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Environmental Stress Crack Resistance of Polyethylene Pipe Materials

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Abstract

Slow crack growth is a phenomenon that can occur in most plastics. Resistance to this type of cracking is critical to insure materials intended for the distribution of fuel gas offer high durability with adequate long-term strength.

This paper will define one particular case of slow crack growth that is widely encountered, called Environmental Stress Cracking Resistance (ESCR). Explanations as to why resistance to slow crack growth is an important resin property will also be given.

An overview will be provided of the various properties which influence ESCR, both in the polymer resins as well as in the test methods themselves. This paper will also describe some of the tests used to measure slow crack growth in polyethylene gas pipe products in the United States and Europe.

Introduction to Environmental Stress Cracking and ESCR

Over the past decade, high density polyethylene (HDPE) materials have improved significantly and now meet more stringent performance standards. Some performance evaluation tests that once took days to run now take months with today's resins. One such performance criteria is Environmental Stress Crack Resistance (ESCR). Because standard test methods for measuring ESCR on plastics take such a long time, sometimes months, the quality of the material is judged acceptable if the failure time exceeds a certain limit. Many times, the test is terminated before an absolute fracture time is determined. Due to these long testing times, new tests and standards have been developed to differentiate these improved materials more easily.

Why is Stress Cracking Important

Because stress cracking results in the breakdown or failure of a plastic material, a plastic part needs to endure its entire designed life before it fails. For polyethylene, this may range from several months for a milk or juice bottle to several decades for a natural gas pipeline or an automotive fuel tank.

In the late 1940's Western Electric was encountering occasional cracking in the low density polyethylene used to jacket wire cables. Bell Labs was asked to investigate the cracking and they found the cause to be from the use of lubricating soaps used during installation. Through this research the Bell Labs Bent Strip ESCR test was born and became the first ESCR test.

What are the different aspects of slow crack growth?

Slow crack growth can manifest itself in different forms, among others, the main ones are:

- stress cracking
- environmental stress cracking

A good starting point in order to understand the differences between those definitions is with ASTM D 883. According to this norm, stress cracking is "an external or internal crack in a plastic caused by tensile stresses

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less than its short-term mechanical strength". This type of cracking typically involves brittle cracking under plane strain conditions (typically at the tip of a microscopic imperfection), with little or no ductile drawing of the polymeric material from its adjacent failure surfaces.

The same kind of definition could be given to the environmental stress cracking (or ESC), which is stress cracking which occurs in an surface active environment. This concerns surface active wetting agents such as alcohols, soaps, surfactants, or other types of wetting agents. The surface-active agents do not chemically attack the polymer or produce any other effect other than to bring about microscopically brittle appearing fractures. In the absence of the surface-active environment these fractures would still occur, but not in any reasonable period of time. The active environment only accelerates the stress cracking (or slow crack growth) process and does not modify the fracture mechanism.

The ability of a polymer to resist environmental stress cracking is known as Environmental Stress Cracking Resistance or ESCR. Different polymers exhibit varying degrees of ESCR. Some grades of HDPE have very good resistance against ESC, while some have marginal resilience. Some polymers, such as polypropylene, are not affected by ESC.

Principle Variables Affecting ESCR in Polyethylene

According to the general use in mechanical properties, the major variables that affect ESCR in polyethylenes can be classified within two categories, including test variables and material variables.

Test variables

The presence and magnitude of a test variable can answer two kinds of needs: either the structure is really undergoing, during its life, such kind of conditions, (e.g. bottles of detergents, pipes under pressure, etc.), or it is not the case and this fact allows the test to be accelerated, implicitly assuming that the phenomenon of crack propagation is only affected from a kinetic point of view.

Constant Stress (Load) or Strain (Displacement) The stress (load) or strain (displacement) that is placed on the specimen undergoing an ESCR test plays a role in the failure time. One speaks about **creep** testing when the controlling variable is the **stress**. When the **strain** controls the tests, it is called a **relaxation** test.

Higher loads impart higher stresses on the test specimen and leads to shorter failure times, but care has to be taken that the failure of the specimen is always due to slow crack growth and not to general yielding. This point can be verified, namely by observing the rupture surfaces of the post-mortem samples. The amount of micro-ductility cannot be too high, but due to the lack in an objective measurement this point is currently under discussion.

