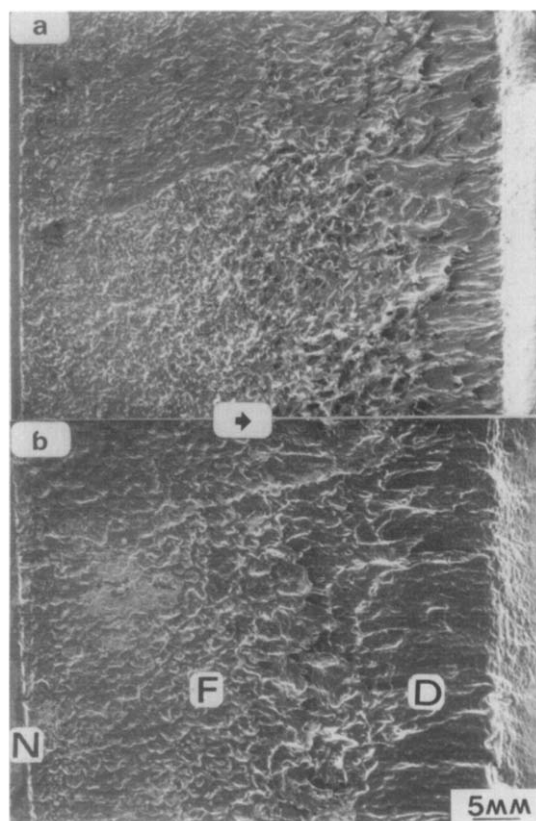


Figure 6 Fractured surface in Igepal (a) after and (b) before the 'Igepal transition'. N, notch, F, fibrillated structure and D, ductile

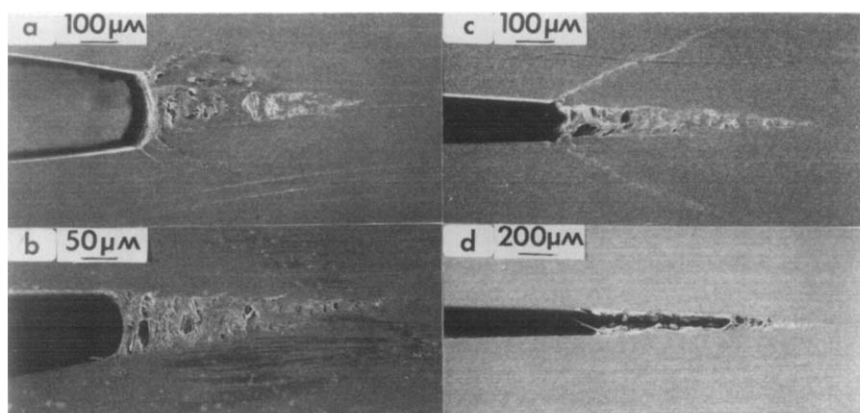


Figure 7 Scanning electron micrographs of damage zones in a central region of the specimen at 50°C and $4.2\ \text{MPa}$ before the 'Igepal transition': (a) after 40 min, in Igepal; (b) after 40 min in air; (c) after 120 min in Igepal; (d) after 120 min in air

300 min in air. Thus, at this stress of $4.2\ \text{MPa}$ before the 'Igepal transition' crazing is enhanced by the Igepal but fracture occurs more rapidly in air.

A qualitative analysis was made of the effect of the secondary craze on the stress field adjacent to the primary craze. This stress field is influenced by the stress concentration produced at the corners at the bottom of the notch. In the absence of crazing or shear yielding this stress field will be elastic, but the formation of a secondary craze or any zone of plastic shear will relax the magnitude of the stress. The relaxed stress field on the boundary of the primary craze governs the time required to fracture the fibrils at the base of the craze. This accounts for the fact that fracture initiated in the air craze before it initiates in the Igepal craze. At 50°C and $5.5\ \text{MPa}$, no secondary crazes were observed in Igepal and the brittle failure times are the same in air and Igepal. Apparently at $5.5\ \text{MPa}$, the failure time is too short to form secondary crazes.

