Stress-cracking of polyethylene in organic liquids

Köksal Tonyali*, Charles E. Rogers
Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA

and Hugh R. Brown
IBM Research Center, 650 Harry Road, San Jose, CA 95120, USA

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The crack growth behaviour of low density polyethylene in various organic liquids shows that there is a correlation between the crack speed and the solubility parameter of the environment. The detergent solutions, which are micellar in water, were found to be more effective in cracking the specimens than solutions without micellar structure. The addition of small amounts of solubilizates, such as xylene, to the micellar solution increased the crack growth rate. Williams' flow model is found to be inadequate to describe the crack growth behaviour. A qualitative model for crack propagation considers that the combination of the sorption properties of the polymer and viscous flow of the swollen material leads to crack growth.

(Keywords: fibril breakdown; fracture; low density polyethylene; micellar solution; stress-cracking; stress induced absorption; viscous flow)

INTRODUCTION

Polymers find wide application in such disparate areas as pipelines, coatings and electronic devices because of their chemical stability, in addition to other properties. As a result, they are often exposed to aggressive environments in which the combination of chemical or physico-chemical effects with stress leads to early failure. This is a particular problem when there is no obvious interaction of the chemical environment in the absence of stress. Polyethylene is a polymer which is used in large amounts by industry, but fails under low stresses in the presence of environments such as alcohols, detergents and silicone oils[1,2].

Williams and his coworkers[3-5] were the first to apply linear elastic fracture mechanics (LEFM) to environmental stress-cracking (ESC) of polyethylene. They suggested that there exists a unique relationship between the stress intensity factor (K_I) and crack speed ($\dot{c}$). They showed that a K_I–$\dot{c}$ plot consisted of three regions, namely Regions I, II and III, which they believed to be controlled by relaxation, hydrodynamic flow properties of the environment, and the mechanical properties of the material in air, respectively. The unique relationship between K_I and $\dot{c}$ and the existence of three regions of crack propagation have been confirmed in some cases[6-9]. However, the current authors[10-13] have recently shown that LEFM applied to the system only at low K_I levels and that Region II was not controlled by the flow properties of the environment. We used detergent solutions with various concentrations as the environment and measured the K_I-independent crack speeds in Region II. In contrast to Williams' model, we found that the constant crack speed increased with detergent concentration. Since the viscosity of the solution is an increasing function of detergent concentration, his model would predict a crack speed that decreased with increasing detergent concentration.

The purpose of this paper is to extend our work to study the crack propagation behaviour in various organic environments. The data are compared with existing models of crack propagation. A new qualitative model to describe crack growth is proposed.

EXPERIMENTAL

Test methods

Low density polyethylene in the form of beads was obtained from Dow Chemical Corporation (Dow low density PE 681, melt flow index = 0.23). The beads were pressed into a sheet in a compression moulding apparatus at 185°C. The sheets had dimensions 150 mm × 150 mm × 1.35 mm. Specimens 12 cm long and 3 cm wide were cut out from the sheets. A razor blade was used to introduce a 3 mm notch to the specimens. All tests were carried out at 20°C using single edge notched specimens and a stress level of 0.13 MPa (yield stress = 11.3 MPa). A crack propagation test rig was used to monitor the crack length with respect to time[10].

Environments

The following liquids were used as environments: methanol, ethanol, ethylene glycol, diethylene triamine, methyl cellosolve, Igepal CO-630, sodium hydroxide, nonyl phenol, xylene, water, and in some cases, mixtures of two or more of these liquids.

Data analysis

The crack length–time plots were smoothed and the crack speed ($\dot{c}$) at each data point was obtained using a

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* Present address: Department of Physics, Washington State University, Pullman, WA 99164, USA.

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spline fitting computer program[10]. The stress intensity factor (K_I) was calculated using the usual equation,

$$K_I = Y\sigma c^{1/2}$$

where Y is the shape factor[14], σ is the applied stress and c is the crack length.

