Evaluation tests on PE-HD geosynthetic barriers after exposure tests

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ABSTRACT: For the evaluation of the durability of a high density polyethylene polymeric geosynthetic barrier accelerated oxidation tests are carried out by using high-pressure autoclaves. The ageing tests are followed by several evaluation tests on the exposed specimens. A comparison of the evaluation test results with those obtained from the same test on an unexposed control sample provides typically a basis for acceptability. The following characteristics are used: tensile properties, oxidation induction time (OIT) values, melt-flow rate (MFR), oxidation onset temperature (OOT) and strain hardening test (SHT) modulus. The sampling and the preparation/treatment of oxidation induction time (OIT)-specimens for measurements on PE-HD GBR-P made of bulk thickness or at layers in different depths are discussed. The effects of sampling from the inner core, from the surface or from the entire thickness are shown. The effects of the orientation of the exposed surface in a crucible of a differential scanning calorimeter are discussed. The use of a cover plate above the OIT-specimen is discussed. Lifetime prediction is shown on the basis of defined acceptance criteria for the changes of the following properties: elongation at break in uniaxial tensile tests, strain hardening modulus, MFR and OOT.

Keywords: High Density Polyethylene (PE-HD), Polymeric Geosynthetic Barrier (GBR-P), Melt-Flow Rate (MFR), Oxidation Induction Time (OIT), High-Pressure Oxidation Induction Time (HP-OIT), Oxidation Onset Temperature (OOT), Strain Hardening Test (SHT), Differential Scanning Calorimeter (DSC), High-Pressure Autoclave Test (HPAT), Notched Constant Tensile Load (NCTL) Test

1 INTRODUCTION

For the foreseen service life of geosynthetic barriers their durability must be determined. The durability of GBR-P depends on various mechanisms that cause degradation, i.e. reduction of mechanical or hydraulic performance. These mechanisms of degradation may be the attack by e.g. oxygen accelerated by elevated temperature, exposure to ultraviolet light, or repetitive mechanical stress and catalysed possibly by chemicals or the solvation, i.e. change in physical properties due to absorption of liquid chemicals.

Establishing the durability of PE-HD GBR-P exposure testing is carried out by first exposing a specimen to simulated and/or accelerated environments (weathering, leaching, oxidation or chemicals) under controlled conditions. It is followed by one or more evaluation tests of selected physical/mechanical tests on the exposed specimen. A comparison of the evaluation test results with those obtained from the same test on an unexposed control sample typically provides a basis for acceptability.

In most cases few evaluation tests are used after ageing tests: comparison of tensile properties, comparison of OIT-values or HP-OIT-values and change in mass.

Nowadays further tests provide opportunities to check the ageing stage of geosynthetics especially for PE-HD GBR-P. The SHT acc. prEN 17096:2017 is a very promising property which can be fast determined on rather small specimens. MFR acc. to ISO 1133-1 is a very common test for quality control but it provides also very good indications on the ageing of the polymers. The stabilization against oxidation can be determined via the oxidation induction temperature / time by means of DSC acc. to ISO 11357-6. Beside the widely practiced isothermal OIT tests dynamic oxidation induction temperature - also called OOT - is used. In the dynamic technique, the sample is heated at a defined constant heating rate under oxidizing conditions until the reaction begins. Oxidation tests in high-pressure autoclaves acc. to ISO 13438:2004 provide the opportunity to monitor the changes in oxygen pressure during running tests.

2 OXIDATION TESTS IN HIGH-PRESSURE AUTOCLAVES

2.1 *Test device*

For the oxidation tests high-pressure autoclaves acc. to ISO 13438:2004 were used. Specimens were immersed in a 0.01 mol/l $NaHCO_3$ solution at a temperature of 80 C at three different over-pressures of 5 bar, 25 bar and 50 bar with pure oxygen (O_2). Specimens were taken for evaluating the stage of the ageing after different immersion durations.