The difference between the crazes in Igepal and air in the stress range below the 'Igepal transition' stress is shown in Figure 8 at 50°C and $3\ \text{MPa}$ after 2 and 6 h. The craze grows faster in Igepal and after 6 h it is twice the length of the one in air. Complete failure occurred in $1.3 \times 10^3\ \text{min}$ in Igepal and $2.5 \times 10^3\ \text{min}$ in air. Thus, when the stress is below the 'Igepal transition' stress, the Igepal makes the craze grow faster and also decreases the time to failure.

Figures 9a and b are detailed micrographs of the damage zones in Igepal and air. Both damaged zones have the same general characteristics of a craze. The primary difference is that the surface of the fibrils in Igepal appear to be somewhat smoother than that in air. This suggests that Igepal produces some plasticization of the fibrils.

DISCUSSION

The most important result is that the time for failure must exceed a critical value before the Igepal accelerates the fracture process. This critical time will be called the 'Igepal transition time', ITT. Prior to the ITT, the stress dependence and the temperature dependence of the failure times in Igepal and air are identical. After the ITT, the activation energy was reduced from $118\ \text{kJ mol}^{-1}$ in air to $69\ \text{kJ mol}^{-1}$ in Igepal and the stress exponent, n (equation (1)) was reduced from a

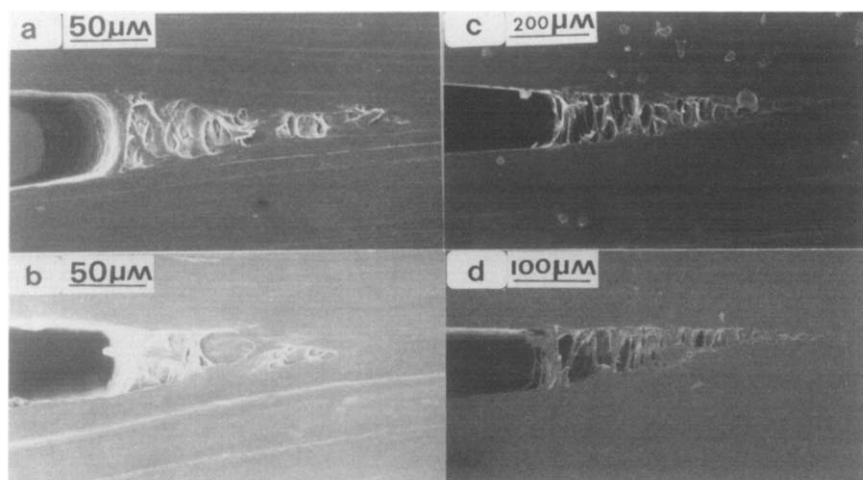


Figure 8 Damaged zones at 50°C and 3 MPa after the 'Igepal transition': (a) in Igepal 2 h; (b) in air 2 h; (c) in Igepal 6 h; (d) in air 6 h

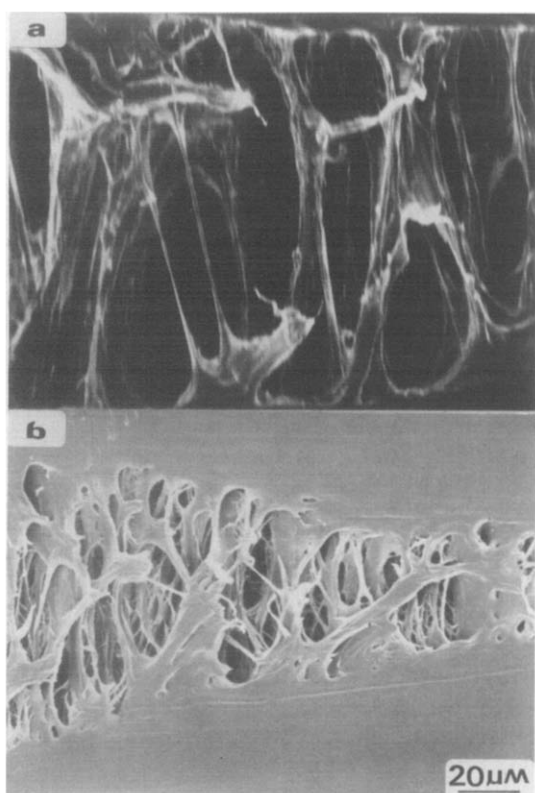


Figure 9 Fibrillated structure (a) in Igepal at 50°C, 3 MPa, 360 min and (b) in air at 80°C, 2.4 MPa, 130 min

