1. Introduction

1.1 The Definition of Environmental Stress Cracking

Service life is always one of the important factors people will consider when picking the right material. People used to use a lot of metals, and nowadays plastics are developed so much that they have replaced metals to a large extend. So the failure problems of plastics get more concerns than ever. Among all the failures happened on plastics, 15%-20% are caused by environmental stress cracking [1]. It is very interesting to both chemists and physicists as it involves, stress enhanced absorption, permeation, thermodynamics of mixtures, local yielding, cavitations, fibrillation and fracture. [2]

Environmental Stress Cracking (ESC) in plastics is the failure of plastics due to the action of both stress and surface-active substances (known as stress cracking agents). Stress can be external or internal stress and these surface-active agents can be alcohols, soaps, dyes, agents containing moisture. [1,2,5] The source of the stress is often unavoidably processed in during moulding. So even there's no applied external stress, ESC is still possible. The source of fluid contact is sometimes primary, but the existing of adhesives, paints, lubricants and cleaning agents are the most often reasons[1,3,4].

ESC is not a chemical reaction between the polymer and the active environment even though it results from the interaction of the polymer with certain chemicals. The stress-cracking agents accelerate the process of macroscopic brittle-crack formation but not in a way of chemical degradation of polymer [5].

1.2 The Cause of ESC

When polymer subjects to a high tensile force in the temperature above glass transition temperature (Tg), the material will reach a yielding point before ductile fracture happens. The time to fracture decreases with the increasing of tensile force. How about the tensile force is low enough that no locally yielded sites generate? What will be the change in the material?

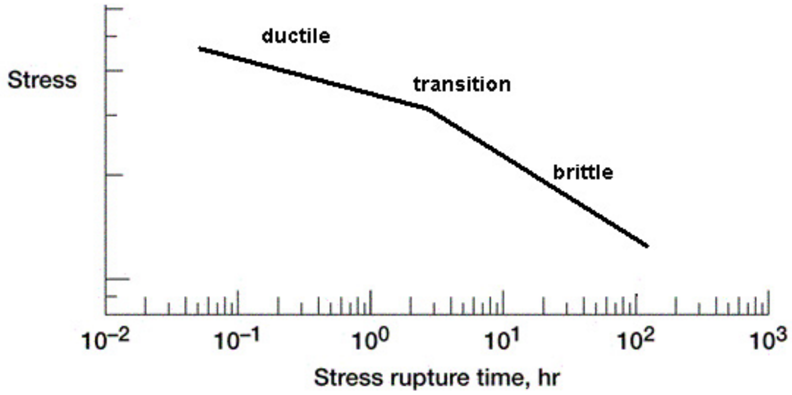

Fig 1.1 Time dependent creep ruptures strength of an amorphous plastic showing ductile to brittle transition

From the figure above, we can see, when the material exposes to a low force for a sufficiently long time, the material will have brittle fracture in the last. Many factors can accelerate this procedure, for example higher temperature, dynamic fatigue and contact with specific fluids (ESC)[6].

The fracture mechanism under high stress and low stress is different:

When material is subject to high stress, a high density of locally yielded sites will be generated and grow, when the yielded sites are big enough to merge with each other, the sites become a big one and eventual macroscopic yield failure happens. However, when material is subject to low stress, only a few sites will be micro-yielded and grow slowly. The chance to meet the neighbors and coalesce is very little. But these yielded zones cavitate and fibrillate to become crazes, which eventually reach a critical length for fast crack. The absorption of fluid plasticizes polymer and reduces yield strength [2].

Another explanation about these two fracture mechanisms is “tie molecules”. In amorphous polymers, crack formation due to ESC begins with craze formation. Highly drawn fibrils hold together these craze regions and bridge the micro-cracks and prevent their propagation and coalescence; For semi-crystalline polymers, tie molecules connect the crystalline laminas through the amorphous phase [5]. The tie molecules play an important role in the mechanical properties of the polymer, since it is the bridge for transmission of load. Stress cracking agents lower the cohesive forces that maintain the tie molecules between the crystalline laminas. Thus cracking is initiated at stress values lower than the critical stress level of the material [5].

The fracture mechanism for a polymer with lamellae crystalline structure, e.g. Polyethylene, is shown in figure 1.2 – 1.4.

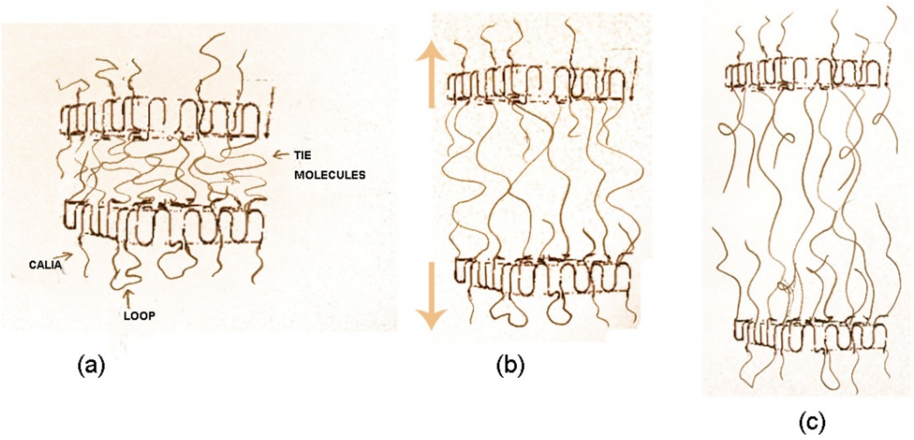

Fig 1.2 Initial steps in the deformation of polyethylene [7]

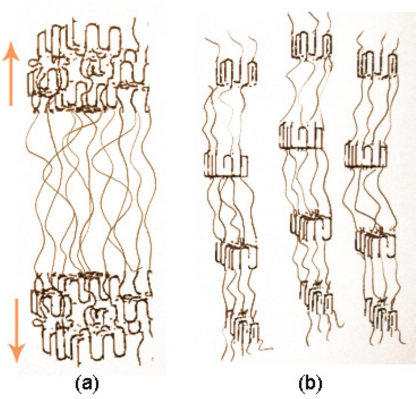

Fig 1.3 Steps in the ductile deformation of polyethylene [7]

There are three different kinds of intercrystalline materials in a semi crystalline polymer: cilia are chains suspended from the end of a crystalline chain while loose loops are chains begin and end in the same lamellae; the third kind is tie molecules, which are chains begin and end in adjacent lamellae.

