

A theory of the environmental stress cracking of polyethylene

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It is proposed that the environmental stress cracking of polyethylene is caused by stress-induced swelling and plasticization of certain favourably oriented amorphous regions in polyethylene. The criteria for stress-induced swelling together with the criteria for little swelling at zero stress show that a vigorous stress cracking agent will have a solubility parameter close to that of polyethylene and a large molar volume. Some detergents fit into this category.

INTRODUCTION

It has been known for 30 years that polyethylene can show low stress, apparently brittle failure in the presence of certain environments (*ESC*). This effect was observed by Roberts¹ when studying the swelling and dissolution of polyethylene in organic solvents and by workers at The Bell Telephone Company² who were concerned by cracking caused by soaps in polyethylene cable jackets. This phenomenon is normally observed in alcohols, ketones and phenols, esters such as phosphates and phthalates, detergents and soaps, some animal, vegetable and mineral oils, halogenated hydrocarbons^{3,4} silicone oils and low molecular weight polyethylene. It has frequently been suggested that *ESC* occurs in the presence of mobile polar liquids⁵ but it is not clear that this description applies to all the above stress cracking materials. Polyethylene is known to fail fairly rapidly under load when immersed in vigorous swelling liquids^{1,6}, such as hexane or xylene, which are often described as solvents although at room temperature there are no solvents for polyethylene. The failure under these circumstances is ductile but occurs just as quickly under constant stress situations as in an active alcohol⁶. Although it has been suggested that *ESC* liquids are surface active agents, attempts to correlate cracking efficiency with ability to wet the polymer have not been successful⁶.

The effect of polymer morphology, molecular weight and its distribution on *ESC* resistance has been studied extensively⁵. Crack resistance normally increases with increasing molecular weight and with the removal of very low molecular weight material.

Marshall *et al.*⁹ made a considerable advance to the technique of measuring *ESC* resistance of polyethylenes when they showed that the principles of fracture mechanics can be applied to the system⁹. It has since been shown^{10,11} that, in common with environment controlled fracture in other materials, there are two regions of crack growth rate in polyethylene: a slow region where crack growth rate is controlled by stress intensity and 'activity' of the environment; and a fast region where environment viscosity is the most important parameter and stress intensity has only a minor influence. Howard⁵ observed that, in some systems, the variation of time to fail in the Bell Test with temperature mirrored the variation of the detergent viscosity with

temperature; in those systems therefore, times to fail were probably controlled by the second, high speed region of crack growth. Shanahan and Schultz¹² showed that low stress 'activity' of a series of different molecular weight silicone oils was the same, but at high stresses the crack growth rate was controlled by silicone viscosity.

A MODEL FOR ENVIRONMENTAL STRESS CRACKING IN THE SLOW CRACK GROWTH REGION

It has recently been shown that low stress *ESC* in polyethylenes is probably a failure of the amorphous regions^{13,14}. To cause this failure the environment must be absorbed into these regions so it is initially worth examining their swelling properties, both with and without an applied stress. The failure properties of the swollen material will then be examined.

We shall assume that the amorphous regions can be considered as thin sheets of crosslinked rubbery material sandwiched between inextensible crystalline lamellae. A similar crosslinked rubber model has been used with some success to describe the swelling of polyethylene in compatible organic liquids and vapours.

The rubber is described by the combination, devised by Treloar¹⁵, of the Flory-Huggins theory of polymer solutions with the Gaussian theory of rubber elasticity. In this model the free energy changes related to a small increase of solvent in the rubber are equated with the work done by the external forces. It can be shown¹⁵ that:

$$t_1 V_1 = RT \left[\ln(1 - v_2) + v_2 + \chi v_2^2 + \frac{\rho V_1}{M_c} v_2 l^2 \right] \quad (1)$$

where t_1 is the stress in the 1 direction, l_1 is the extension ratio in that direction, χ is the Flory-Huggins interaction parameter, V_1 is the solvent molar volume, M_c is the molecular weight of the rubber between crosslinks, v_2 is the volume fraction of rubber in the solution, and ρ is the density of the unswollen rubber.