2.2 *Test samples*

In the study a smooth 2 mm thick black coloured PE-HD GBR-P with density of 0.942 g/cm³ was used. As stabilizers Irgafos 168 – a hydrolytically stable phosphite processing stabilizer and Irganox 1010 – a sterically hindered phenolic antioxidant were used. Irganox 1010 is a phenolic primary antioxidant used for processing and long-term thermal stabilization. It protects the polymers against thermo-oxidation degradation. The PE-HD GBR-P contains carbon black and the resin is a linear low density polyethylene. Due to the density of the GBR-P - including carbon black - it will be called PE-HD as this is the common practice that the density of the final product is the decisive factor for the categorisation of PE GBR-P.

Additionally pressed sheets - made from the same re-granulated PE-HD GBR-P - in thicknesses of 1 mm, 4 mm and 10 mm were tested in high-pressure autoclave tests (HPAT).

3 TEST RESULTS

3.1 *Oxygen pressure*

The three HPAT run at 6 bar, 26 bar and 51 bar for around 160 d, 75 d and 75 d respectively. The experience from other HPAT on e.g. PE-HD plastic pipes (Zanzinger et al, 2014) or on polypropylene geotextiles (Hausmann et al., 2016) is that the polymer degradation can be determined by the change of the oxygen-pressure in a HPAT. In this study too many withdrawals have been made. Therefore a judgment of the change of oxygen-pressure could not be used in this study.

3.2 *Oxidation induction time*

3.2.1 *Test conditions*

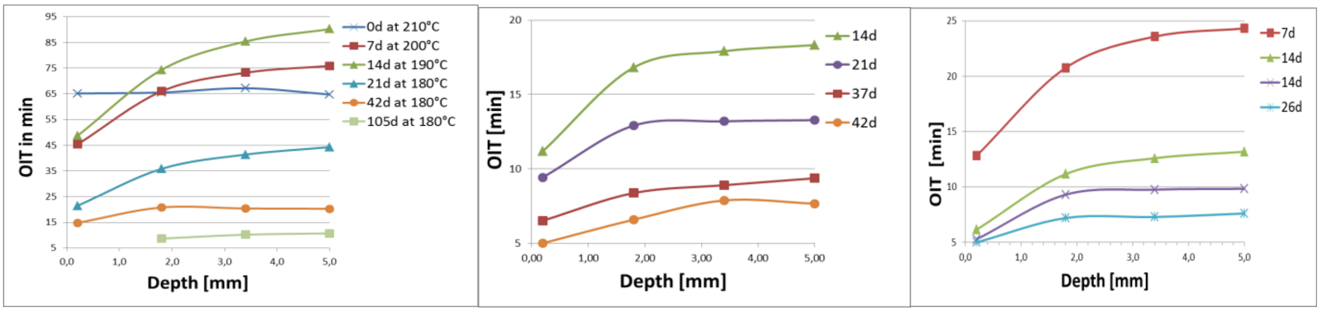
OIT was determined acc. to ISO 11357-6. Most tests on aged specimens were performed at a constant temperature of 180 °C. Un-aged specimens and specimens up to 14 d immersion in the HPAT were tested at temperatures up to 210 °C. In this study crucibles with a 3 mm diameter piercing in the lids are used.

Two measurements were made per specimen. Here for a specimen of 2 mm by 4 mm was cut in two halves. Each half specimen was tested by putting the cut cross-section surface on the bottom of a crucible each. It was demonstrated by Sauer (2016) that in this case the two exposed surfaces of the specimen in the DSC device were exposed identically as the entire test plates were exposed in the HPAT before. This procedure was seen to be the most representative simulation.

3.2.2 *OIT distribution*

On the 10 mm thick pressed plate the OIT was measured on 400 µm thick specimens taken at the surface, at depths of 1.8 mm, 3.4 mm and 5.0 mm. Fig. 1 shows that there is a strong consumption of stabilizers - represented as OIT - at the surface in comparison with the measurements in the deeper part of the test plate. It is very clear that the stabilizers are consumed first at the surface whereas the stabilizer content inside the plate is still higher.