RESULTS AND DISCUSSION

Effect of ethanol concentration on the K_I–$\dot{c}$ plots

A stress intensity factor (K_I) against crack speed ($\dot{c}$) plot (*Figure 1*) shows the effect of ethanol concentration on the constant crack speed. All curves seem to be almost identical and display a number of regimes of crack growth with increasing stress intensity factor. Pure ethanol also gave the same curve. Region I starts at a K_I value of 0.13 MN m$^{-3/2}$, at which crack initiation takes place. In this region, the crack speed is a function of the stress intensity factor and increases rapidly with K_I. Region I ends at about $K_I = 0.2$ MN m$^{-3/2}$, where a new region begins with a K_I-independent crack speed. This region is replaced by another region at $K_I = 1.0$ MN m$^{-3/2}$ which is called the 'crack deceleration region'. In this region, crack blunting occurs (not shown in the plot). The constant crack speed is 0.017 mm h^{-1} for all concentrations of ethanol in water.

Constant crack speed in various organic liquids

Tests have been made to study the effect of various organic environments on the constant crack speed. *Table 1* shows both the liquids used as aggressive environments with their various properties[15,16] such as surface tension (γ), viscosity (η) and the solubility parameter (δ), and the constant crack speeds obtained in each environment.

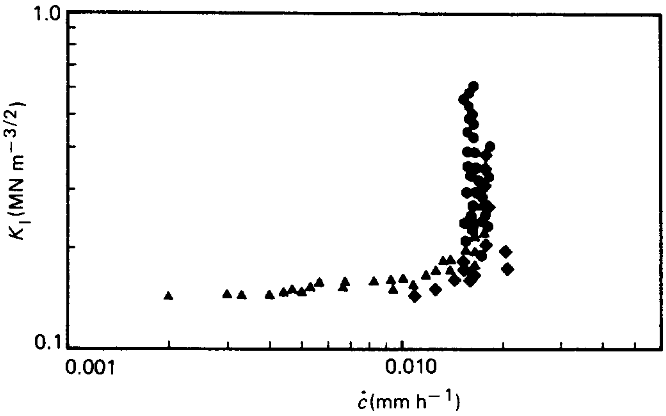

Figure 1 Effect of ethanol concentration (wt%) on the K_I–$\dot{c}$ plot: ●, 5%; ▲, 10%; ◆, 20%; ●, 40%

The results in *Table 1* show clearly that there is no specific correlation between the constant crack speed and the surface tension of the liquids. Organic liquids generally have low surface tensions and spread on polymer surfaces readily. This process has been considered for some time to reduce the surface energy for crack formation[17,18]. However, our attempts to extend this correlation to stress-cracking of polyethylene have not been successful. This perhaps can be best seen in *Figure 1*. The increase in ethanol concentration leads to a lower surface tension which has absolutely no observable effect on the constant crack speed.

Attempts to correlate the environment viscosity with the constant crack speed do not succeed either. Williams and coworkers[4,5] and Bubeck[9] have suggested that the constant crack speed region in a K_I–$\dot{c}$ plot is controlled by the flow properties of the environment. We have substantiated elsewhere[12,13] that this is not the case in polyethylene–detergent solution systems, as an increase in the detergent concentration resulted in both an increase in the constant crack speed and an increase in viscosity. As can be seen from *Table 1*, although Igepal CO-630 has the highest viscosity of this set of fluids, it gives rise to the largest constant crack speed. If the behaviour was flow controlled, one would expect to obtain the highest crack speed in methanol. The observations in this work, therefore, suggest that the hydrodynamics of the fluid is not important in stress-cracking of polyethylene.

Inspection of *Table 1* shows that a relationship may exist between the solubility parameter of the environment and the constant crack speed. The solubility parameter of polyethylene is 16.4 MPa$^{1/2}$ (Ref. 16). The data in *Table 1* show that the constant crack speed increases as the solubility parameter of the environment approaches that of the polymer. Diethylene tramine (DETA) does not follow this trend. A possible explanation may be that the structure of DETA is quite different from that of polyethylene. DETA may well deviate because of H-bonding. In such a case, the solubility parameter would be unreliable. The dependence of the constant crack speed on the solubility factor suggests that the organic liquids act as plasticizers. Similar observations in poly(phenylene oxide) have been made by Kambour *et al.*[19], who found that a minimum value of critical strain to cause crazing was obtained at $\delta_{\text{polymer}} = \delta_{\text{liquid}}$ when the critical strain was plotted against the solubility parameter.