In this equation the left-hand side represents the work done by the external forces; the term $RT[\ln(1 - v_2) + v_2]$ is the partial molar entropy of dilution and $RT\chi v_2^2$ the partial molar enthalpy of dilution — both from the Flory-Huggins

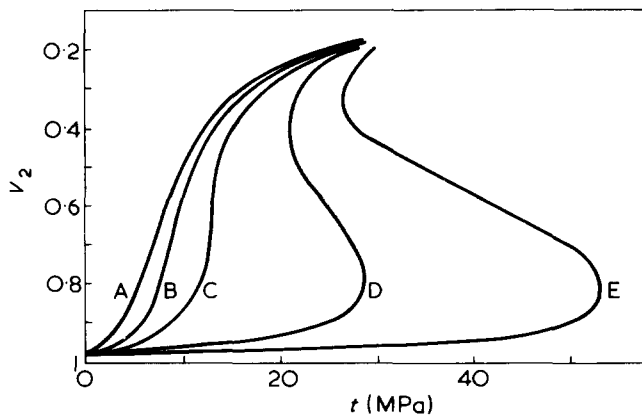


Figure 1 The relationship between stress and swelling. A, $V_1 = 10^{-3} \text{ m}^3$; B, $V_1 = 6 \times 10^{-4} \text{ m}^3$; C, $V_1 = 3 \times 10^{-4} \text{ m}^3$; D, $V_1 = 10^{-4} \text{ m}^3$; E, $V_1 = 5 \times 10^{-5} \text{ m}^3$

theory. The term $RT\rho V_1 v_2 l_1^2/M_c$ is concerned with the free energy change due to the expansion of the rubbery network. As the lamellae are considered inextensible, then $l_2 = l_3 = 1$. Therefore:

$$t_1 = \frac{RT}{V_1} \left[\ln(1 - v_2) + v_2 + \chi v_2^2 + \frac{\rho V_1}{M_c v_2} \right] \quad (2)$$

We shall consider swelling in two regimes as follows.

Swelling in a poor solvent and zero applied stress

The first requirement of a stress cracking agent is that it should not swell the material significantly under zero applied stress, so we shall examine the condition for this to be the case. Starting with equation (2) assume $t_1 = 0$ and $1 - v_2$ is small. Therefore:

$$\ln(1 - v_2) + 1 + \chi + \frac{\rho V_1}{M_c} = 0$$

Let $RT\rho/M_c = 5 \text{ MPa}$, a value suggested for the amorphous sections of polyethylene¹⁶ and $T = 300\text{K}$. We shall consider two possible values of V_1 : $5 \times 10^{-5} \text{ m}^3$ a value typical for low molecular weight solvent, and 10^{-3} m^3 a value more suitable for detergents. In the first case $\rho V_1/M_c = 0.1$ and in the second = 2.0, so for low molecular weight materials the swelling is controlled mainly by the value of χ but as the molecular weight increases the swelling decreases at constant χ .

It is worth noting that there is a relation between χ and the solubility parameters of polymer and solvent δ_p and δ_l of the form:

$$(\delta_p - \delta_l)^2 = \frac{RT\chi}{V_1}$$

The difference in solubility parameters, $\Delta\delta$, necessary to cause a particular degree of swelling will therefore decrease rapidly with increasing molar volume.

Swelling in a poor solvent under an applied tensile stress

Solutions of equation (1) are shown in Figure 1 for a series of solvents which have been chosen to give a swelling of 2% under zero applied stress. Since we are assuming that only the amorphous regions swell, this would correspond to a swelling of less than 1%, calculated on the total polymer volume. It is clear from these plots that the stress required

to swell the material to a swelling such as 25% increases rapidly with decreasing molar volume. Therefore, for a given zero stress swell ratio the most efficient swelling agents under stress are those with a large molar volume. In the case of no crosslinking and large χ the value of t_1 necessary to cause instability is given approximately by:

$$\frac{RT\chi}{V_1}$$

which equals $(\delta_p - \delta_l)^2$.