When a large tensile load is applied as shown in the arrow direction in Fig1.2 (b), some tie molecules cannot be pulled out any more (Fig1.2(c)) and lamellas break up into small units as shown in Fig1.3(b). For a small tensile load, the large-scale fiber pullout is not attained, the loading situation will stay like Fig1.2(b) for a long time, but after a critical time, most of tie molecules disentangle from the matrix and load cannot be supported by the remaining few tie molecules, thus happens the brittle fracture in Fig1.4.

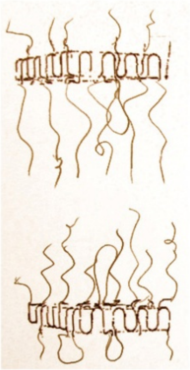

Fig 1.4 Final step in the brittle failure of polyethylene [7]

Any stress cracking agent will help the tie molecules to be pulled out from the lamellae [5].

1.3 The Prediction of ESC

Now there’s still no exactly effective way to calculate or predict the influence of a given fluid on a certain polymer.[2] Some kinds of severe ESC fluid can be absorbed by polymer very quickly, and the fast decreasing of hardness and strength would cause a fast fracture. Not all the liquids have this significant impact even though almost every kinds of fluid are more affinitive than air.

As there are tens of thousands of fluids in the world, as well as thousands of plastics, how can we know if this plastic is safe to use in contact with a particular fluid? But as no system way is found to calculate the impact, what we can do is prediction or testing.

There're some generalizations made by scientists who work on this area for a long time. Normally amorphous thermoplastics or thermoplastics in their amorphous state are more prone to ESC than the semi-crystalline state or thermoset. As the structure of the crystalline is more packed, not like the loose structure in the amorphous phase. So fluid cannot go into crystalline as easy as amorphous phase. For the thermoset, as it's cross-linked between molecular chains, the diffusion of fluid also meets barrier. Another rule is about hydrogen bonding. More details about hydrogen bonding will be discussed later in this chapter. D.Wright[2] found that fluids with modest hydrogen bonding are most likely to be severe or moderate stress cracking agents. But also in Bistra'spaper[5], she indicated that fluids with a low hydrogen bonding are prone to be severe or moderate ESC agents. In Isaksen's early works[8], he carried out experiments on many fluids tried to correlate fluids parameters to ESC, but found no close relation between hydrogen bonding and ESC. It's possible this rule only works in some kinds of polymers but maybe not for all the plastics.

Fluids with a high molar volume have fewer possibilities to be severe stress cracking agents [2]. Because high molar volume leads to high viscosity and it's not easy to move freely with a high viscosity. Similar rule is plastics with high melt flow index suffer from reduced ESC resistance[2], as it's not easy for the movement of fluid molecules in polymer chains with large molecular weight.

Amorphous plastics are most susceptible to ESC at temperatures that approach their Tg[2]. This due to the increased free volume in polymers as Tg is approached, which facilitates fluid permeation into the polymer.

Early research indicated total solubility parameter of the fluid was the most critical factor. This parameter is from the total cohesion energy of the substance. If the polymer and fluid have similar total solubility parameter, then the polymer tends to absorb more fluid than the one doesn't have a similar total solubility parameter. This theory only works well with the solubility parameter less than 10, it's not able to predict the performance between polymer and fluid which have a total solubility parameter more than 10[2].

With more research on solubility parameter, scientists found the total cohesion energy of a liquid, E, can be divided into at least three separate parts either by experiment or by calculation[9]. In the three-parameter Hanson approach, these parts quantitatively describe the non-polar (atomic), dispersion interactions, E_D, permanent dipole-permanent dipole (molecular) interactions, E_P, and the hydrogen-bonding (molecular) interactions, E_H.

$$E = E_D + E_P + E_H \tag{1}$$

Dividing this equation by the molar volume, V, gives the respective Hansen cohesion energy (solubility) parameters.

$$E/V = E_D/V + E_P/V + E_H/V \tag{2}$$

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{3}$$

The total cohesion energy divided by the molar volume is the total cohesion energy density. The square room of this is the Hildebrand total solubility parameter, δ. The SI units for these are $MPa^{1/2}$.

Now there're more models used to predict this ESC phenomenon. Isaksen[8] used polar parameter to predict ESC for HDPE and he established a reasonable correlation between equilibrium absorption and time to fail together with polar solubility parameter. In his study, polyethylene, which has the lowest polarity of all polymers, is the most rapidly attacked by fluids of (similar) low polarity.

Hansen and Just [10] reported the results that confirm ESC phenomena in plastics depend on the size and shape of the test liquid's molecules as well as their Hansen Solubility Parameter (HSP) relative to those of the polymer.

Peter J. Walsh and A.J. Lesser [11] probed a hypothesis for predicting a critical stress associated with of ESC. An experimental technical involving contact angle measurements of a sessile drop as function of stress is used. But they still need further experiments to look at the effect of contact angle on ESC.

1.4 Assessment by Testing

There are a variety of test methods available for assessing the ESCR of thermoplastics. Mainly they are constant strain or constant stress testing. But constant strain test is always less severe than the equivalent test involving the application of a constant load because the stress in the sample induced by constant stain will decay with time due to stress relaxation.

1.4.1 Constant Strain Tests

Constant strain tests are most commonly used because they are cheap to carry out. The problem for this kind of tests is stress relaxation mentioned in the paragraph above.

