The effect of concentration of an environmental stress cracking agent on slow crack growth in polyethylenes

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Slow crack growth was measured in three polyethylene copolymers by a notch tensile test at 50°C in Igepal Co-630. The concentration of Igepal was varied from 0 to 100%. The largest reduction in time to failure occurred in the concentration range between 0% and 0.1%. From 0.1 to 20% concentration, the additional effect was much less. A minimum in time to failure occurred at ~50% concentration. There is a significant increase in failure time when the concentration is increased from 50 to 100%. If the failure time is $<10^3$ min in air, Igepal has practically no effect.

(Keywords: polyethylene; slow crack grwoth; concentration)

INTRODUCTION

Nonylphenoxy polyethoxy is commonly known as Igepal Co-630. It is also called an environmental stress cracking (ESC) agent and is used to accelerate slow crack growth in polyethylenes (PEs). Often the Igepal is used at 10% concentration in water at 50°C. Ward *et al.*[1,2] have measured slow crack growth in 22 PEs in air and Igepal as shown in *Figure 1*, where the percentage reduction in failure time by the Igepal increases as the resistance to slow crack growth increases. For failure times of $< \sim 10^3$ min, there was practically no difference between failure times in air and Igepal.

The general mechanism whereby an ESC agent accelerates failure has been discussed by Isaksen *et al.*[3], Bernier and Kambour[4], Tonyali *et al.*[5,6], Brown[7] and Frayer *et al.*[8]. Isaksen *et al.*[3] used 15 different solvents and found that ESC efficiency depended on the chemical nature of the solvent and was high if the absorption was limited. Bernier and Kambour[4] studied 28 solvents and found that crazing was maximized when the solubility parameter of the solvent equalled that of the polymer. Tonyali *et al.* and Brown confirmed the findings by Bernier and Kambour. The solubility parameter of Igepal is 20 MPa$^{1/2}$ and for PE it is 16.4 MPa$^{1/2}$ which agrees with the above result.

Brown *et al.*[9] have extensively observed the failure mechanism of slow crack growth with the optical microscope. They found that a craze forms immediately upon loading the notched specimen. The time to initiate fracture in the fibrils at the base of the craze is the most important indicator for determining the resistance to slow crack growth. The subsequent time for complete failure is related to this initiation time. Consequently, the effect of the Igepal depends on the penetration of the Igepal into the fibril of the craze. Since the stresses that act on the boundary of the craze are low, as shown by the work of Wang *et al.*[10,11], the fracture of the fibril most likely involves a process of disentanglement rather than chain scission. As pointed out by Tonyali *et al.*[5,6] and Brown[7], the Igepal acts like a lubricant to promote chain sliding.

With regard to the effect of Igepal concentration on ESC in PE, the published data are limited. Tonyali *et al.*[5,6] found a linear relationship between crack speed and Igepal concentration for concentrations up to 25%. Chang and Donovan[12] studied the effect of stress intensity on crack growth in low density PE (LDPE) in Igepal concentrations up to 10%. They found that as the stress intensity increased the rate of crack growth increased but there was no effect of Igepal up to concentrations of 10%. Beyond a certain stress intensity, the rate of crack growth became constant with respect to stress intensity, but the rate increased from 4×10^{-7} m s^{-1} at a concentration of 0.4% to 11×10^{-7} m s^{-1} at a concentration of 10%. In this investigation, the concentration was varied from 0.1 to 100%. The research was conducted on three linear LDPE (LLDPE) resins used for gas pipes whose failure times in air varied from 10^2 to 6×10^5 min. The effect of concentration was also investigated for a range of stress intensities which produced the brittle type fracture that is characteristic of slow crack growth.

The results show that the effect of concentration on slow crack growth is most pronounced for resins whose resistance to slow crack growth is greatest. Also, the resistance to slow crack growth generally exhibits a minimum value at ~50% Igepal.