In cases were effects on the surface are relevant such like e.g. stress cracking the OIT at the surface should be taken into consideration instead of the OIT of the entire specimen.



(a) 6 bar (b) 26 bar (c) 50 bar

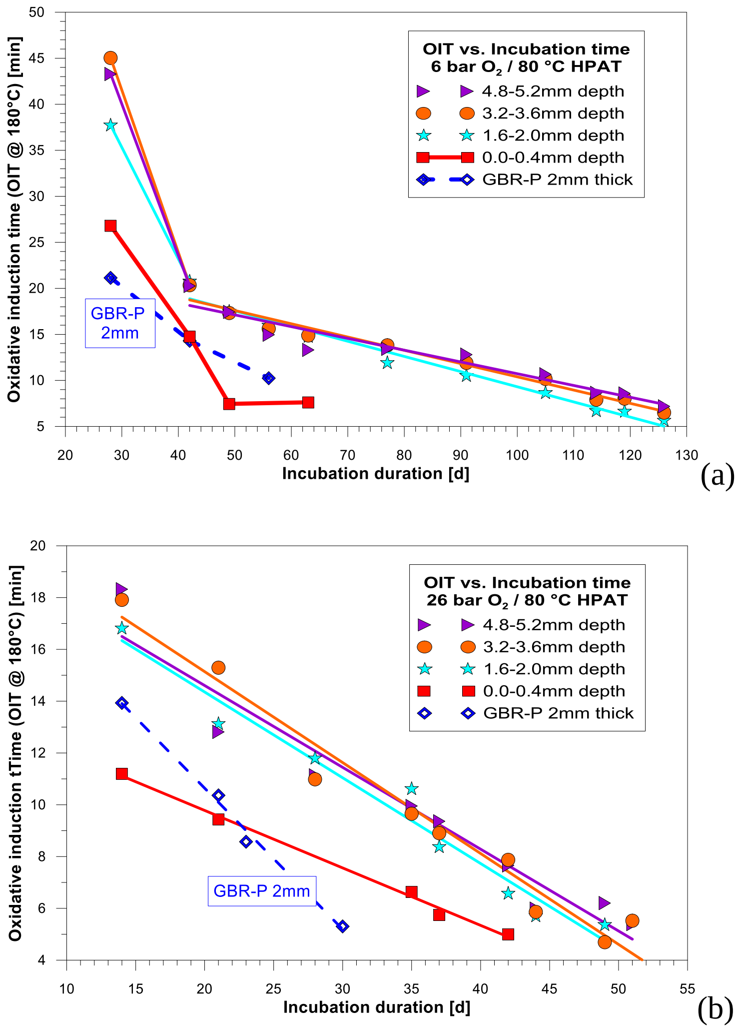
Figure 1. OIT-values (at different oxygen pressures) at different depth in a pressed 10 mm thick plate

3.2.3 *Stabilizer consumption*

Fig. 2 shows the change of the OIT as a function of the incubation duration in three HPAT. The specimens were taken from the 10 mm thick test plate in four different depths and additionally from a 2 mm thick GBR-P. It can be seen that in beginning a strong decrease of the OIT took place. It will be followed by a less fast decrease afterwards. This might be due to the consumption of the process stabilizer first followed by the consumption of the long-term stabilizer.

The OIT-values of the GBR-P are mainly between the OIT values of the specimens from the surface and from the 1.8 mm depth. This is reasonable as the GBR-P is exposed from double sides, whereas the specimens from the 10 mm plate can be seen as single-sided exposed specimens only.

Figures 3 to 5 show the OIT-values of the GBR-P as a function of time for three HPAT at three different O_2-pressures. The curves follow two mechanisms for the consumption of the stabilizers. The process stabilizer might be consumed first and rather fast. The second stabilizer demonstrates a longer activity to protect the polymer from degradation. For practicality a 1% residual OIT-value has been chosen as an arbitrary criterion to determine the time until consumption of the stabilizer. The results are shown in Tab. 1.



