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Oxidative induction time: A quality assurance measurement to predict environmental stress-cracking

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ABSTRACT: Oxidative induction time may predict environmental stress cracking in relation with the type of HDPE, the seaming parameters, the welding machine and the ageing of the geomembrane. This information can be usefull and could also prevent loss of time.

1 WHAT IS THE STRESS CRACKING ?

Stress cracking can be defined as a brittle failure of a plastic in contact with a specific environment without which no failure would occur for the same stress level. This environment can be composed of wetting agents, soaps, oils or detergents. It must be noted that, without tension, this environment doesn't induce any chemical (oxidation, hydrolysis,...) or physical effect (swelling,...) on the considered plastic.

The stress cracking phenomenon doesn't happen with any type of plastic : only the highly crystalline materials will be concerned (the polyethylene has a crystalline structure at ± 50 to 65 %).

Stress cracking occurs very often near the geomembranes seams. It is not surprising because :

-on the one hand, we can easily imagine that, during the welding operation, this zone has undergone some modifications able to change the material behaviour (modifications caused by the thermal energy brought by the welding);

- on the other hand, in this area, there are scratches caused by the welding machine wheels during the clamping of the joint. These defects can be responsible for the initiation of the stress cracking failure.

Some parameters have an effect upon the behaviour to stress cracking.

- The structure parameters have of course a leading influence on the material behaviour. In practice, it is however difficult to make only a characteristic change in order to know its precise influence.

- The thermal-mechanical history (time, speed, pressure and temperature of transformation,...) has a certain influence because it has an effect upon the structure configuration : orientation, internal stresses, crystallinity. Unfortunately, it isn't always possible to estimate the weight of each parameter.

- The stress level applied is an important parameter; under a certain critical value, the phenomenon doesn't occur.

- The temperature is an accelerating factor of the phenomenon.

- The environment is also of great importance. The liquids (soaps, wetting agents,...) have a growing reactivity with a high pH, a low viscosity and a low surface tension. Thus, a 5 or 10 % solution of wetting agent in water is more aggressive than a 100 % one because the viscosity and the surface tension are lower. It must be noted that the intermediate mixtures lead to gels difficult to use.

2 STRESS CRACKING TESTS

2.1. Test method

The experimental device adopted has been realised according to ASTM D2552 recommendations ("Environmental stress rupture of type III polyethylenes under constant tensile load).

The apparatus (see figure 1) is composed of an immersion tank which can contain a maximum of 20 test specimens, loaded at different percentages of their yield stress by static load (in tension-shearing

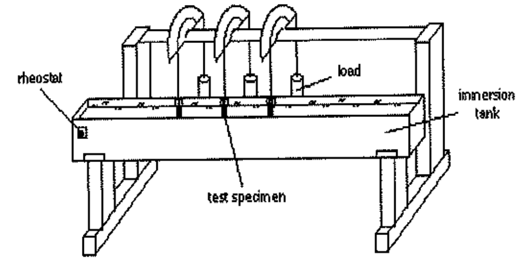

Figure 1 Drawing of the apparatus

stress). A lever system with a mechanical advantage of 3:1 is used to impose the desired loading on each specimen.

The surface-active agent in which the specimens are immersed is a 10 % solution of a specific wetting agent : a nonylphenoxypoly(ethyleneoxy)ethanol, heated at the constant temperature of 50°C. A submersion heater and controller are used to maintain the test temperature.

The test specimens are dumbbell shaped; their narrowest section is 6 mm in width and contains a double thermal welding.

2.2 Observation of the phenomenon

Tests have been realised on two specimen types of the same composition but showing different stress cracking behaviours. Analyses performed on the specimens after the stress cracking tests revealed that the type 1 membrane was more degraded (surface oxidation) than the type 2 one.

Thus, we have :

- type 1 specimens (degraded material);
- type 2 specimens (non-degraded material).