1.4.4.1 Bell Telephone Test (BTT) for Flexible Materials

In the test, a strip of the material is bent. The maximum surface strain is given by:

$$\varepsilon = t/\,(w-t) \qquad (4)$$

Where w is the width of the holder and t is the material thickness. This method is quite crude and cheap and only really used for quality control testing of polyethylene.[2]

1.4.2 Constant Stress Tests

1.4.2.1 Single Cantilever for Rigid Materials

It's a simple method without dedicated investment. A strip of the material is clamped to the edge of a sturdy bench. The fluid is applied to the upper surface. As a control it is recommended that the same configuration be run concurrently in the absence of the fluid. [2]

1.4.2.2 Tensile Creep Test

A high temperature tensile creep rupture testing device which is applicable to both rigid and flexible materials was developed by Rapra. [2] It's quite similar to the common test at constant load. It involves application of a tensile stress and the recording of the time to rupture. Even though the name is high temperature creep testing device, it's also possible to work in normal temperature. This is the device on which the creep tests in this paper carry out.

1.5 Aim of the Project

The aim of this project is to investigate the properties of a POE hose, especially the environmental stress cracking resistance property. And if there's any relatively simple way to predict if the hose can be used to contain the given fluid.

2. Experimental

2.1 Materials

In this chapter, different tests are explained. All the materials used in the following tests were taken from the POE hose (SPX DN13) (figure 2.1), which is a commercial product of LK Pex. The raw material used for the hose was POE. It is a kind of thermo elastomer made by in-situ polymerization of ethylene and octene in metallocene catalyst. The soft chain structure of octene and crystallized ethylene chain make POE not only stiff but also easy to process. The saturated structure makes it excellent ageing-resistant material. Now it's widely used in cable industry, automotive industry as well as household appliance industry.

Fig 2.1 Photo of a specimen cut from the hose

2.2 Apparatus

2.2.1 Tensile Test

The aim of the tensile test is to get the stress and strain for the hose to break in 4 kinds of liquids. They were xylene, acetic acid, Igepal CO-630 and water.

Tensile test was carried out in the Rheology Lab, Department of Materials and Manufacturing Technology, Chalmers University of Technology. The model of the tensile test machine was ZWICK. LK Pex modified the grip of the tensile test device in order to fit the shape of hose. Figure 2.2 is a photo of tensile test device (left) and a close look of the new grip (right). For the new grip, it's clear to see how it works in figure 2.3. There are two pieces of sample holders holding the ring. When the grips go upwards, the upper piece of sample holder will also go upwards and thus the elongation of the ring.

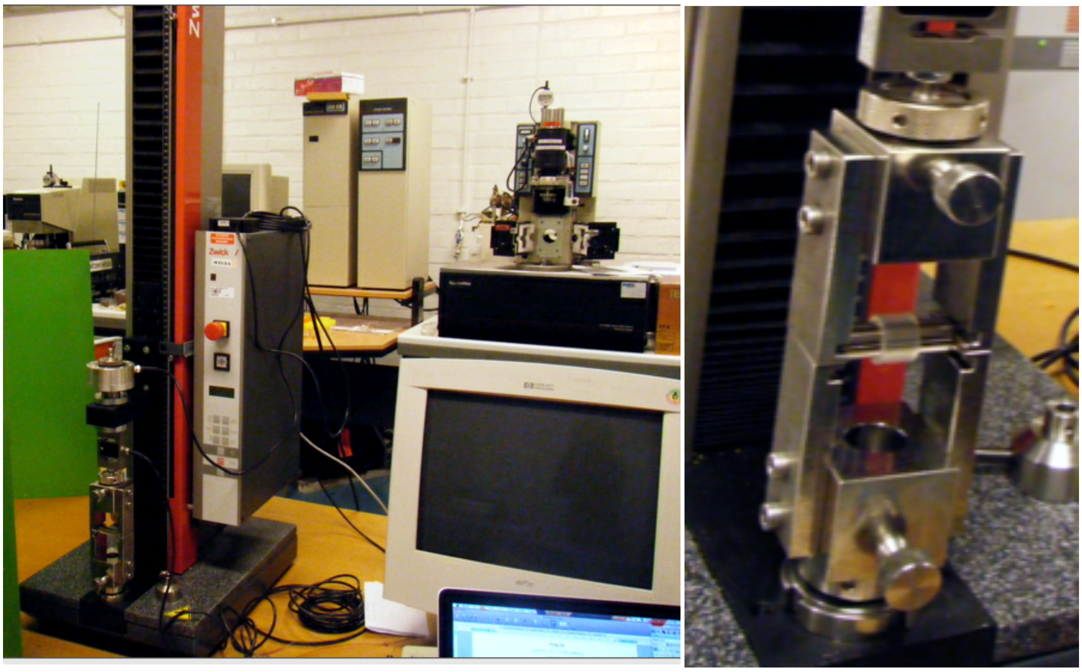

Fig 2.2 Photo of tensile test machine and a close look of new grip

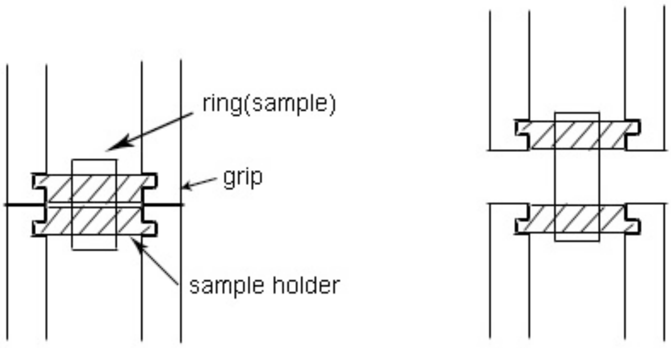

Fig 2.3 Sketch of the grips before test (left), in the test (right)

Here is the process for the experiment: a section of hose (ring) with a length of 12 mm (Fig 2.1) was cut from a long hose and fixed in the machine as shown in photo. The crosshead can travel with a speed preset on the software. Then the crosshead would drive the movement of grips. So the hose got elongation. Once the crosshead began to move, one kind of liquid was applied on the outer surface of the ring using a burette. There was a hole designed in the bottom base of the device to accept the liquid from the hose for the sake of protecting the device. To assure that there's always liquid on the ring, the liquid should be applied on the surface very often until the break happened.

The 2000N load cell was used in the experiment and speed set for crosshead was 20mm/min for the first minute and 2mm/min later on.