EXPERIMENTAL

Three PE gas pipe materials were used in this investigation. Their material parameters are listed in *Table 1*. Materials A and C are compression-moulded

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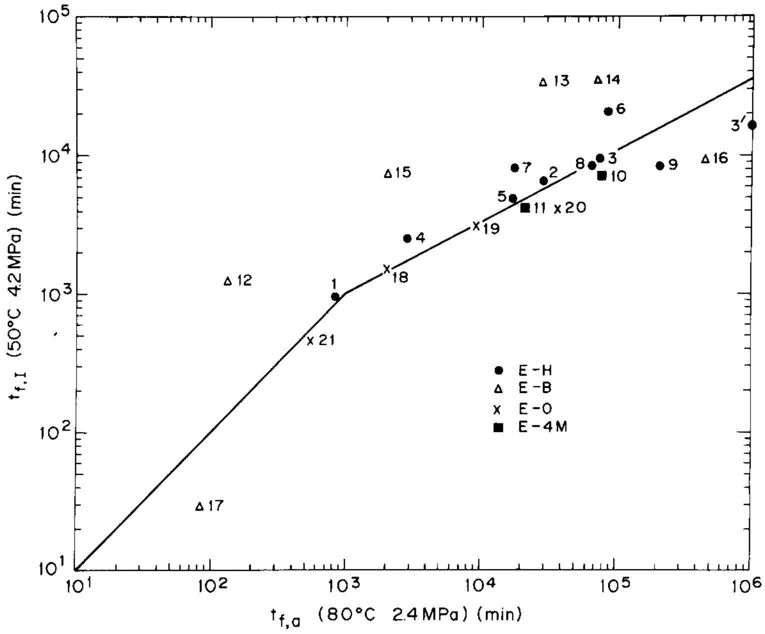

Figure 1 Time to failure in Igepal *versus* time to failure in air for different comonomers: (E-H) hexene; (E-B) butene; (E-O) octene; (E-4M) 4-methyl pentene

Table 1 Material parameters

Material	M_n	M_w	MI	ρ ($g\,cm^{-3}$) at 23°C	σ_y (MPa)	Composition (branches/1000C)
A	15000	170000	0.20	0.9445	19.6	4.9 butyl
B	–	128000	1.15	0.9440	18.0	4.5 hexyl
C	–	128000	1.15	0.9465	20.7	4.5 hexyl

plaques 10 mm thick and slowly cooled. Material C is from a gas pipe with an outer diameter of 114 mm and wall thickness of 10.8 mm. The geometries of the notched tensile specimens taken from the compression-moulded plaque and from the pipe are shown in *Figure 2*. All specimens have a 3.50 ± 0.05 mm notch and 1 mm deep side grooves. Details of the notching procedure are given by Lu *et al.*[13]. The specimens were designed so that fracture occurred under plain strain conditions. The tests were conducted at 50 ± 0.5°C with stresses from 2 to 4.2 MPa. These low stresses insured that brittle failure occurred. The specimens were enclosed within a thin rubber sack which contained the Igepal solution. The concentrations of the Igepal Co-630 from the GAF Company were 0.1, 1, 5, 10, 20, 30, 50, 75 and 100%.

A dial indicator was used to measure the overall creep deformation of the specimen. Simultaneous measurements of the crack opening displacement with a microscope showed that the dial indicator also tracked the changes in the crack opening displacement as shown in *Figure 3*. Consequently, the dial indicator could be used to determine the time of fracture initiation.

Duplicate tests were done for each set of test conditions. Generally, the times of failure for the pair of tests agreed within ±15%.