Higher strains must, in a certain way, play the same role as the load does, but the reaction of the material to this kind of solicitation will not be same, and failure times can be different.

The type of mechanical variable (stress or strain) that has to be applied to the sample, and consequently the kind of test that has to be implemented depends on the service conditions existing in the final application.

Testing Environment Temperature It has been shown that the higher the test environment temperature, the faster the ESC onset.

High temperatures are used, like stress/strain and surface active agent, as an accelerating variable. This assumes that the deformation processes that occur in the material will only be shifted in time and not in nature which would make the extrapolation of the results to lower temperatures difficult.

One has to be careful when choosing testing temperature because of the recrystallization processes. Above certain temperatures the molecular arrangement of the resin under test can be altered and lead to unrealistic results.

Stress Crack Reagent Nature and Concentration It is known that, depending on the type of surface agent used for the test, the accelerating factor (i.e. the shift in the failure times) will be different. For example, tests running in water will produce higher times to failure than tests implemented in an solution of water and detergent.

In the case of the most commonly used stress crack reagent, *Igepal*® CO-630, as the concentration of water in the stress cracking media increases or the contrary, the faster the ESC onset, but in an approximate range of 0.15% to 60% of *Igepal*® CO-630 in water, times to failure seem to keep relatively constant.

This fact has been used to accelerate ESCR as measured by ASTM D1693, the so-called "Bent Strip" ESCR test. Originally, ASTM D1693 specified (in a footnote) that 100% *Igepal*® was to be used for all conditions. Most often employed as a quality control "go/no go" test, the length of time to failure became excessive for many materials and a more aggressive 10% by volume *Igepal*® solution was substituted in order to cause more rapid failure. The latest revision of ASTM D1693 reflects this practice in Table 1.

Presence of a Notch The fact that a sample or a piece of pipe is notched allows the crack propagation to start earlier, because of the introduction of a critical defect. Brittle failures are typically facilitated due to the state of stresses and strains generated in the sample by a notch. Therefore, the way the notch is milled, especially its geometry (notch length and notch tip radius) may affect the times to failure. This factor is as important as the stress, temperature and the surface active agent.

Sample Preparation Crystallinity can also be influenced by the cooling rate during sample preparation. Crystallinity increases when the cooling rate increases (more amorphous phase) and ESCR is reduced, while holding all other properties equal.

Material variables

The major material variables that affect ESCR in polyethylenes include molecular and microstructural variables.

Molecular Weight Fracture is concerned with the premature failure of the strength properties of the affected materials. In polymers, strength is strongly dependent on molecular weight. As the melt index of a polymer decreases, the average molecular weight increases. This means that the polymer's chains on the average contain more molecules. It also means that higher proportions of the chains are long in comparison to the total number of chains present. All other things being equal, stress crack resistance of polyethylene improves as molecular weight increases (melt index decreases). This can again be explained with the concept of tie molecules that create links between the different sets of crystalline lamellae.

Molecular Weight Distribution (MWD) In general, "narrow" molecular weight distribution polyethylenes have poorer ESCR values than do "broader" molecular weight distribution polymers all other things being equal. This generalization should, however, be viewed with caution as a large number of other factors, including catalyst type and co-monomer distribution have larger degrees of influence on ESCR than does MWD. This is nevertheless explained with the presence of higher molecular weights, that generate longer tie molecules.

Chain Branching and/or Density ESCR is directly influenced by the type, length and complexity of chain branching. For polyethylenes, density is a convenient, if not wholly accurate, measure of short chain branching. As a general rule of thumb, as branching increases, so does ESCR. Thus, as density decreases, ESCR generally increases. ESCR appears to be particularly sensitive to subtle variations in crystal structure and thus to differences in short chain branching.

Microstructure of the Solid State The resistance to slow crack growth (ESCR) usually decreases as the amount of crystallinity increases in the resin. Crystallinity is closely related to density and is generally explained in terms of number of tie molecules, that give its consistency to the material. These tie molecules are determined by the resin manufacturing process and catalyst type. While holding everything else constant, materials with higher crystallinity, and thus higher densities will exhibit lower ESCR values.