Brown[20] suggested that stress can be expected to have a profound effect on the absorption of the liquids into polyethylene. Thus the crack tips are highly stress concentrated regions in which swelling is enhanced. Organic liquids swell the polymer and act as plasticizer, and hence, the swollen part of the specimen flows easily

Table 1 Effect of various organic environments on constant crack speed

Environment	γ' (dyn cm^{-1})	V (cm^3 mol^{-1})	η (cp)	δ (MPa$^{1/2}$)	$\dot{c}$ (mm h^{-1})
Methanol	22.69	40.7	0.59	29.6	0.015
Ethanol	22.27	58.5	1.22	26.5	0.017
Ethylene glycol	53.00	55.8	21.00	32.9	0.000
Methyl cellosolve	35.00	79.1	1.72	24.8	0.032
Diethylene triamine	–	108.0	–	25.8	0.004
Sodium hydroxide (10%)	80.00	–	–	–	0.000
Water	74.00	18.0	1.00	47.8	0.000
Igepal CO-630	32.00	–	250.00	20.0	10.020

Table 2 Effect of diethylene triamine–methyl cellosolve–sodium hydroxide mixtures on constant crack speed

Environment	$\dot{c}$ (mm h^{-1})
Diethylene triamine (DETA)	0.004
Methyl cellosolve (MeCell)	0.032
70% DETA+28% MeCell+2% NaOH	0.016
49% DETA+49% MeCell+2% NaOH	0.023

under the applied stress. The degree of swelling in the polymer could be predicted by making use of the solubility parameters of the fluids, e.g. by using a Flory–Huggins relationship.

The difference between the solubility parameter of the liquid and that of polymer can be used as a measure of plasticization efficiency. It can be seen from *Table 1* that when the difference approaches zero cracking becomes easier.

Effects of mixed solvents on the cracking behaviour

We showed elsewhere[12,13] that the detergent concentration in aqueous solutions affected the constant crack speed. It is of interest to extend this work to other solvent mixtures. In this section, we will discuss three systems, namely the diethylene triamine (DETA)–methyl cellosolve (MeCell)–sodium hydroxide (NaOH) system, the ethylene glycol–Igepal CO-630 system and the ethanol–Igepal CO-630 system. The Igepal CO-630–xylene–water solution will also be discussed.

Table 2 shows the effect of the DETA–MeCell–NaOH solution on the constant crack speed. The amounts of the liquids in *Table 2* are all percentages by weight. 10% NaOH in water did not produce any observable crack growth (see *Table 1*) and thus we assume that sodium hydroxide is a non-aggressive environment. As can be seen from *Table 2*, the constant crack speeds in DETA and MeCell are 0.004 and 0.032 mm h^{-1}, respectively. It seems that the cracking behaviour is controlled by the amount of MeCell in the mixture. The solution of 70% DETA–28% MeCell–2% NaOH gives rise to a speed of 0.016 mm h^{-1}. An examination of *Table 1* shows that this behaviour is expected since the solubility parameter of DETA is larger than that for MeCell. The chemical structure of DETA is quite different from that of polyethylene and also strong H-bonding may affect the prediction of the solubility parameter; hence DETA is not a good cracking agent.

Variation of the concentration of ethanol in water between 5 and 40% (also 100%) showed no effect on the constant crack speed (see *Figure 1*). A possible explanation for this behaviour may be that the equilibrium solubility of ethanol in polyethylene is low and its diffusion into the bulk is rapid, so that within the concentration range we used equilibrium is reached quickly. Equilibrium solubility of ethanol should change with ethanol concentration in solution. But absolute sorbed concentration is low and hence small concentration changes will not have a large effect on the crack speed. Therefore, the change in ethanol concentration does not affect the crack speed. An alternative explanation for this behaviour will be suggested later in this section.