RESULTS

Figure 3 shows the simultaneous observations of overall creep by the dial gauge and crack opening displacement by the microscope. Both curves show the same pattern of acceleration and deceleration. Crack initiation as observed by the microscope occurs at the time, t_B, which is indicated by the arrow. The creep curves also exhibit their initial acceleration at t_B. Many of such observations show that the time when the initial acceleration occurs in the creep curve also corresponds to the initial fracture

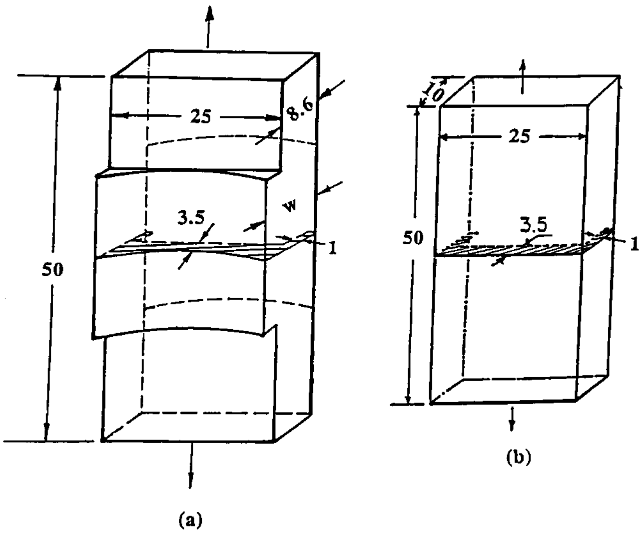

Figure 2 Geometry of slow crack growth specimens from the pipe (a) and the compression-moulded plaque (b). Dimensions in mm

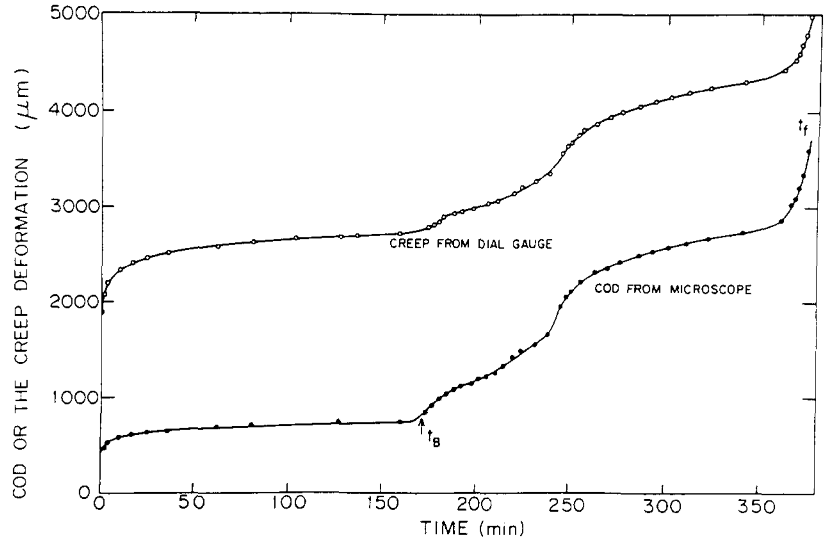

Figure 3 Simultaneous observations of the slow crack growth process by measuring the creep deformation by a dial indicator and the notch opening by a microscope for a specimen tested at 80°C in air