The tests study the behaviour of series of identical test specimens, loaded exactly in the same way, with stresses, varying from 15 to 70 % of material yield stress σ_{yield}. The failure time of each specimen is recorded, with a maximum test duration of 400 hours.

- For type 1 specimens, the stresses vary from 15 to 50 % of σ_{yield}.
- For type 2 specimens, we have recorded that, for 40 % of σ_{yield}, there was no failure during the 400 hours; so the stresses vary from 40 to 70 % of σ_{yield}.

2.3 Results

We can observe that (figures 2 and 3) :

- The type 1 specimens fail by stress cracking, a brittle failure occurring at the edge of the seamed region and developing in the perpendicular direction to the applied stress.
- The type 2 specimens fail in a ductile way, by a several hundred percents elongation of the zone at the edge of the seam.

These test results have been put on diagrams giving the evolution of the failure times related to the applied stresses (effective stresses applied calculated by measuring the real dimensions of all the seams at the place of the failure) and curves have been adjusted to the test results (figures 2 and 3). As we can see on figures 2 and 3, if the type 2 specimens can support stresses up to about 50 % of σ_{yield} , for the type 1 specimens, brittle failures may already occur for stresses of 25 % of σ_{yield}. So we can conclude that it is essential to limit the tensions in geomembranes in a very severe way.

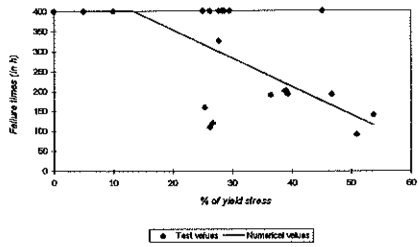

Figure 2 Type 1 : evolution of failure times related to the effective stress in the seam.

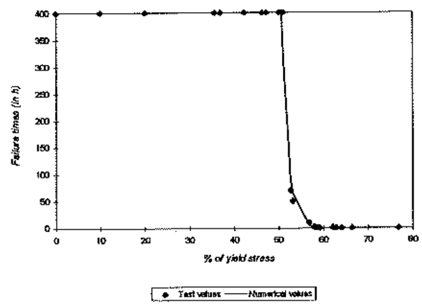

Figure 3 Type 2 : evolution of failure times related to the effective stress in the seam

3 OXIDATIVE INDUCTION TIME (OIT)

It is the time necessary to produce the oxidation of a polyethylene specimen heated at a constant temperature of 210°C and then plunged in an oxidising atmosphere (pure oxygen). The test measures the time during which the antioxidiser prevent the specimen from oxidation.

Analyses of this kind have been performed at several points along type 1 and type 2 test specimens, intact and having undergone a stress cracking test.

- For type 1 specimens (stress cracking), we observed :

OIT values are about 10 minutes;

OIT values are rather uniform along the specimen.

This may be explained by the fact that type 1 specimens have undergone a global surface oxidation on their whole length.

- For type 2 specimens (no stress cracking), we observed :

OIT values are about 20 minutes;

OIT values are very lower (about 10 minutes) at the edge of the seam.

This may be explained by the fact that type 2 specimens have undergone a local surface oxidation in one point.

The oxidations (local and global) are due to the thermal (welding) or environmental (UV action for example) history of the specimen. These oxidations haven't been caused by the stress cracking tests; indeed, OIT values are identical for the intact specimens and for those having undergone a test.

4 INFLUENCE OF THE LOSS OF ANTI-OXIDISING MATERIAL

4.1 Artificial ageing on geomembrane

Geomembranes were aged in a QUV-test to produce an acceleration of the ageing phenomenons, including cycles of :

- 4 h UVB radiation at 60°C and
- 4 h condensation at 50°C;

After 3874 hours, that means more than 5 months exposure at QUV-test, the OIT values were about of 15 minutes (see figure 4).