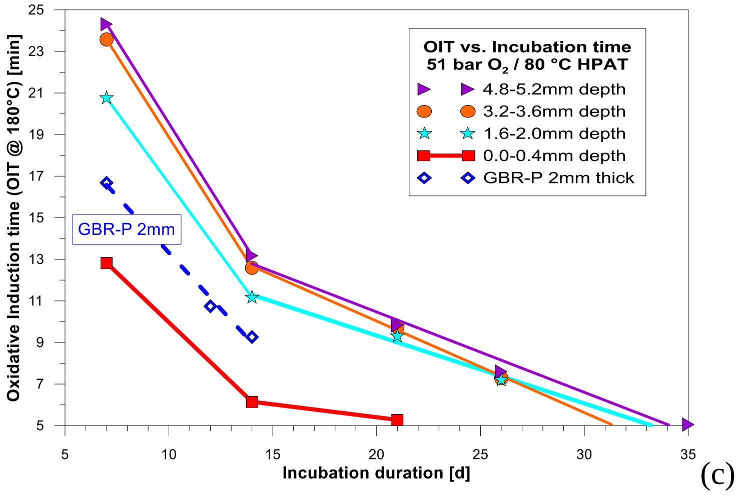


Figure 2. OIT (at 6 bar (a), 26 bar (b), 51 bar (c) oxygen pressure) in different depth of a 10 mm thick plate in comparison with a 2 mm thick GBR-P.

Table 1. Times-until-"consumption of stabilizer" with the acceptance criteria: 1% residual OIT-value.

Test conditions	80°C / 51 bar O_2	80°C / 26 bar O_2	80°C / 6 bar O_2
Time for stabilizer consumption for OIT / d	~18	~23	~64