Tensile tests were carried out with the dry ring and also on the rings with four different agents. They were xylene, acetic acid, Igepal CO-630 and water. Three to four times of repetitions were done for every different liquid.

2.2.2 Creep Test

The rig for the creep test was designed by LK Pex. It's a developed version of tensile creep rupture rig from Rapra[2]. The software used here was Creep Software EC 04 from the company Elastocon AB. A photo of the tensile creep test rig is shown in figure 2.4.

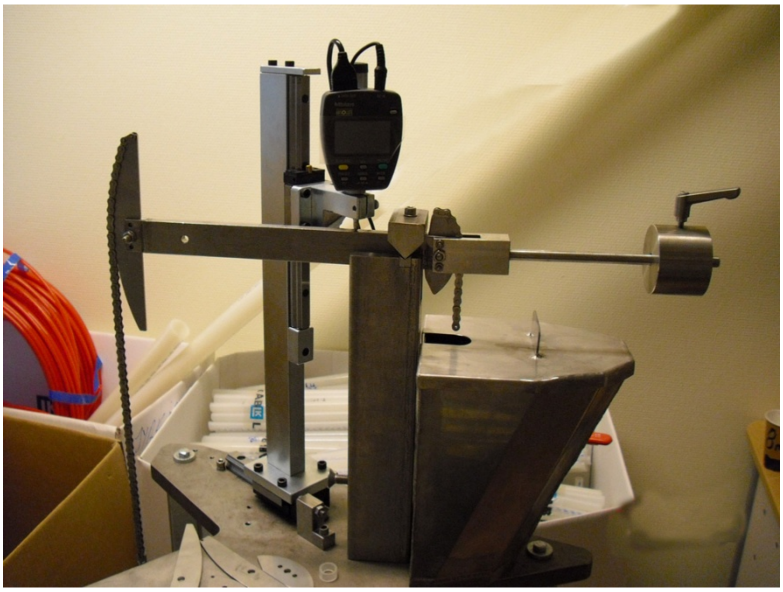

Fig2.4 Photo of creep test machine which is developed from Rapra tensile creep rupture rig

When compare this rig with the one from Rapra, there are several advantages for the new rig designed by the company. First a digital device was installed to measure and record the elongation of specimen. Secondly, the special curve design of the link between the lever and movable head for holding the sample allows more accurate recording of the sample elongation. Also the design of the solvent tank makes it easier to carry out creep tests with several different challenging liquids, as it's easier to change the liquid and safer for the operator.

The validation of the new rig was done by comparing the elongation figure in the digital device with the figure got from a vernier caliper. The result showed that most of the time the figures shown in device were exactly the same as what got from vernier caliper. Even there was difference some times, the difference was small enough to neglect.

By doing the test, first to do was balance the lever with the left side and right side. The left side had the weight of the empty weight pan, weight of pointer from digital gauge and also the self-weight of left side lever. The right side had the weight of one of sample holder, the upper part of crosshead, the weight of right side lever and the counter balance. The lever can be equilibrious by moving the counter balance. After the lever was balanced, the similar specimen was cut as the one in the tensile test, and then dimensions were measured. The specimen was fixed on the sample holder. The sample holder was then placed in the socket of the crosshead. Pour the liquid in the tank and add the weights to the weight pan as soon as finishing pouring the liquid. The time interval for the two procedures should be short because if it delayed, it's possible some of the liquids can be plasticizer for polymer, the property of polymer would change as well as the creep feature.

In the creep tests, the same liquids as in the tensile test were used. They were xylene, acetic acid, Igepal CO-630 and water.

Several pre-tests were done before the formal tests to decide how much weight should be put on the weight pan. The weight should not be too large, otherwise the elongation may exceed the measuring range of the rig and also a large force may not lead to environmental stress cracking due to the generation of a high density of local yielded sites. Meanwhile a too small weight is also not preferred as it may take a longer time for the plastic to have feature changes.

After several pre-tests, a weight of 2.5 kg to 3.5 kg was chosen. And for the sake of time limit of the project, most of the creep tests were stopped in 5 days or when there was an obvious change in the strain rate.

Then came the analysis of data in the last. However, as the POE hose specimen can elongate as much as 10 times of the original length before breaking, it's out of the rig's record ability. Also an elongation of 10 times is not interested for the project as in the real service condition a hose will never elongate so much. So in the test, only a 100% elongation was recorded. And then the strain rate during elongation was analyzed.

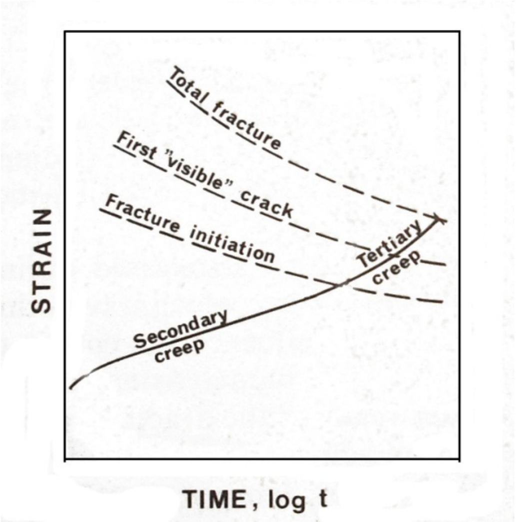

Fig 2.5 A strain logt sketch from uniaxial creep rupture in glass fiber/polyester.[12]

From figure 2.5 we can see, a polymer has three different stages of elongation during the creep test. The first stage is the elastic elongation (not shown in the figure). The secondary creep is a relatively flat stage. After that comes the tertiary creep, which is also the initiation of fracture.[12] In the test, an earlier appearance of the third stage is judged as a quicker fracture initiation.

2.2.3 Swollen Test

The hose we used in the experiment was cross-linked by 0.5% peroxide. The degree of cross-linking is a very important aspect in the characterization of polyethylene based polymers.

The way to carry out swollen test was a classic way first used by P.J. Phllips and W.S. Lambert using boiling xylene [13,14]. Figure 2.6 is the photo of swollen test device.