How Resistance to Slow Crack Growth is Measured

As polyethylene materials have improved over the years, the term slow crack growth (SCG) resistance has been used to identify all the various ESCR test methods described below. The most widely used and oldest SCG test is the Bent Strip ESCR test. Due to limitations of the Bent Strip ESCR method, several alternative ESCR tests have been developed for use in the United States and Europe. All of these tests are intended to reach reasonable failure times by modifying temperature, stress/strain, as well as other testing parameters mentioned above. All of the different methods used to measure the slow crack growth resistance listed below involve a notch to facilitate the failures.

The variations between the tests leads to enhanced difficulty in comparing them. Furthermore, at this point, the fundamental question of the observation of fracture surfaces to determine if the failure is really brittle or not, is not included in a rigorous way in the different procedures. This has to be kept in mind, when looking at the results. The tests are classified by the type of environment the tests are conducted and mention has also been given to the solicitation type.

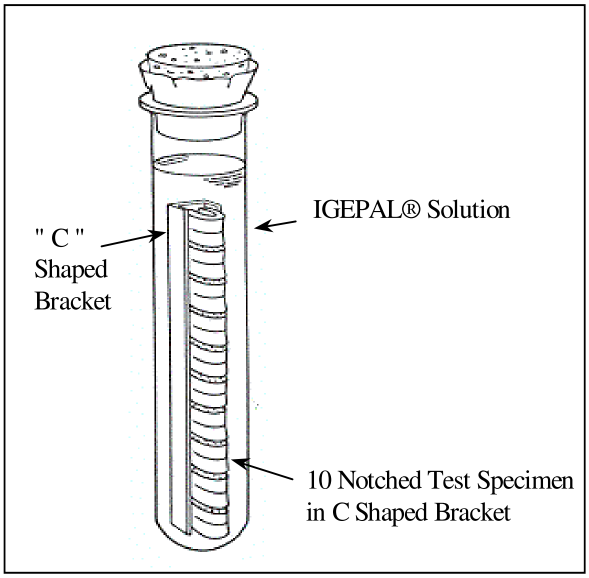
Tests Implemented in Surface Active Environments under Constant Displacement

ASTM D 1693 – Bent Strip ESCR Test

This is one of the original and best-known ESCR tests developed by Bell Labs in the late 1940's.

Ten rectangular shaped specimens are cut from a molded plaque prepared using standard methods. A controlled notch is cut horizontally across each specimen, which serves as a crack initiation point. The specimens are bent and inserted into a "C" shaped bracket, creating a stress in the specimen. A diagram of this test method is shown in Figure 1.

Figure 1 - ASTM D 1693 – Bent Strip ESCR Test



The specimens and bracket are inserted into a tube filled with *Igepal*® solution. The tube is then placed into a heated environment and monitored for cracking (failures). Solution concentration, environment temperature and sample dimensions vary with the test condition specified as illustrated in Table 1.

Table 1 – Standard Test Conditions for ASTM D 1693

Condition		Specimen Thickness		Notch Depth		Bath Temperature
		mm[A]	in.	mm[A]	in.	°C
A[B]	min	3.00	0.120	0.50	0.020	50
	max	3.30	0.130	0.65	0.025	
B[C]	min	1.75	0.070	0.30	0.012	50
	max	2.00	0.080	0.40	0.015	
C[B]	min	1.75	0.070	0.30	0.012	100[B]
	max	2.00	0.080	0.40	0.015	

[A] Dimensional values are not exactly equivalent. However, for reference purposes, the metric units shall be used.

[B] At a temperature of 100°C, a full strength reagent, rather than an aqueous solution of a reagent, is generally used because solutions tend to change their compositions by water evaporation losses during the test period.

[C] For reference purposes, concentration of *Igepal*® will be 10% volume.

These various test conditions introduce different stresses and strains and allow testing of different polymers and still obtain results in a timely manner.

Today, ASTM D 1693 – Bent Strip ESCR test is being specified less frequently because it is not as aggressive towards modern resins. This test is a constant strain test, but polyethylene, like many polymers, relaxes when strained. This stress relaxation allows testing to run without failure for very long time periods (>1,500 hours), even under severe conditions of temperature and *Igepal*® concentrations.