We have shown elsewhere[10,12,13] that the solution structure of the environment played a large role in the cracking behaviour and, furthermore, we attributed the increase in the constant crack speed with detergent concentration as being due to the increase in the number of micelles in the water solution. To investigate the effect of the solution structure further, we used three mixtures, which were 10% (by volume) Igepal CO-630 in each of ethanol, ethylene glycol and water. These solutions were chosen because Igepal CO-630 in ethylene glycol and water gives rise to a micellar solution, but Igepal CO-630 does not form micelles in ethanol[21]. Critical micelle concentrations (CMC) for the ethylene glycol and water solutions are 13.5 and 0.01% (v/v), respectively.

Table 1 shows that Igepal CO-630 is highly aggressive ($\delta = 20$ MPa$^{1/2}$) compared to ethanol, ethylene glycol and water. Thus the constant crack speeds obtained in the solutions of Igepal CO-630 yield information about the relation between the cracking mechanism and the solution structure.

The effect of 10% (by volume) Igepal CO-630 in different solvents is shown in *Figure 2*. Interestingly, one observes the lowest constant crack speed (about 0.02 mm h^{-1}) in the ethanol solution and the highest speed (0.55 mm h^{-1}) in the water solution. The difference is probably related to the fact that the solutions are micellar in ethylene glycol and water. The formation of micelles may create more efficient plasticization at the crack tip because the micelles are composed of a high activity of aggressive detergent molecules. In ethylene glycol and water, no cracking of polyethylene was observed.

A possible explanation may be the following. Comparing the results of the ethanol solutions to those of the detergent solutions, a question arises as to why the constant crack speed is dependent on the concentration of the detergent but not on the ethanol concentration. Although we are not able to explain the entire effect, we can speculate that the cracking process is controlled by the properties of the surfactant solutions and it appears that there is a supply problem of the aggressive environment at the crack tip.

If a solid is exposed to a surfactant solution, it is usually assumed that equilibrium is established rapidly at the interface between the surface and the environment. However, in many cases it is fairly certain that all the interfaces involved will not, in fact, reach equilibrium so quickly. Therefore, the velocity of adsorption at the interface will be a controlling mechanism. For example, Addison[22–28] studied aqueous solutions of a series of

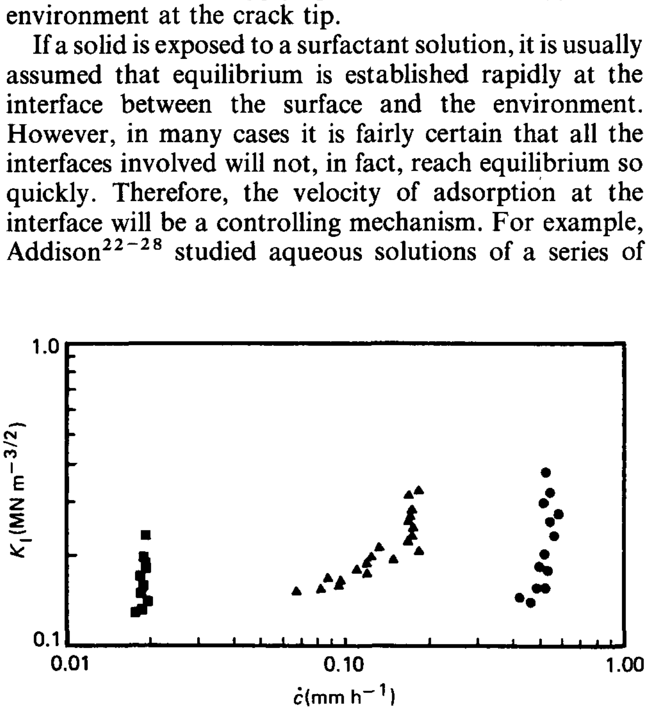

Figure 2 Effect of solution structure on the K_I–$\dot{c}$ plots: 10% (by vol.) Igepal CO-630 in ■, ethanol; ▲, ethylene glycol; ●, water