It will be so necessary to wait about 8 or 9 months

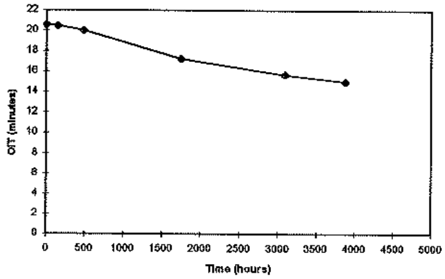

Figure 4 Evolution of OIT values versus exposure time in QUV test.

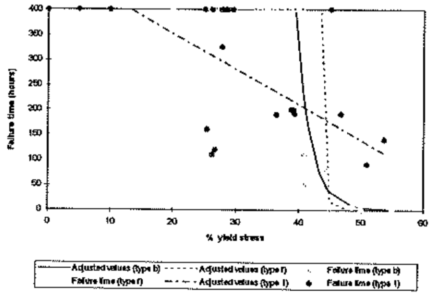

Figure 5 Evolution of failure time versus percentage of yield stress

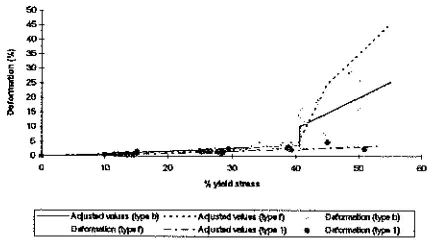

Figure 6 Evolution of deformation versus percentage of yield stress

in order to attempt OIT values of 10 minutes.

The aim of this manipulation is to point out the influence of the exposure time and the comparison with natural ageing.

4.2 Stress cracking on naturally aged membranes

Three types of membranes were tested :

- new membrane (OIT = 23 minutes) seamed with TWINMAT (type f);

- lightly aged membrane (OIT = 20 minutes) seamed with TWINMAT (type b);
- hardly aged membrane (OIT = 10 minutes) seamed with SERROT (type 1).

The results have been plotted on figures 5 and 6.

We observe an evolution of the type of failure in relation with the decrease of OIT (that means the loss of anti-oxidation material) :
- for specimens 1 : brittle failure with deformations quasi equal to zero;
- for specimens f : ductile failure with high deformation (≈ 45 %);
- for specimens b : semi-ductile failure with maximum deformation of about 28 %.

The loss of anti-oxidation material induces a failure more and more brittle.

4.3 Stress-cracking on artificially aged membranes

Only two types of membranes were tested :
- new membrane (OIT = 23 minutes) seamed with TWINMAT (type f);
- aged membrane (OIT = 17 minutes) seamed with TWINMAT (type e).

No essential difference was observed in the behaviour of the membranes due to a too small time of exposure to the QUV test. More information will be given in an other report.

4.4 Comparison of natural and artificial ageing

The results obtained for a same oxidative induction time after natural and artificial ageing are similar. That means that it would be possible to define a good correlation with what happens on site and what it is observed in a laboratory.

5 INFLUENCE OF THE WELDING MACHINE

Two types of machines were tested :
- hot air machine (SERROT);
- hot air and wedged machine (TWINMAT).

The results obtained on seams realised with a new membrane (OIT = 23 minutes) show a very small difference of behaviour.

The type of failure is ductile for the two specimens. The influence of the type of machine seems not to be fundamental for the environmental stress cracking behaviour of the seams.

6 INFLUENCE OF SEAMING PARAMETERS

The speed of seaming and the temperature influence were investigated on membranes seamed with a TWINMAT machine. The seaming parameters were defined as given hereafter :

Specimen type	Temperature (°C)	Speed (m/min)	Pressure (N)
f	450	1.5	1200
g	500	1.5	1200
h	450	3	1200

The results are plotted in the figures 7 and 8.