range of 4.6 to 7.6 in air to 1.8 in Igepal. Consequently, the failure time in Igepal relative to that in air is given by

$$\frac{t_f(I)}{t_f(A)} = \left(\frac{\sigma}{\sigma_1}\right)^{n_A - n_I} \quad (2)$$

where n_A and n_I are the stress exponents in air and Igepal and σ_1 is the stress at the ITT. It is also important to note that the ITT increases as the temperature is decreased. As will be discussed below, the ITT is related to the diffusion coefficient of the Igepal into the crystalline region of the polymer.

Another effect of the Igepal is the production of secondary crazes as shown in *Figure 7*. These secondary crazes relax the stress field at the base of the primary

craze where fracture initiates. As a result, fracture occurs in Igepal after a longer time than in air. This anomalous behaviour occurs prior to the ITT before the Igepal has had the time to accelerate fracture.

Slow crack growth in polyethylenes involves the following two distinct processes as it does in all polymers: the initiation and growth of a craze; and the initiation of fracture at the base of the craze and subsequent crack growth. The role of Igepal on these processes will now be discussed.

When the specimen is first loaded a craze is produced at the root of the notch and its size corresponds to the prediction by the Dugdale theory as shown by Battacharya and Brown⁷ and Lu and Brown⁵ in polyethylenes. A measure for the size of the craze, δ , is given by

$$\delta \sim \frac{K^2}{\sigma_y^2} \quad (3)$$

where σ_y is the yield point. As theorized by Kinloch⁸ and Williams⁹, the craze grows as σ_y relaxes. In general, all ESC agents accelerate the relaxation of the yield point by plasticizing a small volume of the matrix at the tip of the craze. In the case of a semicrystalline polymer, the ESC agent can increase the rate of craze growth by dissolving into the amorphous region just as ESC agents enhance craze growth in completely amorphous polymers. This enhancement of craze growth by Igepal is responsible for the formation of the secondary crazes and for the longer primary craze in Igepal (*Figure 7*).

The process of crack initiation is centred on the fibrils at the base of the craze. Fracture occurs by a disentanglement of the molecules. The most important factor that controls the rate of disentanglement, is the density of tie molecules and the crystals which link the tie molecules. The key role of tie molecules in the fracture process has been emphasized by many investigators, but there is no universal agreement as to the details of the disentanglement process as pointed out by Lustiger¹⁰. Consequently we shall present a viewpoint based on the results of many investigations of slow crack growth in precisely notched specimens of many different kinds of polyethylene under plane strain conditions.

For all polyethylenes, the activation energy for slow crack growth is $\sim 100 \text{ kJ mol}^{-1}$ as shown in extensive investigations by Lu and Brown⁴⁻⁶ and Huang and