ASTM F 1248 – Notched Pipe Ring ESCR Test

This method has been used in the United States for many years to measure ESCR on finished pipe up to 12 inch diameter. A short piece of pipe, typically ½ inch long (around 12mm), is notched using a razor blade in a special notching device (see Figure 2) by rolling the ring over the edge of the blade. This notch depth is 20% of the specified minimum wall thickness and the notch length varies depending on pipe diameter.

Figure 2 - ASTM F 1248 – Notching Apparatus

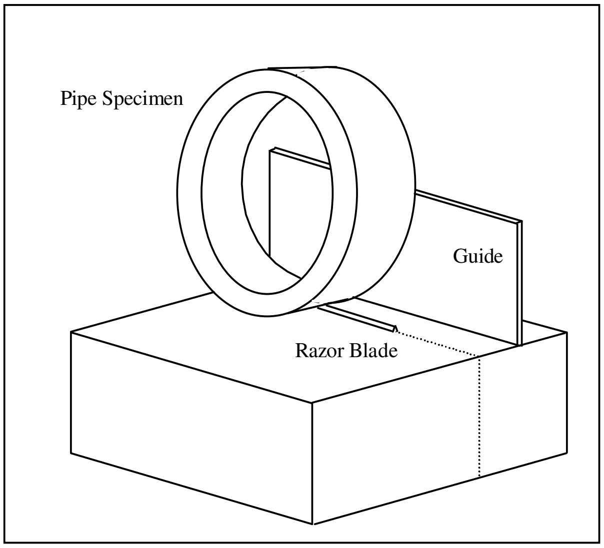
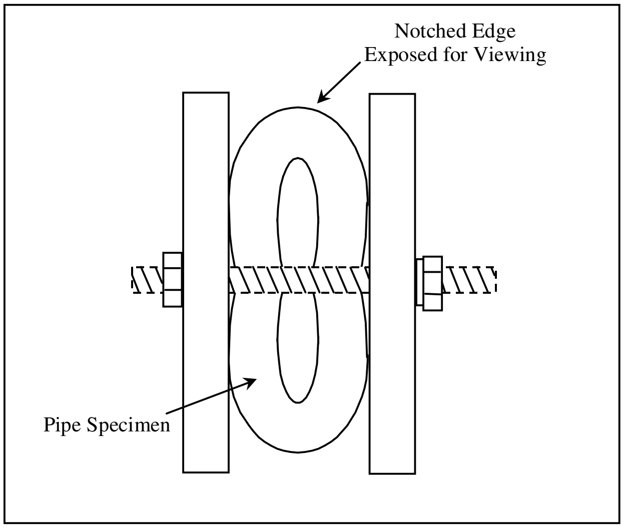


Figure 3 – ASTM F 1248 Testing Apparatus
Notched Pipe Ring ESCR Test Specimen



The notch is positioned in the center of the ring and parallel to the cut edges of the ring. Once notched, the specimen is compressed to deformation in a testing jig with the notch centered on one side, as depicted in Figure 3. The specimen is then placed in a heated *Igepal*® solution bath at 50°C. Failure is considered to be cracking on the surface of the pipe which is visible to the observer with normal eyesight. Time to failures are recorded.

Like the Bent Strip ESCR test, this method places a one time strain on the plastic and then allows the stresses to relax. This can lead to very long failure times of well over 1,500 hours for pipe grade materials and the quality index is greatly diminished when failure times exceed 200 hours.