Effect of swelling on the amorphous regions of polyethylene

It will now be demonstrated that swelling causes plasticization and weakness in rubbery polyethylene. N.m.r. evidence¹⁷ has shown that the amorphous regions of polyethylene can be divided into two regions; an interfacial one where the material is considerably constrained, and a liquid-like region. When the polyethylene is swollen by carbon tetrachloride or benzene the constrained region has been shown to become plasticized and exhibit a liquid-like character¹⁸. In these experiments the maximum swelling of the amorphous regions by benzene was ~50% and the effect was significant at much lower concentrations. Hence plasticization can occur in the amorphous regions of semi-crystalline polyethylene. This plasticization will cause a release of entanglements and consequently a decrease in the strength of the amorphous regions. The strength will also decrease by the same mechanisms that are observed in bulk swollen rubbers. The strength of amorphous crosslinked rubbers is controlled by the segmental viscosity¹⁹, and a decrease of the latter by plasticization inevitably decreases the strength. This has been demonstrated in many rubbers including polyethylene, where Gent and Vickroy²⁰ found, in the course of an investigation of the elastic and photoelastic properties of molten polyethylene, that they could not extend their swollen samples to extensions of more than 10% 'due to the limited extensibility of these highly swollen materials before fracture'²⁰. The equivalent unswollen materials could be extended to 100% extension. There is, therefore, evidence that the swelling of the amorphous regions of polyethylene can cause failure under low stresses and strains.

The complete model

There is good evidence to suggest that ESC is caused by stress-induced swelling and plasticization of those amorphous regions whose bounding lamellae are approximately normal to the applied stress. In these regions the combined actions of stress and the constraints of the lamellae cause sufficient hydrostatic tensions for swelling whose amount is controlled mainly by $(\delta_l - \delta_p)$. The swollen rubber will fail by the normal rubbery viscoelastic mechanisms which are greatly accelerated by the swelling. The stress necessary to cause this failure is of the order of $(\delta_l - \delta_p)^2$ for poor ESC liquids but the cracking is normally observed to be a flaw initiated phenomenon, and this stress need only be at the root of the flaw.

For a fluid to be an ESC agent it must, by definition, not swell the material significantly at zero stress. Swelling at zero stress plasticizes all the amorphous regions of the polymer and decreases the yield stress¹⁸ (as conventionally measured). Failure can easily occur at low stresses but it is not unexpected since the material is clearly greatly affected by the fluid.

PREDICTIONS FOR AN ESC AGENT

An ESC agent must be a material which does not swell the unstressed polymer greatly, which means that it must have a considerably different solubility parameter to polyethylene, or a large molar volume, or both. In addition its effectiveness as an ESC agent will increase directly as $(\delta_p - \delta_f)^2$ approaches zero, with only a small dependence on molar volume. Hence the most effective cracking agents have $\delta \sim 7.9 \text{ (cal/cm}^3)^{1/2}$ (the value for polyethylene) and larger molar volumes. In addition they must be liquid at room temperature. The plasticization mechanism suggests that efficiency will increase as the glass transition temperature of the swelling agent decreases.

The most commonly used and perhaps the most vigorous stress cracking agents are detergents, of which the non-ionic 'Igepal Co630' is a much used example. This material consists of a branched nine-carbon *para*-substituted phenol onto which nine ethylene oxide units have been condensed. It has a molar volume of approximately $6 \times 10^{-4} \text{ m}^3$. The solubility parameter of the hydrocarbon part will be similar to a branched decane of about $7.8 \text{ (cal/cm}^3)^{1/2}$. Poly(ethylene oxide) forms an approximately athermal solution in benzene so it must have approximately the same solubility parameter, $9.2 \text{ (cal/cm}^3)^{1/2}$, which suggests that a value of $8.6 \text{ (cal/cm}^3)^{1/2}$ is not unreasonable for the detergent. This is close to the value of $7.9 \text{ (cal/cm}^3)^{1/2}$ for polyethylene and explains why the material is such a good stress cracking agent. The small but finite adsorption of the detergent in PE has been demonstrated under zero stress^{21,22} and it has been shown to increase under stress²¹. The majority of materials mentioned in the Introduction as stress cracking agents have solubility parameters considerably greater than this with smaller molar volumes so they are not such effective cracking agents at low stress. The solubility parameter of straight chain aliphatic alcohols decreases steadily with molecular weight and it has been shown that their stress cracking vigour increases steadily with molecular weight²³, as predicted by this theory. The solubility parameter of fairly high molecular weight silicone oils varies little with molecular weight so that the independence of 'activity' with molecular weight¹² agrees with the theory.