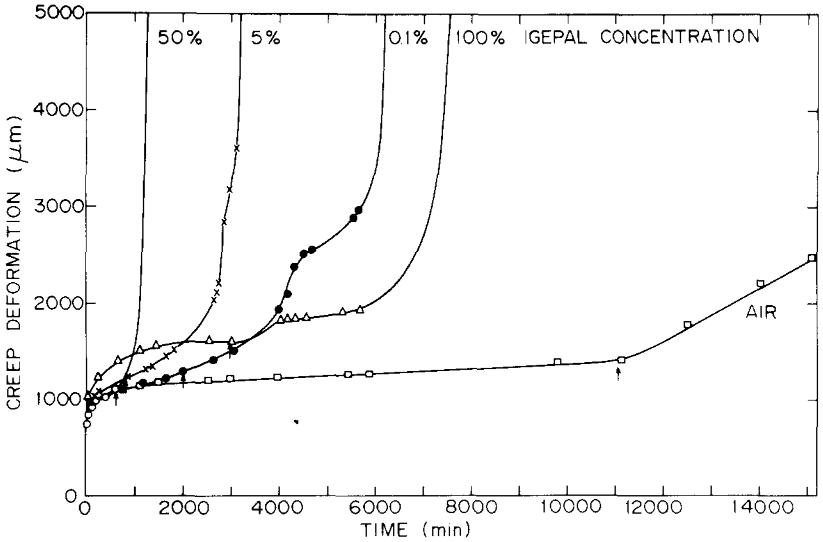

Figure 4 Creep deformation *versus* time for material B (50°C, 2 MPa) for various concentrations of Igepal

Table 2 Times for crack initiation compared to times for complete fracture for material B at 2 MPa

Igepal concentration	t_B (min)	t_f (min)	t_B/t_f
Air	–	–	0.3[a]
0.1%	2000	6600	0.30
5%	800	3200	0.25
50%	400	1200	0.33
100°C	3000	7600	0.39

[a] The average value of t_B/t_f from 20 samples tested in air is 0.3 (ref. 14)

of the fibrils in the base of the craze that forms at the root of the notch.

The relationship between the time for initiation of fracture, t_B, and the time for complete fracture, t_f, is shown in *Table 2*. In air, $t_B/t_f = 0.3$ and for all concentrations of Igepal, $t_B/t_f = 0.3$. In many other PE resins, t_f and t_B are related. These results mean that the resistance to slow crack growth can be measured by the time required to fracture the fibrils that form at the root of the initial notch. Thus, the effect of the Igepal in reducing time to failure is primarily determined by its action on the fibrils located at the root of the notch.

Figure 4 shows the creep curves for various Igepal concentrations. The arrow indicates the time for crack initiation. The shape of the curves indicates that the process of slow crack growth is discontinuous. This discontinuous behaviour also occurs generally in air as observed and discussed by Lu and Brown[14].

The effect of Igepal concentration on the time for failure, t_f, is shown in *Figure 5* for each of the three materials over a range of stresses. One prominent effect is that t_f shows a very large decrease when the concentration is 0.1%. From 0.1 to 10%, the effect of Igepal is relatively small compared to its effect from 0 to 0.1%. The other prominent effect is that the reduction of t_f in Igepal compared to its value in air decreases as t_f in air decreases. For a t_f in air of $< 10^3$ min, Igepal has very little effect for concentrations up to ~20%. This result is consistent with previous data shown in *Figure 1*. The above observations are quantitatively presented in *Table 3* which shows the ratio of t_f in various concentrations of Igepal relative to the value in air. At all concentrations, $t_f(\mathrm{Ig})/t_f(\mathrm{air})$ increases as t_f decreases and becomes 1 at $t_f < 10^3$ min. t_f not only varies with the material, but for a given material, t_f increases as the stress decreases. Thus, in general, the ratio of $t_f(\mathrm{Ig})/t_f(\mathrm{air})$ increases as t_f decreases.

In the neighbourhood of 50% Igepal the ratio of $t_f(\mathrm{Ig})/t_f(\mathrm{air})$ exhibits a minimum value. This is the range of concentrations where the Igepal is most effective in reducing t_f. Beyond the minimum at 50%, t_f increases up to a concentration of 100%. However, the value of t_f at 100% concentration is always less than the value in air.

Microscopic observations of the damage zone are shown in *Figure 6* for the various Igepal concentrations. The lengths of these damage zones are consistent with the effect of concentration on lifetime in that the maximum amount of damage occurs at a concentration of 50%.