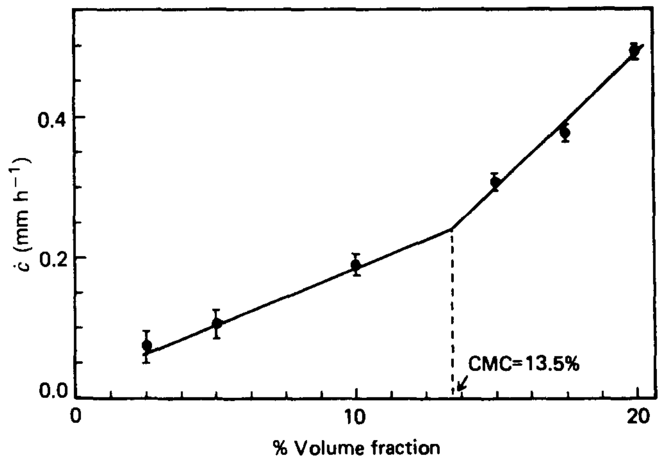

Figure 3 Effect of detergent concentration in ethylene glycol on constant crack speed

aliphatic alcohols up to octanol and observed that equilibrium was attained at the interface so rapidly with alcohols up to butanol that he was not able to detect any measurable time lag for the formation of equilibrium. However, he found that there is a time lag with the other alcohols. He also reported that the rate, at which equilibrium is attained, increases with solution concentration. Thus it appears that in ethanol solution the fibril surface may reach equilibrium instantaneously and hence we would not see any concentration effect.

It has been pointed out that in detergent solutions the time to reach final equilibrium is longer than that in alcohol solutions. Ward and Tordai[29,30] reported that the equilibrium time may be a million times greater than that needed for the diffusion to bring detergent molecules onto the surface. In a micelle, molecules will be oriented in a definite sense, and the final process of adsorption at the interface may require a large activation energy. There is also another possibility that in surfactant solutions there might be a third component with a higher diffusion coefficient than that of the surfactant, so that final quasi-equilibrium is attained quickly with those molecules. For instance, in the 10% Igepal solution in ethanol the interface may be formed readily by ethanol molecules which block the entrance of the Igepal molecules to the surface. Hence a decrease in the rate of cracking would be observed since Igepal is a more effective cracking agent.

Meader and Fries[31] studied the adsorption isotherms of some detergents on wool and cotton, and found that micelles, as well as detergent molecules, were being adsorbed at the interface. Thus, considering that the adsorption process is also concentration dependent, the crack speed should also be controlled by micelle formation.

The reason that the water solution gave rise to the highest crack speed may be that the micelle concentration was high. The concentration of the micelles, $[M]$, is given by the equation[32]:

$$[M]=(\phi-\mathrm{CMC})/N$$

where ϕ is the total concentration of the detergent, CMC is the critical micelle concentration, and N is the aggregation number in a micelle. Thus an increase in ϕ would lead to an enhanced $[M]$ and hence crack speed provided that N is about the same in both ethylene glycol and water. In ethylene glycol, 10% Igepal CO-630 is close to its CMC. However, one should keep in mind that an Igepal CO-630 molecule contains nine ethylene oxide units, which is an average value, and thus a sharp CMC is not observed in general[32]. This is to say that one might have micelles just below the CMC.

The effect of the amount of the detergent in ethylene glycol on the constant crack speed is shown in *Figure 3*. One can see that the constant crack speed increases with concentration. The increase above the CMC is faster because the aggregation of the molecules leads to more efficient plasticization. *Figure 3* also implies that the crack propagation tests can be used to determine the CMC. However, the extrapolation to zero volume fraction does not go to a speed of zero. This may be due to some impurities in the detergent (practical grade reagent); note that the constant crack speed is zero in pure ethylene glycol.

A proposed mechanism for ESC of polyethylene

Igepal CO-630 is a commercial product and possibly it contains small amounts of nonyl phenol and polyethylene glycol. Also, as stated earlier, the given number of oxyethylene groups is an average number. One suggestion is that these impurities may cause cracking of polyethylene. Nonyl phenol is not soluble in water, but is soluble in the detergent. Thus it is carried within the micelle. The inner part of the micelle contains the hydrocarbon end of the molecule as shown in *Figure 4*. Nonyl phenol has a solubility parameter of 19.3 MPa$^{1/2}$, which is close to that of polyethylene (16.4 MPa$^{1/2}$). According to the manufacturer of Igepal CO-630, there is about 1% of nonyl phenol in the product[33]. Hence a plasticization mechanism would be probable for crack propagation.