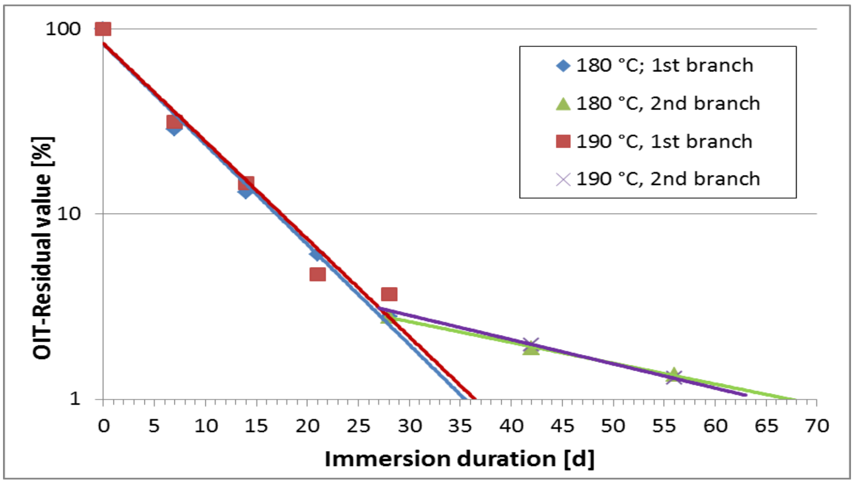


Figure 3. OIT-Residual value of PE-HD GBR-P at 6 bar and 80 °C

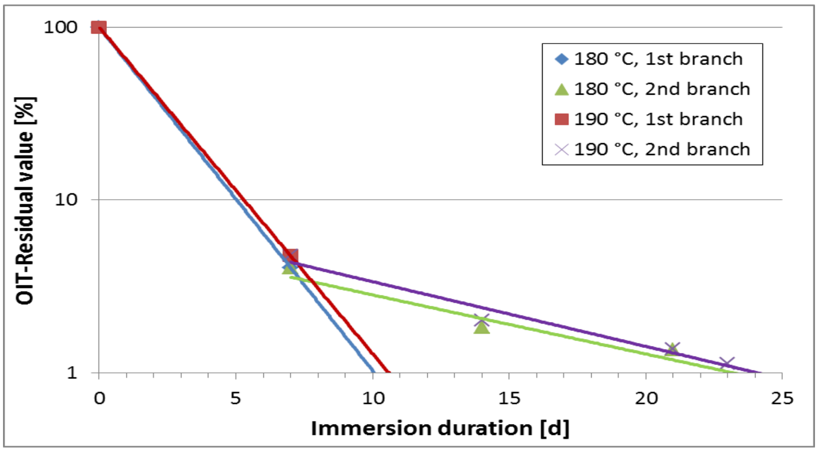


Figure 4. OIT-Residual value of PE-HD GBR-P at 26 bar and 80 °C

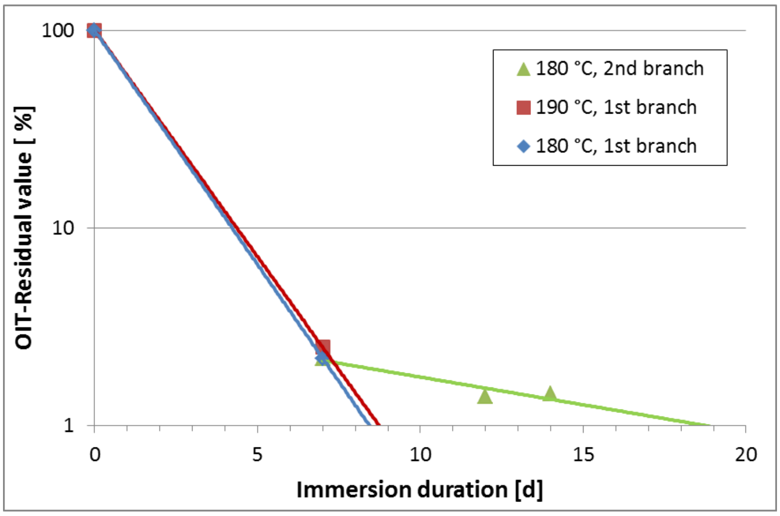


Figure 5. OIT-Residual value of PE-HD GBR-P at 51 bar and 80 °C

3.2.4 *OOT*

Beside OIT-measurements OOT was determined acc. to ISO 11357-6. The OOT declined as well as the OIT-measurements in two-step-process (Fig. 6). The conclusion might be again that the strong drop of the OOT is due to the consumption of the process stabilizer first and then followed by a less strong decrease of the OOT due to the consumption of the long-term stabilizer.

Interesting is that at the end the OOT remains stable at a constant residual value. The end of the second branch (when OOT = constant) is a clearly defined criteria. This has been chosen here as acceptance criteria for the end of lifetime of the sample. The results are shown in Tab. 2.

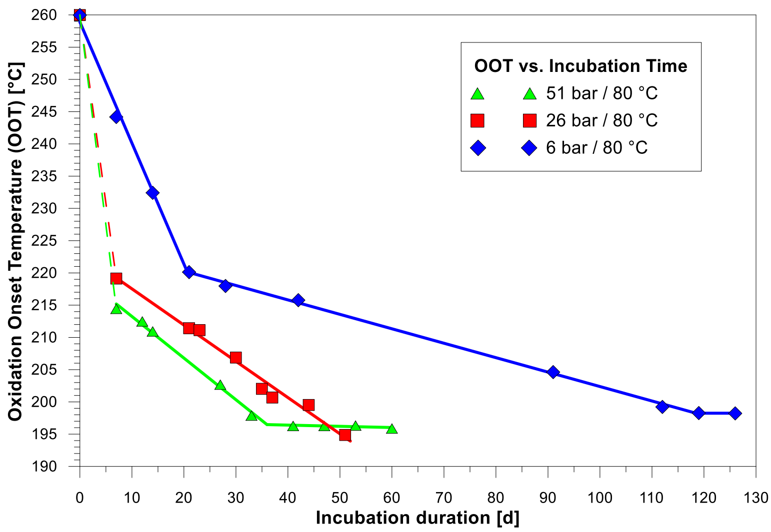


Figure 6. OOT.