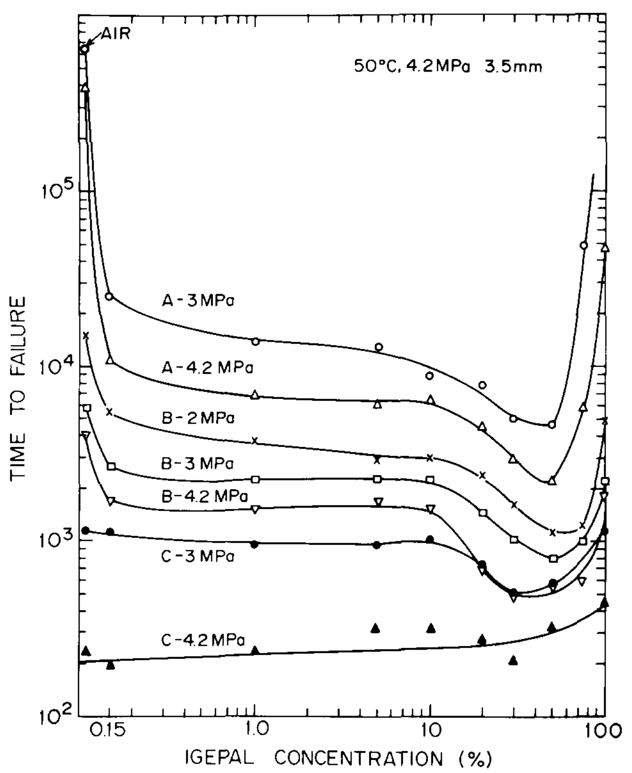

Figure 5 Time to failure *versus* Igepal concentration for the three materials at various stresses

DISCUSSION

The basic mechanism of failure involves the disengagement of the tie molecules from the crystals. Fracture initiated in the fibrils of the craze that forms at the root of the notch when the specimen is first loaded. The applied stresses are too low to produce chain scission. In particular, the time to fracture the fibrils at the base of the craze governs the subsequent time to failure. After fracture initiation there is a general acceleration in the rate of crack growth because the stress intensity increases. However, the rate of disentanglement of the fibrils in the ever present craze governs the process. In some way, the Igepal lubricates the fibrils so that molecules can disentangle faster. The faster the molecules can disentangle, as determined by the molecular properties of the molecules and the stress, the less is the lubricating effect of the Igepal.

This lubricating effect of the Igepal does not increase greatly as the concentration goes from 0.1 to ~20% as

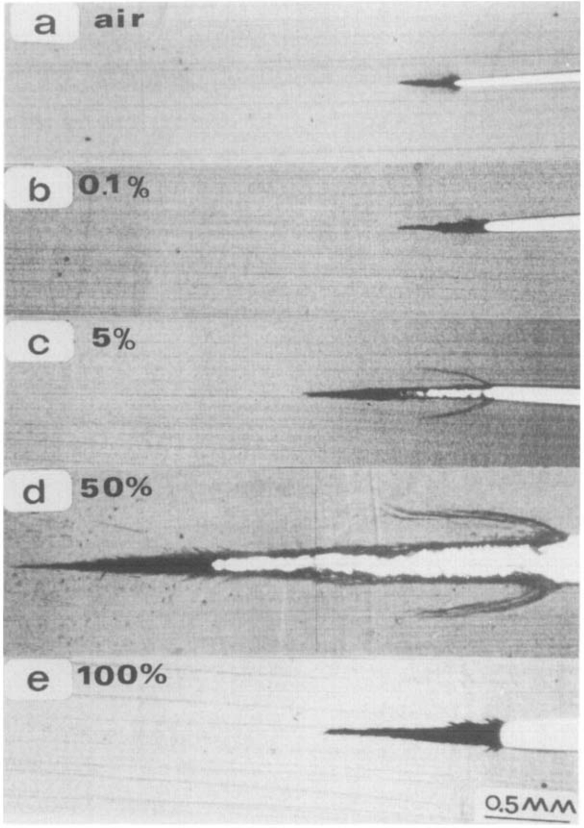

Figure 6 Microstructure of the damaged zone for material B after 600 min at 50°C and 2 MPa for various Igepal concentrations: (a) air; (b) 0.1%; (c) 5%; (d) 50%; (e) 100%