We suggest a crack propagation mechanism for environmental stress-cracking of polyethylene in the detergent solutions which subsequentially involves the following:

1 Fibrillar fracture occurs at the crack tip as illustrated in *Figure 5*.

2 The environment is already at the crack tip or wets the fibrils readily with no restriction, and hence the micelles are adsorbed on the fibril surfaces.

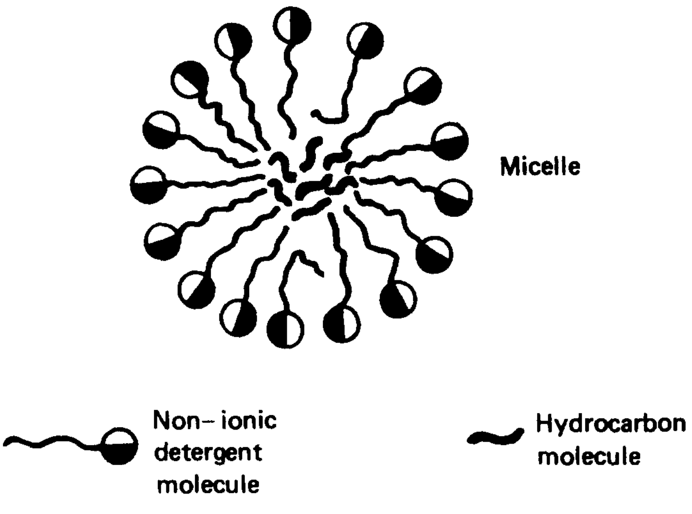

Figure 4 A schematic micelle structure

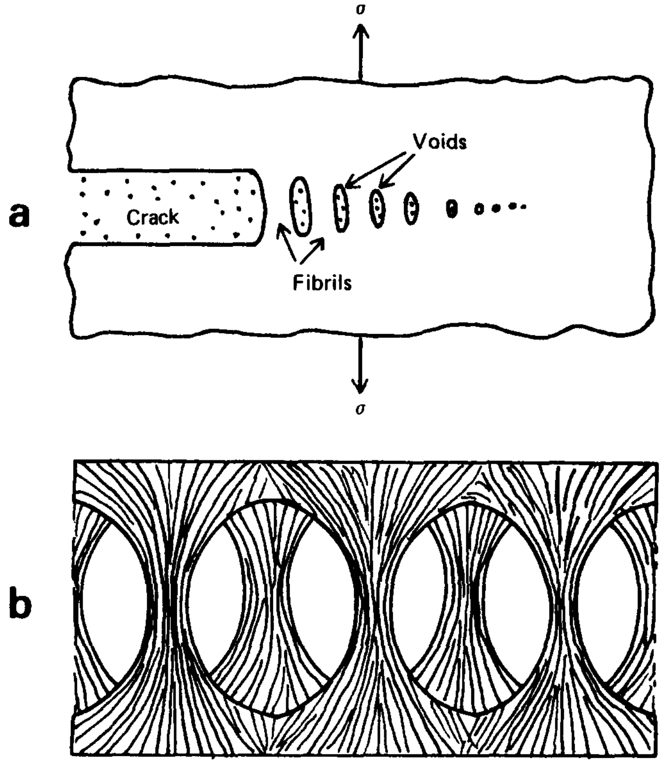

Figure 5 Deformation of the crack tip: (a) fibrillar fracture; (b) schematic fibril structure

3 The aggressive molecules start to diffuse into the material, i.e. the fibrils. However, a problem here is that the diffusion constant into the highly oriented regions of the fibrils is low due to the efficient chain packing[34] and therefore stress-enhanced diffusion may take place at the ends (shoulders) of the fibrils (*Figure 5b*). The shoulders have the most disrupted morphological structure, which helps diffusion and sorption[34]. Isaksen *et al.*[2] and Howard *et al.*[35] have in fact observed that unoriented regions failed first.

4 The plasticized material, which is under stress, flows with subsequent fibril breakdown and, hence, this process leads to crack growth.