Table 2. Times-until-“failure” with the acceptance criteria: end of second branch in OOT-tests.

Test conditions	80°C / 51 bar O_2	80°C / 26 bar O_2	80°C / 6 bar O_2
Time-until-“failure” for OOT * / d	~36	~50	~119

* Start of third branch w/o change of OOT.

3.3 *MFR*

MFR acc. to ISO 1133-1 is widely used in the quality control not only for the production of polyolefin products. In this study the change of MFR after ageing has be investigated. A strong change of the MFR was found after ageing in HPAT (Fig. 7).

For practicality a change in MFR of 350% has been chosen as an arbitrary criterion to determine the time until failure. The results are shown in Tab. 3.

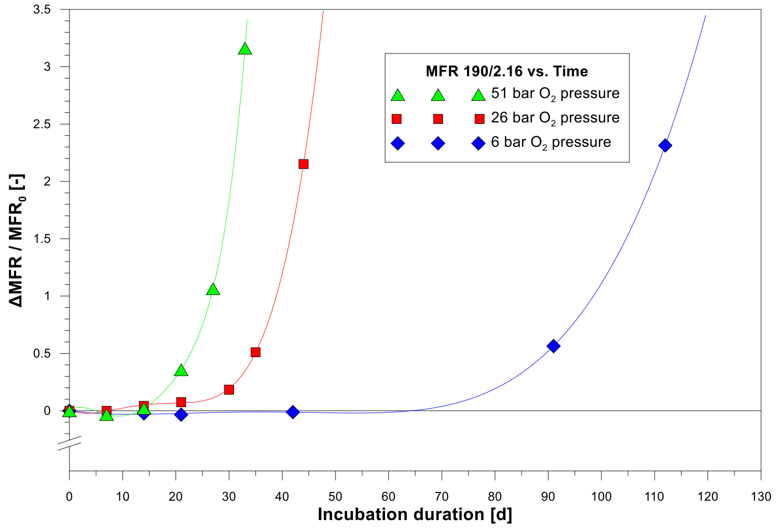


Figure 7. MFR.

Table 3. Times-until-“failure” in MFR tests with the acceptance criteria: 350% change of MFR.

Test conditions	80°C / 51 bar O_2	80°C / 26 bar O_2	80°C / 6 bar O_2
Time-until-failure for MFR 190/2.16 / d	~33	~48	~120

3.4 *Tensile properties*

The most common evaluation test is a tensile test acc. to ISO 527-3. For PE-HD the elongation at break is a rather sensitive parameter for the end-of life of an aged sample. Here an acceptance criterion of 75% residual elongation at break has been used. It is known for phenol stabilized PE-HD GBR-P that the tensile properties do not change significantly as long as the stabilizers are not consumed. After a certain induction time the degradation of the polymer takes place and the properties will drop down dramatically. Therefore a 75% criterion seems to be more reasonable than the commonly used 50% criterion.

The results are shown in Fig. 8 and Tab. 4.