Table 3 Times to failure in Igepal relative to failure times in air for various concentrations

Material and stress (MPa)	$t_f(\mathrm{air})$	$t_f(0.1)$	$\frac{t_f(0.1)}{t_f(\mathrm{air})}$	$t_f(1)$	$\frac{t_f(1)}{t_f(\mathrm{air})}$	$t_f(10)$	$\frac{t_f(10)}{t_f(\mathrm{air})}$
A-3	6.2×10^5	2.25×10^4	0.030	2.0×10^4	0.031	9.0×10^3	0.014
A-4.2	3.9×10^5	1.1×10^4	0.028	6.0×10^3	0.015	6.0×10^3	0.015
B-2	2.0×10^4	5.7×10^3	0.280	3.3×10^3	0.17	3.0×10^3	0.15
B-3	5.8×10^3	2.8×10^3	0.480	2.1×10^3	0.36	2.2×10^3	0.37
B-4.2	3.0×10^3	1.7×10^3	0.560	1.4×10^3	0.36	1.6×10^3	0.53
C-3	1.1×10^3	1.1×10^3	1	1.0×10^3	1	2.0×10^3	≈ 2
C-4.2	2.2×10^3	2×10^2	1	2.2×10^2	1	4.0×10^2	≈ 2

compared to the large effect between 0% and 0.1% concentration. In general, a lubricating film acts in this way. A film of lubricant of critical thickness can make a tremendous change in the coefficient of friction compared to a dry surface, whereas an additional increase in thickness of the lubricating film has a relatively smaller effect. After the asperities on a surface are covered by a lubricant, additional lubricant has a smaller effect on the coefficient of friction.

The result has practical applications for those quality control tests as described in ASTM specifications for evaluating the ESC resistance of PEs. The specifications propose a 100% concentration as the most severe condition for producing cracks. This research shows that a 50% solution is more effective.

The increase in time to failure from 50 to 100% concentration is probably related to the observation that the higher concentration produces a greater blunting of the notch. Instead of forming a craze as is the case at lower concentrations, a shear zone forms at the root of the notch. Details of the progressive change in the structure of the damage zone at the root of the notch as a function of concentration will be presented in another paper. It will also be of interest in a future investigation to measure t_f as a function of concentration between 0% and 0.1%.

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REFERENCES

1 Ward, A. L., Lu, X. and Brown, N. *Polym. Eng. Sci.* 1990, **30**, 1175

2 Ward, A. L., Lu, X., Huang, Y. and Brown, N. *Polymer* 1991, **32**, 2172

3 Isaksen, R. A., Newman, S. and Clark, R. J. 140th National Meeting of the American Chemical Society, Chicago, IL, September 1961, American Chemical Society, Washington DC, p. 515

4 Bernier, G. A. and Kambour, R. P. *Macromolecules* 1968, **1**, 393

5 Tonyali, K., Rogers, C. E. and Brown, H. R. *Polym. Eng. Sci.* 1987, **27**, 82

6 Tonyali, K., Rogers, C. E. and Brown, H. R. *Polymer* 1987, **28**, 1472

7 Brown, H. R. *Polymer* 1978, **19**, 1186

8 Frayer, P. D., Tong, P. P. and Dreher, W. W. *Polym. Eng. Sci.* 1977, **17**, 27

9 Brown, N., Lu, X., Huang, Y. and Qian, R. *Makromol. Chem., Macromol. Symp.* 1991, **41**, 55

10 Wang, X., Fager, L. and Brown, N. *Polymer* 1989, **30**, 453

11 Wang, X. and Brown, N. *Polymer* 1989, **30**, 1456

12 Chang, P. and Donovan, J. A. *Polym. Eng. Sci.* 1990, **30**, 1431

13 Lu, X., Qian, R. and Brown, N. *J. Mater. Sci.* 1991, **26**, 881

14 Lu, X. and Brown, N. *J. Mater. Sci.* 1991, **26**, 612