Xylene was supplied by Fisher Scientific, analytical reagent grade.

Fig 2.6 Photo of the device for swollen test

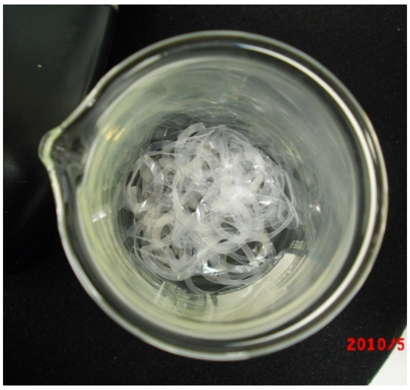

Fig 2.7 Photo of thin films from POE hose for swollen test

Thin films[15] (figure 2.7) from the POE hose of known weight were immersed in boiling xylene (138 ^{0}C – 140 ^{0}C) in a stainless-steel basket for 72 hours to allow the extracting of uncross-linked polymer. Afterwards the basket with the remaining part of the film was transferred into a xylene-containing flask and held at 110^0C oil-bath for 24 hours. This was for the swelling of the cross-linked matrix. The sample was transferred to a clean dry tared weighing bottle for weighing without delay. Here it should be very careful as the sample should not be squeezed and the transfer of specimen should be made quickly. The surfaces should not be subjected to excess blowing. After recording the weight in swollen state, the sample with opened weighing bottle was transferred to a vaccum oven (Heraeus Vacutherm, Thermo Scientific) at 110^0C for 24 hours. Two groups of POE hose made in different times were used in the experiments with 3 repetitions in each group. Estimates of percentage of extractables were obtained using the weight loss of POE. The molecular weight between crosslinks was estimated using the Flory-Rehner equation as follows[14,16,17]:

$$V_2 = (W_2/\rho_2)/[W_2/\rho_2+(W_1-W_0)/\rho_1] \quad (5)$$

$$v = -[\ln(1-V_2)+V_2+\chi V_2^2]/V_1(V_2^{1/3}-V_2/2) \quad (6)$$

$$Mc = \rho_2/v \quad (7)$$

Where v is the effective network chain density,V_2 is the volume percentage of polymer in a swollen sample, V_1 is the molar volume of solvent, χ is the Flory-Huggins polymer/solvent interaction parameter, W_0 is the weight of polymer before swelling, W_1 is the weight of polymer after swelling, W_2 is the weight of polymer after vacuum drying, ρ_1 is the density of solvent, and ρ_2 is the density of polymer. In the calculation of MW, the values of V_1 and χ are 136 mL/mol and 0.37, respectively.[14]

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2.2.4 Density test

Density test was done in SP (Swedish National Testing and Research Institute) Gothenburg. Figure 2.8 is the photo of the device for density measurement.

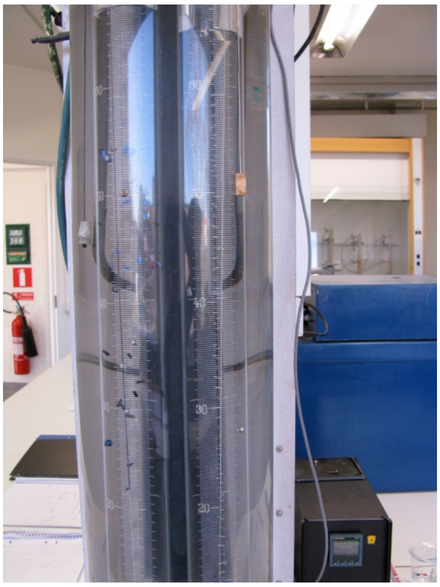


Fig 2.8 Density Gradient Column in SP, Gothenburg

First prepare the liquid in the column. Fill a certain amount of 2-propanol in a flask with a thin pipe in the bottom part. The thin pipe goes down until the bottom of the column. Add water to the flask with a certain slow speed. Because of gravity, the liquid in the flask will go to the column through the thin pipe. As there's difference in the density of water and 2-propanol, there will be a density gradient of the liquids in the column. It takes one day to finish filling the column. Let the liquid stay still for 1-2 days to assure no bubbles in the column. Now there's a linear relationship between the position of the liquid and density in the middle part of the column. Two small floats with pre-known densities (907.3 kg/m^3 and 898.5 kg/m^3) are put in the liquids. Then the densities of the liquids in the position of the floats could be known. So when a sample with unknown density was put in the column and stay still between the two floats, the density of the sample can be estimated.

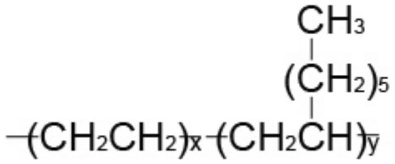
3. Results and Discussion

3.1 Calculation of the Total Solubility Parameter of POE

The cohesive energy density or solubility parameter of polymers cannot be calculated via the heat of vaporization, because the energy for separating the molecular chains is always larger than breaking down the polymer into small molecules. An indirect method is to find the best solvents for the polymer. The solubility parameters of the polymer would then equal that of the solvents. Alternatively the molar attraction constants (G) for sub-molecular groups may be used to provide a calculated value[18]. Values for groups in POE are given below:

$-CH_2-$ = 133; $-CH-$ = 28; $-CH_3$ = 214;

For POE used in the experiment, the percentage of ethylene and octene are treated as commercial secret by the supplier. The structure of this polymer is:



$$-(CH_2CH_2)_x-(CH_2\overset{\substack{CH_3\\|\\(CH_2)_5\\|}}{CH})_y$$

$$\delta = d \cdot G/M \qquad (8)$$

Where M is the molecular weight of a repeat unit (28x+112y) and d is the density (0.909 g/cm^3, density test will be presented later in this article).