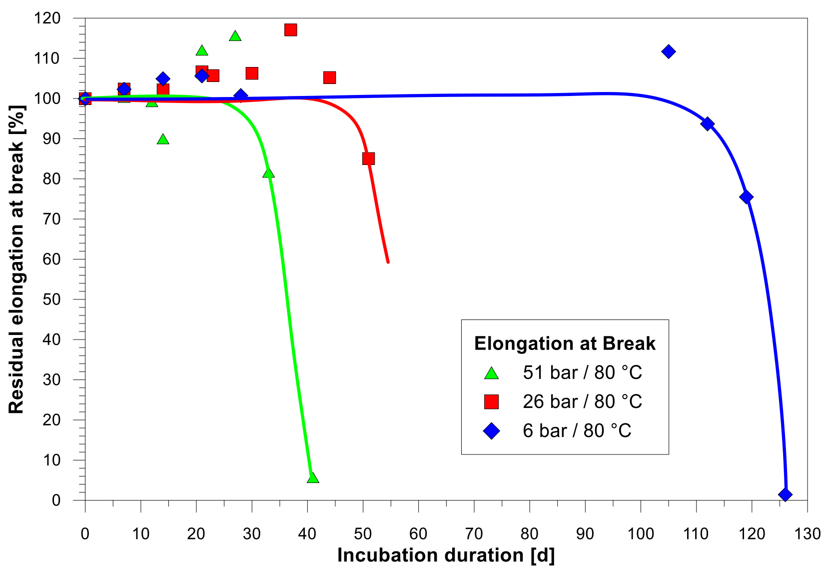


Figure 8. Elongation at break.

Table 4. Times-until-“failure” with the acceptance criteria: 75% retained tensile elongation at break.

Test conditions	80°C / 51 bar O_2	80°C / 26 bar O_2	80°C / 6 bar O_2
Time-until-failure for ε_b / d	36-37	~51	~118

3.5 *Strain hardening modulus*

From previous studies (Zanzinger et al., 2015) it is known that the stress cracking resistance expressed as single-point NCTL failure times correlates well with strain hardening modulus $<G_p>$ acc. to prEN 17096:2017. In this study $<G_p>$ was determined after ageing of the samples.

Here an acceptance criterion of 40% residual strain hardening modulus has been used as an arbitrary criterion to determine the time until failure. The results are shown in Fig. 9 and Tab. 5.

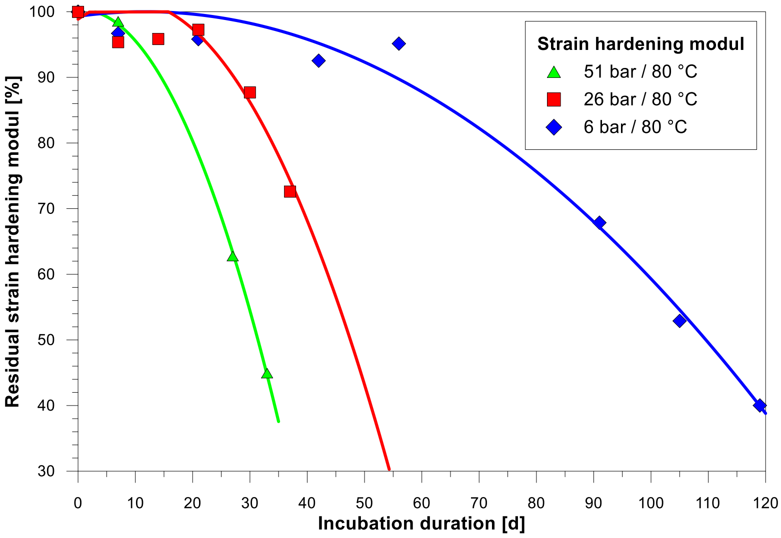


Figure 9. Strain hardening modulus.

Table 5. Times-until-“failure” with the acceptance criteria: 40% retained strain hardening modulus.

Test conditions	80°C / 51 bar O_2	80°C / 26 bar O_2	80°C / 6 bar O_2
Time-until-failure for $<G_p>$ / d	~34	~50	~119

4 LIFETIME ESTIMATION

From the above described tests “times-until-failures” have be determined for different acceptance criteria shown in Tables 2 to 5 at a test temperature of 80 °C at different O_2-pressures. Those failure times were used to extrapolate the failure times at 80 °C and 0.21 bar atmospheric conditions (Fig. 10). The lowest extrapolated failure time at 80 °C and 0.21 bar O_2-pressure was found for elongation at break ε_b with 731 d given in Tab. 6. The other tests showed extrapolated failure times in the similar range between 731 d and 911 d.

Table 6. Times-until-“failure” at atmospheric conditions for different evaluation tests.