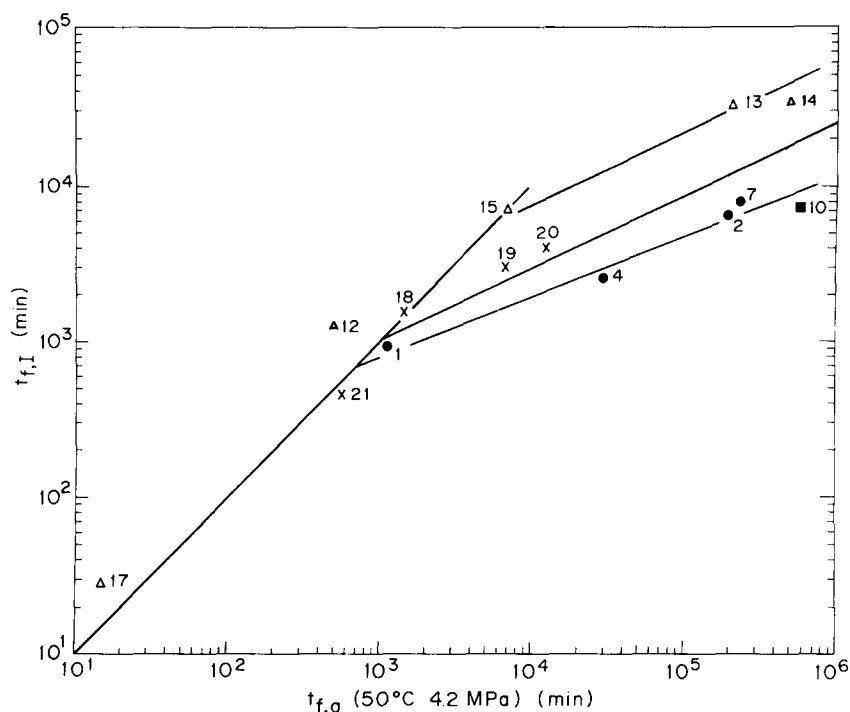


Figure 10 Failure time in Igepal versus failure time in air for a variety of polyethylene copolymers at 50°C and 4.2 MPa: ethylene-butene copolymers (Δ); ethylene-octene copolymers (\times); ethylene-hexene copolymers (\bullet); ethylene dimethyl pentene copolymers (\square)

Brown^{11,12}. This value is about the same as that for the α transition as reviewed by Kambour and Robertson¹³. The most current review of the mechanism of the α transition by Boyd¹⁴ states that the α transition is associated with molecular chains in the crystals. Therefore, these results suggest that the disentanglement process involves motion of the tie molecules in the crystalline region. Huang and Brown^{11,15} have presented a model of the interaction between tie molecules and the crystal based on measuring the effect of molecular weight and density of short branches. Not only is the number of tie molecules important, but the thickness of the lamella crystals between the short chain branches is a factor. Lu *et al.*^{16,17} have shown that thermal treatments which change the distribution of lamella thicknesses have a large influence on slow crack growth in polyethylenes.

It is our view that the rate determining process for fracture initiation is the disengagement of the tie molecules from the crystals. This process takes place in the fibrils at the base of the craze which are produced immediately upon loading. It is proposed that in order for the Igepal to accelerate fracture, it must interact with the crystalline region. This means that the Igepal must diffuse into the crystal whereas it need only diffuse into the amorphous region to promote craze growth. Since the diffusion into the crystal region is relatively slow, it is suggested that the ITT is related to the time required by the Igepal to diffuse into the crystalline region in order for it to accelerate the fracture process. Klein and Briscoe¹⁸ measured the diffusion coefficient of Igepal into polyethylene. From their data, the diffusion coefficient is estimated to be $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ at 50°C. Since the fibrils in the craze are $\sim 0.1\text{--}1 \mu\text{m}$ in diameter, it should only take 1–100 s for the Igepal to be absorbed into the amorphous region. This time should also be sufficient to enhance craze growth. However, at 50°C, the ITT is 800 min and about the same value was observed in an

investigation of 22 other polyethylenes by Ward *et al.*² (Figure 10). Based on the size of the fibrils and the time for the Igepal to become effective, a diffusion coefficient of $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ can be calculated; this value pertains to diffusion into the crystalline region.

The question arises as to why the Igepal molecule should enhance the rate of brittle failure. Igepal has a very low solubility in polyethylene and thus does not produce large scale plasticization which would lead to the blunting of the notch and thus prevent the formation of the craze. Possibly the long Igepal molecule tends to align itself with the tie molecules in the fibrils and thus decrease the frictional stress between the tie molecules and the crystals. It is proposed that the rate of disentanglement of the tie molecules from the lamella crystals determines the lifetime.

CONCLUSIONS

Igepal has two roles in the process of slow crack growth. It enhances craze growth by plasticizing the amorphous region. This caused the formation of secondary crazes only in Igepal at higher stresses. The secondary crazes increased the failure time in Igepal relative to that in air by relaxing the local stress at the notch. Igepal enhances fracture by interacting with the crystalline region of the fibrils at the base of the craze. The interaction of the Igepal with the crystal reduces the activation energy from 118 kJ mol^{-1} in air to 69 kJ mol^{-1} . Because the Igepal must diffuse into the crystal before it accelerates fracture, there is a delay time which corresponds to the 'Igepal transition time'.

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