For POE used in this test,

$$G = (133+133) \cdot x + (133+28+133 \cdot 5+214) \cdot y = 266x+1040y$$

$$G/M = ()/(28x+112y) = 9.5 - y/(x+4y) = 9.5 - 1/(x/y+4)$$

$$G/M_{min} = 9.5-0.25 = 9.25 \quad (\text{when } x/y \to 0)$$

$G/M_{max} = 9.5-0 = 9.5$ (when $x/y \to \infty$)

$\delta_{min} = d \bullet (G/M)_{min} = 0.909 \bullet 9.25 = 8.408\ (cal/cm^3)^{1/2} = 17.24\ MPa^{1/2}$

$\delta_{max} = d \bullet (G/M)_{max} = 0.909 \bullet 9.5 = 8.636\ (cal/cm^3)^{1/2} = 17.70\ MPa^{1/2}$

So the total solubility parameter for POE is between 17.24 and 17.70 $MPa^{1/2}$.

As polarity comes from the misalignment of positive electric charge center and negative electric charge center, normally molecules with symmetrical structure have a low polarity.

The structure of the main chain of POE is very regular and symmetrical. The side group $–(CH_2)_5CH_3$ has a very low polarity, plus normally polymer has a long chain, side group would stay on the two sides of main chain, which causes an even lower polarity.

So, POE has a very low polar solubility parameter.

3.2 Tensile test

Before showing the result of tensile test, here is some explanation of calculation of stress and strain.

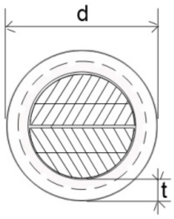


Fig. 3.1 Cross-section view of initial ring on the sample holder

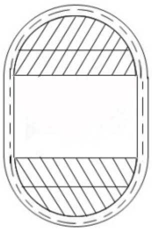


Fig 3.2 Cross-section view of ring and sample holder during a test

The length of the dash line in the schematic is the length of ring used in calculation. As the ring has an initial thickness of around 2.2 mm, during the test, ring was becoming thinner and thinner, the actual thickness at a certain time cannot be known.

After some measurements of thickness during the test and also for the sake of an easy calculation, following assumption is made:

When the crosshead travels between 0-10 mm, the length of the ring which contacts the ring holder is the initial ring length which is 46.472 mm.

When it goes between 10-20 mm, the length is 46, when it goes between 20 - 30 mm, the length is 45; and the like. At last before the break, as the ring is so thin that the thickness can be neglected. The length of ring which contacts the holder is 40.3.

$\sigma = F/A_0$ (9)

$A_0 = 2 \bullet t \bullet w$ (10)

w is the width of the ring;

$\varepsilon = (l-l_0)/l_0$ (11)

l_0 is the initial length of the ring; l is the length of ring at a certain time;

True stress $\sigma_t = \sigma \bullet (1+e)$; (12)

True strain $\varepsilon_t = \ln(1+e)$ (13)

Table 3.1 shows the result of the different test groups in tensile test. The result shows in Table 3.1 is the mean value of 4-5 repetitions in the corresponding group. As mean values, they can better represent the property of material but stress-strain plot of material from beginning of the test to the end cannot be gained from the mean value. So Table 3.2 shows the result of typical run in each group, which has the closest value as the mean value. The further analysis is based on these typical tests.

Table 3.1 Result of tensile test

Sample	Stress(MPa)	Strain	True stress(MPa)	True strain
Dry specimen	23.21	5.37	147.87	1.85
Specimen with water	23.40	5.26	146.43	1.83
Specimen with xylene	18.79	4.95	111.73	1.78
Specimen with acetic acid	20.92	5.08	127.12	1.80
Specimen with Igepal CO-630	23.15	5.30	145.80	1.84

Table 3.2 Result of typical run in each test group

Sample	Stress(MPa)	Strain	True stress(MPa)	True strain
Dry specimen	22.99	5.44	148.12	1.86
Specimen with water	24.17	5.35	153.40	1.84
Specimen with xylene	18.14	4.86	106.27	1.77
Specimen with acetic acid	20.47	5.04	123.61	1.80
Specimen with Igepal CO-630	22.90	5.32	144.67	1.84

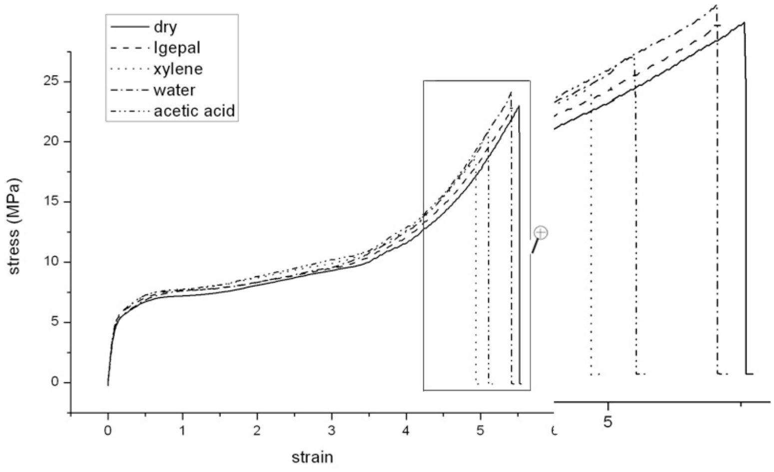


Fig 3.3 Stress-strain chart of samples in different agents

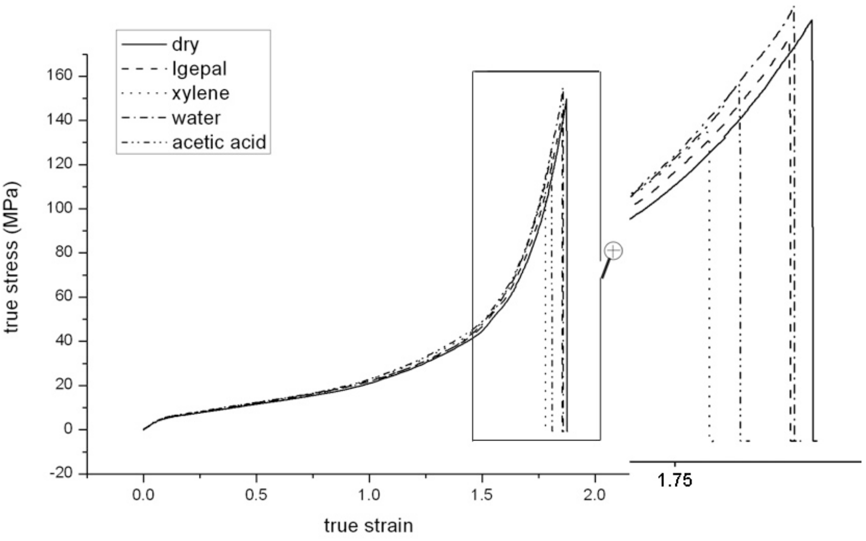


Fig 3.4 True stress-true strain chart of samples in different agents

From these figures, we can see:

1. No big difference is shown between the dry samples and samples in water or Igepal.
2. Acetic acid and xylene have quite big influence on the ring. The stress to break decreases 25% for sample in xylene compared with dry sample. While for acetic acid, it is 14%. The decreasing is large enough to convince people the impact of xylene and acetic acid on POE hose.