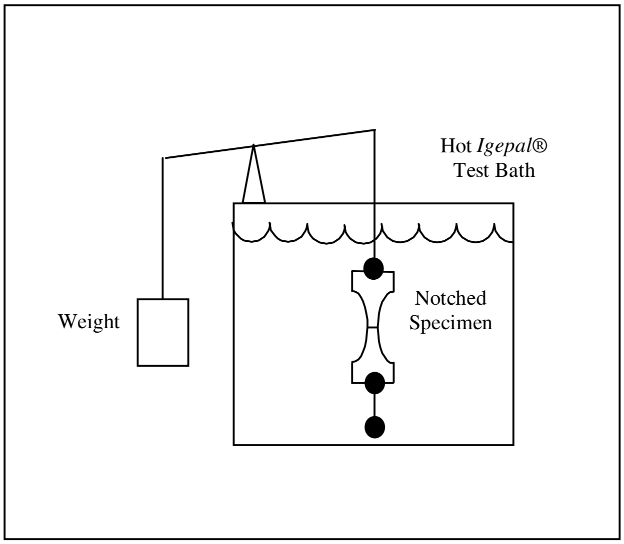
Tests Implemented in Surface Active Environments under Constant Load

ASTM D 5397 Appendix – Single Point Notched Constant Tensile Load (NCTL) Test

The NCTL test is typically used in the United States to test Geomembrane materials, but other PE materials, including some pipe resins, have been tested to gauge slow crack growth performance.

Typical test conditions are 50°C in a 10% *Igepal®* solution and the applied load is 30% of the sample's yield stress. The depth of the notch is 20% of the thickness of the sample. This method is shown in Figure 4.

Figure 4 - ASTM D 5397 Appendix – Single Point Notched Constant Tensile Load (NCTL) Test



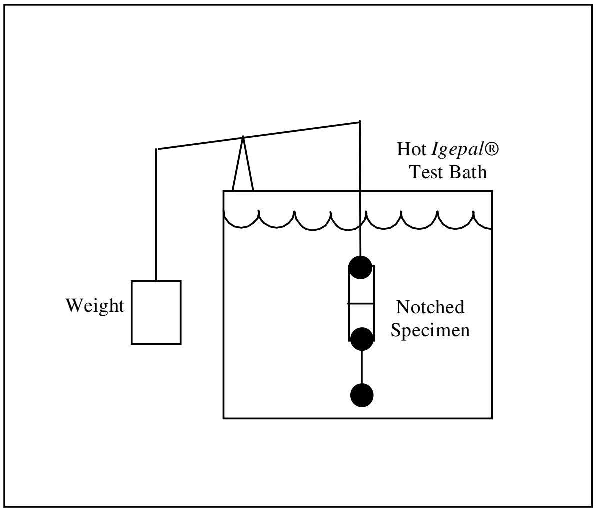
Time to failure is recorded and results pertain only to the test conditions and do not imply relative performance at other conditions of stress, temperature, etc. Failures that occur in the brittle mode are key indicators of slow crack growth performance.

The Full Notch Creep Test (FNCT)

This method is being accepted throughout Europe as the standard method to test PE Pipe grade materials that exhibit very high ESCR values. The FNCT test has been preferred to the PENT test in Europe, as it leads to shorter failure times. This is due to its particular specimen design and to the presence of a surface-active environment.

No generally accepted test conditions have been established yet for the FNCT test, contrary to the PENT test. Nevertheless, the FNCT test is being increasingly discussed in the European PE pipe industry, up to the point of establishing material specifications prior to giving a detailed description of the test method. Figure 5 diagrams this method.

Figure 5 – Full Notch Creep Test (FNCT)



Typical test specimens measure 10 x 10 x 100 mm and are machined directly from pipe or from a molded plaque. Specimens are notched on all four sides, ensuring that the notches are coplanar, with typical notch depth of 1500 microns. The specimen is inserted in the grips of the tensile creep machine with typical loads set between 4 and 5 MPa. The testing environment is temperature controlled at 80° or 95°C and a surface wetting agent such as *Igepal®* is circulated in the bath. Time to failure is recorded for each sample.