The observation of the tendency curves shows :
- a very light influence of the speed of seaming parameter when it is defined by classical value. In the two cases the failure remains of ductile type;
- the deformations of the specimens type h (T° = 500°C) are relatively smaller than the one of the specimens type f and g (T° = 450°C). The type of failure for specimens welded at higher temperatures is of semi-ductile type. The elevation of

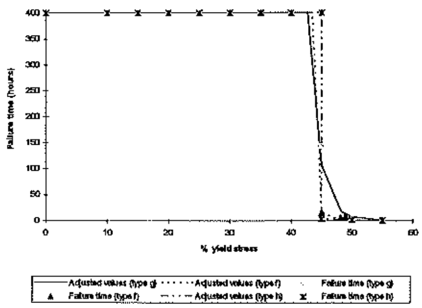

Figure 7 Evolution of failure time versus percentage of yield stress

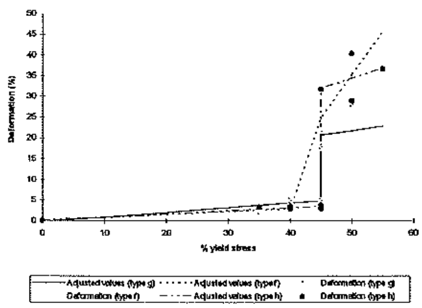

Figure 8 Evolution of deformations versus percentage of yield stress

temperature seems to induce a modification of failure type (from ductile to brittle type).

It would be interesting to investigate other temperatures and speeds in order to define maximum and minimum parameter values it is suitable not to exceed.

7 INFLUENCE OF HDPE TYPE

Two types of HDPE membrane specimens (c and d) were tested. They are characterised by :

	Type c	Type d
Thickness (mm)	2	2
Density	0.945	0.940
Yield stress (N/mm²)	16	18
Deformation at yield point (%)	12	12
Stress at break (N/mm²)	> 30	28
Deformation at break (%)	800	700
Cristallinity ratio (%)	45.9	45.2
Oxidative induction time (min)	23	23

The two samples c and d were welded with a TWINMAT machine.

The failure time was recorded, as well as the type of deformation (see figures 9 and 10).

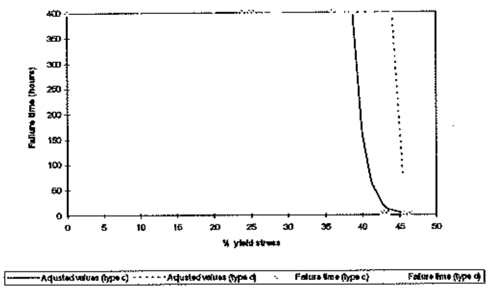

Figure 9 Evolution of failure time versus percentage of yield stress

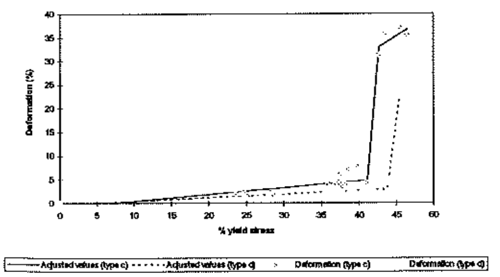

Figure 10 Evolution of deformation versus percentage of yield stress

The curves are lightly translated, indicating a welding of higher quality for d type but the failure was of ductile type for the two membranes. The type of HDPE doesn't seem to be a fundamental factor of influence for environmental stress cracking behaviour.

8 CONCLUSIONS

The tests show clearly that the most important parameters related to the environmental stress cracking behaviour of the seams of geomembrane in HDPE is the oxidation of the membrane, that means the loss of anti-oxidising material.

It will be also important to limit the values of the seaming parameters, and in particular the temperature, because increases far from a certain value induces a less ductile failure.

It is necessary to determine exactly what are the maximum and minimum values for each parameters (temperature, loss of anti-oxidising material, type of HDPE, pressure, speed of seaming,...) in order to guarantee a good behaviour of the seam; that needs more experiments, essentially between OIT of 17 and 10 minutes to define evolution curves.

However, it seems to be possible to correlate OIT and stress cracking behaviour what would be of the prime interest because it would permit to replace long stress cracking tests by very short OIT measurement. It would be so possible to incorporate OIT measurements in Quality Control procedures.

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