Igepal CO-630 is the most commonly used stress cracking agent for evaluating polyethylene or ethylene copolymer because it has a solubility parameter of 20MPa which is not far from PE's 16.4MPa or POE's 17MPa. But here there was little influence of Igepal CO-630 on tensile test. One of the reason is Igepal CO-630 has a relatively high molar volume (600cm^3/mol), the degree of absorption is low under zero stress, but increases with increasing stress.[2] But experiments also show that there is little difference between Igepal and air in the rupture test which is less than 15 hours. This means Igepal is a slow runner. Tensile test was less than 20min for each specimen. This explains why Igepal has little influence here.

3.3 Creep test

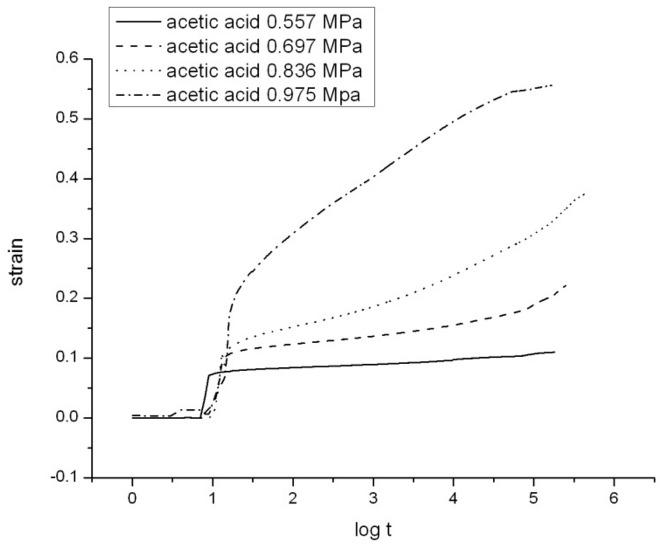


Fig 3.5 Strain-logt plot of POE in acetic acid with a range of loading

There are some small fluctuation in the beginning of the curves, it's because weight pan was held by hand when loading these weights on the pan. Small movement of the weight pan caused by hand was recorded.

From figure 3.5 we can see an earlier third stage comes with a relative large loading, which means an earlier fracture will happen. What can also be observed is that the curve for stress of 0.975 MPa (with a loading of 3.5kg) is different from those with smaller loadings. It doesn't have a flat stage. Possible because this loading is large enough that the equilibrium stage of the external force and force from tie molecules quickly passed.

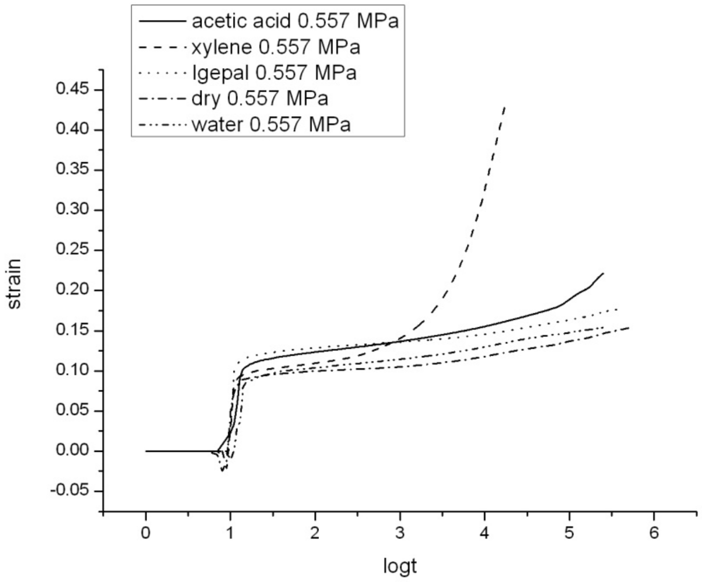


Fig 3.6 Strain-logt plot of POE in different fluids with a constant stress of 0.557 MPa (with a loading of 2.5kg)

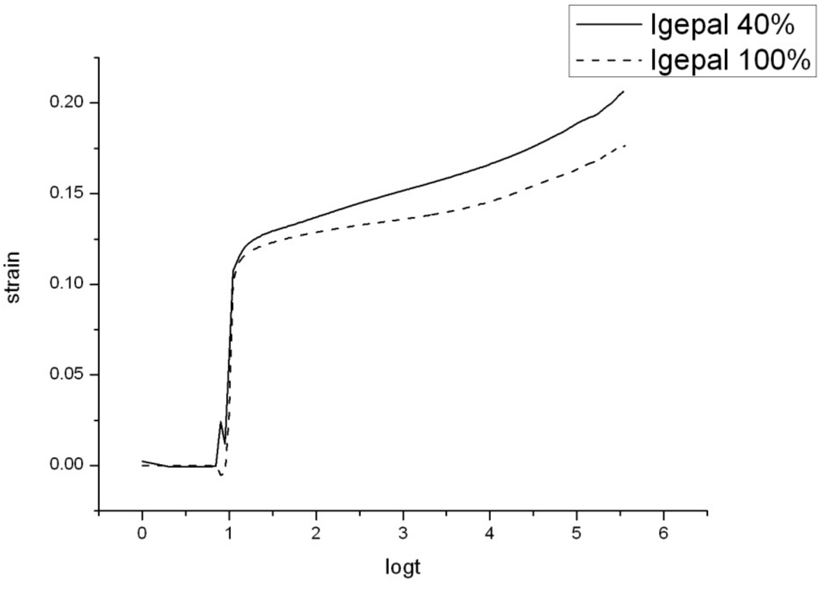


Fig 3.7 Strain-logt plot of Igepal in concentration of 100% and 40% with a constant stress of 0.557 MPa (with a loading of 2.5kg)

From the above two figures, we can see:

Almost no influence was brought by water compared with sample in air. They have same modulus as well as the shape and trend of the curves.