DISCUSSION

The concept that low stress ESC failure is interlamellar has had support for some time^{5,6,22} and has recently been demonstrated experimentally^{13,14}. As this is the case, the resistance to failure will depend upon the number of tie molecules, and this has been shown to depend upon molecular weight as the chain ends collect in the interlamellar regions. Hence the variation of cracking with molecular weight can be explained. Marshall *et al.*²⁴ showed that in HDPE homopolymer the stress cracking just accelerated, or reduced to lower stress intensity — an effect that was already there in failure in air. This agrees well with our

concept of selective plasticization of interlamellar regions.

It has been known for many years that environmental stress cracking is initiated more readily under polyaxial stresses than under uniaxial stresses. This is because the proportion of random flaws in the material which have lamellae at their base, oriented so as to cause swelling in the amorphous phase, will increase with increasing biaxiality.

It is interesting to note that solvent crazing in amorphous thermoplastics is controlled by a term of the form $(\delta_1 - \delta_2)^{25,26}$, and in addition Gent's theory of crazing²⁷ suggests that hydrostatic tension causes the material to be transformed to a rubber. It therefore seems possible that solvent crazing is caused by an elastic instability similar to that described here.

REFERENCES

- 1 Roberts, R. B. *Trans. Faraday Soc.* 1946, **42**, 20
- 2 Decoste, J. B., Malm, F. S. and Wallder, V. T. *Ind. Eng. Chem.* 1951, **43**, 117
- 3 'Alakathene Handbook', ICI Plastics Division, UK, March 1964
- 4 Howard, J. B. *SPE J.* 1959, **15**, 397
- 5 Howard, J. B. in 'Engineering Design for Plastics' (Ed. E. Baer) Reinhold, New York, 1964
- 6 Isaken, R. A., Newan, S. and Clark, R. J. *J. Appl. Polym. Sci.* 1963, **7**, 515
- 7 Martin, J. R., Johnson, J. F. and Cooper, A. R. *J. Macromol. Sci. (C)* 1972, **8**, 57
- 8 Marshall, G. P., Culver, L. E. and Williams, J. G. *Plast. Polym.* 1970, **38**, 95
- 9 Marshall, G. P., Linkins, N. H., Culver, L. E. and Williams, J. G. *SPE J.* 1972, **28**, 26
- 10 Williams, J. G. and Marshall, G. P. *Proc. Roy. Soc. London (A)* 1975, **342**, 55
- 11 Bandyopadhyay, S. Personal communication
- 12 Shanahan, M. E. R. and Schultz, J. *J. Polym. Sci. (Polym. Phys. Edn)*, 1976, **14**, 1567
- 13 Bandyopadhyay, S. and Brown, H. R. *J. Mater. Sci.* 1977, **12**, 2131
- 14 Bandyopadhyay, S. and Brown, H. R. *Polymer* 1978, **19**, 589
- 15 Treloar, L. R. G. 'The Physics of Rubber Elasticity', 3rd Edn. Oxford University Press, 1975
- 16 Peterlin, A. *Polym. Eng. Sci.* 1977, **17**, 183
- 17 Mandelkern, L. *J. Polym. Sci. (C)* 1975, **50**, 457
- 18 McCall, D. W. and Anderson, E. W. *J. Polym. Sci. (A)* 1963, **1**, 1175
- 19 Gent, A. N. in 'Fracture Vol. VII' (Ed. H. Liebowitz), Academic Press, New York, 1972
- 20 Gent, A. N. and Vickroy Jnr., V. V. *J. Polym. Sci. (A-2)* 1967, **5**, 57
- 21 Seimya, T., Yamamoto, H. and Sasaki, T. *J. Polym. Sci. (A-2)* 1970, **8**, 595
- 22 Frayer, P. D., Tong, P. P. L. and Dreher, W. W. *Polym. Eng. Sci.* 1977, **17**, 27
- 23 Shchukin, E. D., Soshko, A. I., Nikityuk, O. A. and Tynnyi, A. N. *Soviet Mater. Sci.* 1971, **7**, 160
- 24 Linkins, N. H., Culver, L. E. and Marshall, G. P. Presented at 2nd Cambridge Conference on Yield, Deformation and Fracture of Polymers, 1973
- 25 Bernier, G. A. and Kambour, R. P. *Macromolecules* 1968, **1**, 393
- 26 Vincent, P. I. and Raha, S. *Polymer* 1972, **13**, 283
- 27 Gent, A. N. *J. Mater. Sci.* 1970, **5**, 925