Evaluation test	Time-until-failure for 80 °C at 0.21 bar / d
Oxidation onset temperature (OOT)	~ 781
Melt-flow rate (MFR)	~ 911
Elongation at break ε_b	~ 731
Strain hardening modulus $<G_p>$	~ 848

Fig 11 shows in a classic Arrhenius plot the estimated lifetime at atmospheric conditions for ambient temperatures. Here typical activation energy E_A of 90 kJ/mol was used for the extrapolation from a test temperature of 80 °C to lower temperatures. As a result of this lifetime estimation a 100 year service life could be given at 40 °C and 0.21 bar atmospheric conditions for ageing tests described above.

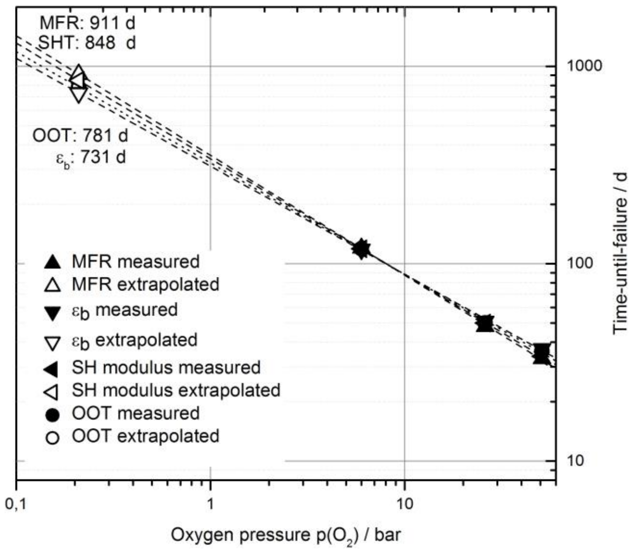


Figure 10. Time-until-failure as function of oxygen pressure.

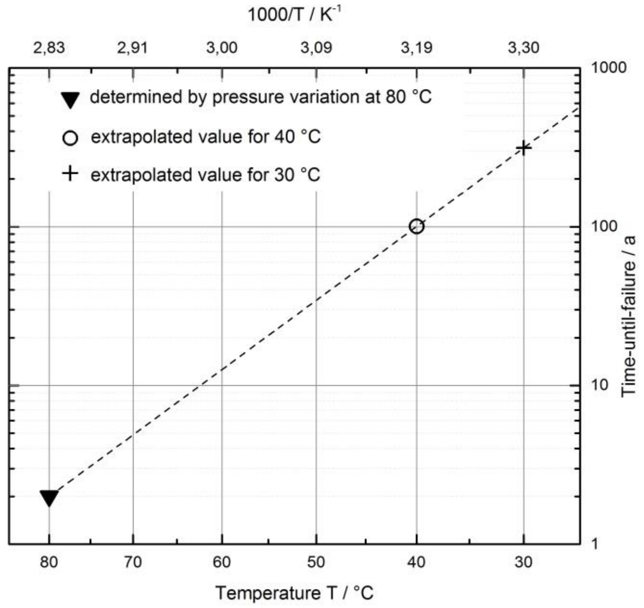


Figure 11. Arrhenius plot for E_A = 90 kJ/mol.

5 CONCLUSIONS

High-pressure autoclave tests provide a highly interesting and fast opportunity for accelerated oxidation tests at reasonable elevated temperatures on PE-HD geosynthetic barriers. HPAT were determined at a test temperature of 80 °C with three different O_2-pressures for up to 160 d test duration. Lifetime estimation was based on four different evaluation tests. For the lowest failure time a service life of 100 years at 40 °C was found. OIT measurements showed the times for stabilizer consumption. It was demonstrated that this is more severe at the surface in comparison with the OIT measurements over the bulk thickness of a PE-HD GBR-P. The tests on OOT, on MFR, on elongation at break and on strain hardening modulus showed very promising results and should therefore be used in the portfolio with the regard to evaluation of ageing tests for PE-HD GBR-P.

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