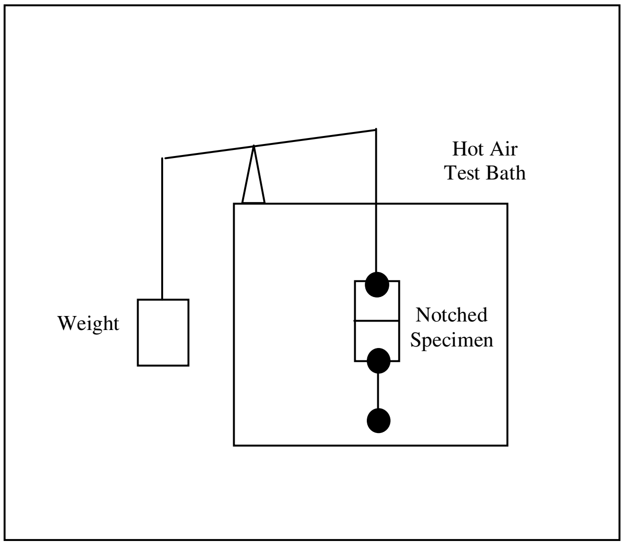
Tests Implemented in Air under Constant Load

ASTM F 1473 - The Polyethylene Notch Tensile (PENT) Test (constant load)

The PENT test is being used in the United States to test PE Pipe grade materials that exhibit high ESCR values, as this test generally provides results in a more timely basis. A standard for this test is also being developed in Europe under the ISO protocol. Typical test conditions are 80°C air and 2.4MPa stress. A diagram of this test method is shown in Figure 6.

Specimens are machined directly from pipe or from a molded plaque. Typical samples measure 10 x 25 x 100 mm. A single notch cut into the test specimen acts as a crack initiation point and the depth of the notch is dependent on sample thickness. Side notches are made to ensure triaxial state of stress, which favor brittle failure while giving rather regular and straight crack front. Typical notch depths are 138 microns on the front and 40 microns on each side. The applied load expedites the cracking mechanism, leading to sample failure. Failure is classified as a complete separation at the notch, indicating a brittle failure. Time to failure is recorded for each sample.

Figure 6 - ASTM F 1473 –
Polyethylene Notch Tensile (PENT) Test



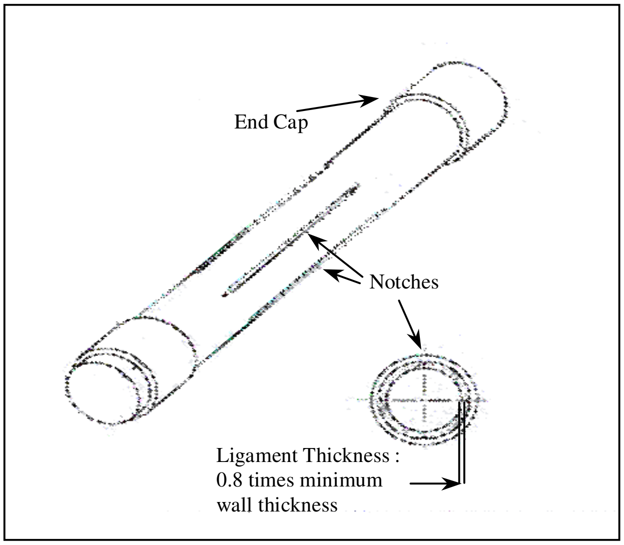
Tests Implemented in Water under Constant Load

ISO 13479 - Notch Pipe Pressure Test

This method is accepted as the standard method to test PE pipes throughout Europe.

The specific performance levels are detailed in the respective pipe standards (i.e. ISO 4427 for water and ISO 4437 for gas). Typically a minimum of 165 hours is set for PE pipe materials. Specimen are prepared using by machining four longitudinal notches in the outside walls. These notches are 20 percent of the wall thickness and are equal in length to the outside diameter of the pipe. Figure 7 illustrates the dimensions of the test specimen.

Figure 7 - ISO 13479 - Notch Pipe Pressure Test



End caps are fitted on the notched pipe specimen for hydrostatic pressure testing in water at 80°C. The pressure level (stress) is dependent on the material type and pipe series. These pressure levels are calculated to give normal plain-pipe hydrostatic stress levels of 4.0 MPa in PE80 materials and 4.6 MPa in PE100 materials. Hydrostatic pressure testing continues until failure, upon which the time is recorded.

Summary

This document was developed to provide the reader with an understanding of what Environmental Stress Crack Resistance (ESCR) is, why it is an important property in polyethylene products, and some of the factors which influence this property. This paper should also give the reader a general understanding of the various tests used to measure ESCR specifically for the polyethylene materials used in gas distribution.

References

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