Igepal CO-630 has a smaller modulus compared with dry sample, but in the limited time recorded in the experiment, still there's no big difference of the shape of the curve.

Acetic acid shows a third stage after about 15 hours.

Obviously xylene is the most severe ESC agent among all the fluids shown here. It has a third stage in less than 8 hours. And from the observation of sample after creep test, xylene was the fluid POE absorbed most.

Table 3.3 HSP of four fluids in the test.[9]

Fluids	δ_D	δ_P	δ_H	δ_T
Xylene	17.8	0-1	3.1	18
Acetic acid	14.5	8	13.5	21.3
Igepal CO-630	/	Appr. 10	/	20
Water	15.5	16	42.4	47.9

POE has a total solubility parameter between 17.24 and 17.70, and a polar solubility parameter closes to 0 and hydrogen bonding closes to 0. As early work[8]was done by other scientists that they correlated polar solubility parameter to ESC and got a good simulation on HDPE. From the data here, xylene has the closest polar solubility parameter and it is the most severe ESC agent, but xylene also has the closest total solubility parameter. As lack of more data to support, it cannot say we have the same conclusion here.

But we can see from this group of data, that total solubility parameter has a same sequence as the severity of ESC in the range of fluids which have similar molar volume. Xylene has the closest total solubility parameter, follows acetic acid as well as Igepal CO-630, and last comes water which has a largest difference in total solubility parameter.

From figure 3.7 we can see molar volume is very important factor.

However, because of the measuring range of the rig which is less than 25mm, while the elongation of POE to break is around 220mm, it's not possible to record ring's time to rupture. For this reason, a figure like figure 1.1 cannot be obtained from the creep tests here. Also if a ductile to brittle transition existing for POE cannot be judged. It's difficult to compare the result with other literatures, e.g. the influence of crystallinity or cross linking degree on ESC, as most of the papers evaluate ESC by rupture time of material.

The result from creep test is similar with the result got from tensile test. Then it's possible to have the assumption that tensile test can predict ESC of chemical agents with a small molar volume. The time for tensile test is much less than that of creep test. But for these small molecules, they can immerse in polymer with less hindrance. Even the time is short, they can still impact the property like chain entanglement of polymer.

3.4 Swollen test

Table 3.4 Percentage of extractables, molecular weight between crosslinks and average chain length between crosslinks of POE hose

Specimen nr.	Extractables (%)	M_w between crosslinks	Average CH_2 units
1	38.3	651.9	47
2	39.1	656.2	47
3	37.4	649.5	46
4	39.2	648.5	46
5	38.7	652.3	47
6	38.4	649.2	46

So the molecular weight between crosslinks is around 650 g/mol, and average CH_2 units between crosslinks are 46-47.

Compared with the work done by Liao[19], they did swollen test on another grade of POE and with the same procedure, but the result was very different from the result we get here. The average molecular weight between crosslinks is 4108 g/mol for 0.5 wt% crosslinking agent and the extractable rate is 20.8%. And the POE they used was Engage 8003 from Dow Chemical and the density is 0.885 g/cm^3 which has a lower density than the POE used here. It's possible it's not a linear polymer and has more branch than the polymer we use. Branch could increase the molecular weight between crosslinks a lot. Another reason could be the different use of crosslinking agents.

3.5 Density Test

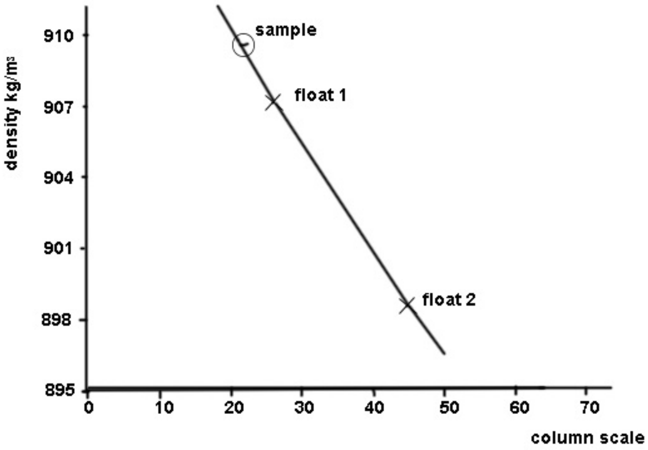


Fig 3.8 Result of gradient column test

Read from the figure we can see the density of the POE hose is 0.909 g/cm^3.The densities of amorphous phase and crystalline phase are 0.852 g/cm^3 and 1.008 g/cm^3, respectively.

As degree of crystallinity $f_c = (\rho - \rho_a)/(\rho_c - \rho_a)$ (14)

$f_c = 36.5\%$

4. Conclusion

In all the four fluids tested on POE, xylene has the most severe ESC impact on POE, followed by acetic acid and Igepal CO-630, while water almost has no impact on POE. Compare with the ESC prediction models mentioned in the beginning of the article, total solubility parameter fits best with the result. That is, for the agents tested on POE, the more closer are the total solubility parameter of the agent and that of the material (POE), the more severe effect on ESC. Tensile test were in some agreement with the creep tests. Within in range of agents tested on POE, tensile tests were helpful towards investigating the severity of ESC but limited to fluids having a small molar volume.

Recommendations for Further Research

Creep test on more fluids can be carried out in the future. For example fluids with a close total solubility parameter but different polar solubility parameter or close polar solubility parameter but different total solubility parameter compared with POE. Also POE with different grades can be tested to see how the relation goes with density and molecular weight between cross links with ESCR.

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