We will now examine the steps of the crack growth model. First, the fracture is fibrillar at the crack tip. This is evident from the fracture surface of polyethylene. Second, we consider that the environment is already at the crack tip. Williams *et al.*[4,5] suggest that the crack speed is controlled by the flow properties of the environment at the crack tip. Bubeck[9] showed experimentally that there is a dry craze zone in front of the crack tip and concluded that Williams' model applied. We have proposed earlier that Williams' model is inadequate to describe the crack growth behaviour. Both here, in *Table 1*, and elsewhere[12,13] we have shown that the crack speed is not related to the viscosity. Bubeck's observation of the dry craze zone at the crack tip does not require that flow controls crack growth rate. It is possible that the length of the active, wet craze zone decreases as the detergent concentration increases. It is the fibrils in this region that must break for the crack to extend. Also, in the surfactant solutions, a concentration dependence may be observed if the interface between the surface and solution does not reach equilibrium readily.

To determine whether the mechanism involves plasticization, we have used micelles containing a swelling agent, xylene. It is known that a solubilizate can be carried by a micelle[32]. Depending upon the detergent and solubilizate structure, the solubilizate is located in the inner part or outer part of the micelle. An example is shown in *Figure 4*. The circular part of the detergent molecule is assumed to be the ethylene oxide end of Igepal CO-630 and the long end is nonyl phenol. If one adds a hydrocarbon compound to the solution in water, it will locate itself in the inner part of the micelle since it is not soluble in the water and ethyleneoxy part. For our purpose, we have chosen xylene as the solubilizate since it is a good plasticization agent ($\delta = 18\,\mathrm{MPa}^{1/2}$) for polyethylene. Thus, once the micelles are adsorbed at the crack tip (or on the surface of the fibrils), the diffusion of xylene molecules can take place. This process will cause plasticization of that local area and hence the material under stress will flow (viscous flow). *Table 3* shows the effect of the addition of xylene to the detergent solution. An increase in the amount of xylene increases the constant crack speed. However, it is reasonable to expect that too large an amount of xylene would not give the same effect, as the crack tip would then blunt due to the gross swelling of the specimen[36,37].

In the detergent solutions, the additions of 0.0, 0.2 and 0.5% nonyl phenol to 10% Igepal CO-630 solution increased the constant crack speeds to 0.60, 0.65 and 0.68 mm h^{-1}, respectively. Therefore, it seems plausible that nonyl phenol is one of the impurities that contributes to stress-cracking of polyethylene. Other impurities, as suggested earlier, may be the compounds of low molecular weight polyoxyethylated nonyl phenol which are present in Igepals. This observation may be taken as evidence suggesting that small amounts of nonyl phenol as seen above, and/or other polyethylene oxide adducts in Igepal CO-630, may cause or at least accelerate stress-cracking. Thus we believe that stress-cracking is brought about by plasticization of the stressed regions in the specimen.

In other environments, which do not contain micelles, a similar mechanism is thought to take place. Cracking may not be as efficient as in the case of the micellar solutions. In the latter, the localized plasticization is more profound because of the larger amounts of the plasticizer molecules in the micelles. As we discussed earlier, the solubility parameter of the environment also affects the cracking behaviour. In pure liquids, such as Igepals, the formation of the aggressive interface between the fibril surface and the liquid would not be a problem since the liquid had only one phase and hence a faster crack speed would be obtained.

CONCLUSIONS

The following conclusions can be drawn from our studies:

1 Surface tension of the environment does not affect the cracking behaviour.

Table 3 Effect of xylene in detergent solutions on constant crack speed

Environment	$\dot{c}$ (mm h^{-1})
5% CO-630	0.40
5% CO-630+0.17% xylene	0.51
5% CO-630+0.50% xylene	0.59

2 The viscosity of the environment does not control the K_I-independent crack speed.

3 The solubility parameter of the environment appears to affect the stress-cracking behaviour.

4 The solution structure of the environment is found to be important. Micellar solutions are more effective in stress-cracking of polyethylene. The crack speed is thought to be a function of the micelle concentration in the environment.

5 The stress-cracking mechanism of polyethylene involves a plasticization phenomenon. The mechanism is probably controlled by the viscous flow rate of the swollen polymer under stress, by the diffusion constant of the environment into the polymer, and by the rate of formation of the interface between the fibril surface and the liquid.

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