Predicting HDPE OIT ageing performance from a revised short duration test

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ABSTRACT
Increasingly engineers are seeking to verify HDPE Polyethylene geomembrane durability characteristics by testing oxidative induction time before and after accelerated ageing of the material. Typically, 90 days of ageing in air is required in an oven at 85 °C which requires a significant time for material specification conformance testing prior to installation. This paper reports on studies undertaken to refine the high-pressure oxidative induction time test process to allow this material durability indicator to be characterized in a shorter period. The study included assesses the response of different HDPE material formulations and skin conditions to the test procedure. Different sample preparation procedures were also examined. A proposed alternative durability test process is proposed for consideration.

Keywords: Oxidation Induction Time, OIT, HPOIT, Oven Aging

1. INTRODUCTION

1.1 Measurement of antioxidant stabilisers

Polyethylene geomembrane is made from a base resin and small quantities of carbon black, antioxidants and stabilisers. Carbon black improves UV performance, the antioxidant additives enhance durability performance (Muller, W. 2007). The performance of antioxidants is usually characterized by determining the Oxidative Induction Time (OIT). For this, a small specimen of material is exposed to an oxygen environment at elevated temperature and pressure and the time for oxidization to start is measured using the Differential Scanning Calorimetry (DSC) method. There are two procedures for measuring OIT, Standard Oxidative Induction Time (S-OIT, ASTM D3895) and High-Pressure Oxidative Induction Time (HP-OIT ASTM D5885). The tests differ to assess the performance of different antioxidant components (Ewais et al. 2014). Some of the common additives used in polyethylene geomembranes such as Hindered Amine Light Stabilizers (HALS) are damaged at the high S-OIT test temperature (200 °C) their performance can be measured at the lower test temperature of the HP-OIT test (150 °C). This paper is focusing on the HP-OIT test and the influence test variability and sample preparation can have on results.

1.2 ASTM D5885 High Pressure Oxidative Induction Time

ASTM D5885 requires that a sample of geomembrane is compression molded to a thickness of 0.25mm according to ASTM D 4703. A specimen 6.4mm diameter is punched from the molded sheet with a specimen mass of 5mg. The mold procedure, often referred to as plaquing, normalized the samples thermal history and standardizes sample thickness. Industry practice is often to test material trimmed from the geomembrane sheet to the required mass without plaquing.

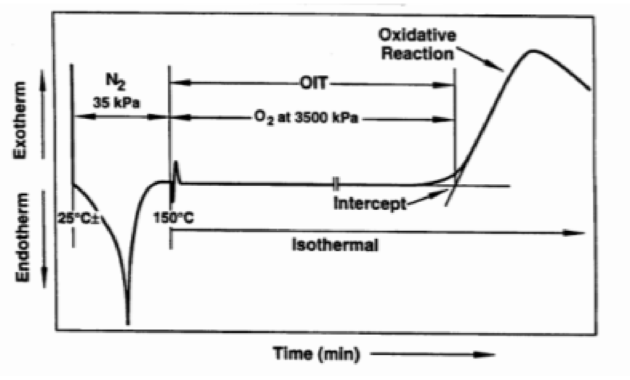

Figure 1 . Testing Temperature Curve (ASTM D5885-17).

ASTM D5885 advises that poor sample uniformity will adversely affect results and provides additional preparation processes to homogenize samples prior to plaquing. In this paper when homogenizing material the Cryogenic Grinder (X2) process was used. The prepared specimens are placed in a crucible and tested in a DSC machine. The DSC temperature is increased to 150 °C and 3,500 KPa with an inert atmosphere (Nitrogen). When stabilized oxygen is introduced and the time from the introduction of oxygen to the on-set of oxidation is used to describe the OIT value Figure 1. HP-OIT values for materials tested ranged from around 400 minutes to over 2,000 minutes.

To characterize a geomembrane's durability performance samples are aged in an accelerating environment and the OIT is measured before and after aging. This result is usually referred to as "percentage retained" and is calculated by dividing the aged OIT result by the unaged result. The reference ageing environment used is air at 85 deg C according to ASTM D5721.

The Geosynthetics Research Institute (GRI) specification for HDPE (GM13) is used by material manufacturers and design engineers as the minimum material properties and testing frequencies. This standard nominates a minimum unaged HP-OIT level of 400 minutes with a test frequency of every 90 MT for unaged material. HP-OIT after oven ageing (OA) in air at 85 deg C for 90 days should be greater than 80% of the unaged value and is only required to be tested when verifying a material formulation.

1.3 Project Material Testing Requirements

Australian engineers and regulators increasingly are requiring higher material acceptance testing frequencies than the minimum requirements of GM13. The landfill guidelines for the state of Victoria (publication 788.3) as one example require un-aged HP-OIT testing every 10,000 m^2 (approx. 19MT) of geomembrane which is around 5 times more frequent than the GM13 standard. Formulation oven ageing tests are accepted but are often required to be recent, less than 12 months old, with some specifications requiring results that are less than 4 months old. It is not uncommon that oven ageing tests must be undertaken on material produced for the project. Oven ageing materials for 90 days adds significantly to the timeline for the supply and approval of project materials.

The increased frequency of HP-OIT testing and oven ageing tests provides a quantity of data previously not readily available. These data allows us to explore the effect of HP-OIT test repeatability and material behavior. Alternative approaches to the current 90 day test comparing an un-aged specimen with a 90 day aged specimen have also been explored seeking to reduce the time to characterize this durability characteristic.

2. TEST VARIABILITY

ASTM D5885 lists test repeatability as 6.5% and reproducibility as 25%. Koerner (2016) showed repeatability at 0.02 and reproducibility at 0.09. Published papers typically show CoV values from research laboratories of between 2% and 10% (Rowe et al, 2019). When assessing durability performance by the comparison of two HP-OIT results variability is compounded and variability of the oven ageing process applies cumulatively to the durability result variability. As with any testing there is inherent variability, this variability can be due to a number of factors in terms of the HP-OIT test the following factors can contribute to the variability.

2.1 Product Consistency

How well the additive package was distributed throughout the product. When one considers the relatively low levels of antioxidant package introduced to the base resin the mixing of this material can have a significant impact on the performance of the product. A second factor which could possibly influence the results, relates to multi layered geomembranes which consist of two or more resin types containing additives which could interact with each other.

2.2 Laboratory Reproducibility

During the study several material specimens were tested in different laboratories. Multiple tests were performed, average results are shown in Table 1. While statistically valid conclusions cannot be drawn from this limited amount of data it does confirms that reproducibility is a factor to consider when interpreting results.

Table 1 - Laboratory results of Material consistency

Material	Lab A	Lab B	Lab C	Lab D	Range
Material D sample 1	944	913			3%
Material D sample 2	800	759			5%
Material C sample 1	1216	1054			15%
Material C sample 2	962	834			15%
Material B sample 1		348	398		14%
Material A sample 2		373	425		14%
Material B sample 2			451	415	9%
Material B sample 1			398	351	14%
Material A sample 2			536	466	15%
Material A sample 2			425	373	14%

2.3 Sample Size

This ties in with product consistency above, were product variability is considered a factor a greater number of specimens are tested in order to mitigate the variability. In the case of ASTM D5885 a single specimen with a mass of 5 ± 1mg is tested Figure 2.

Figure 2 . Specimen Containers.

2.4 Specimen Preparation

There are a number of areas where sample preparation can influence the measurement of the HPOIT values, these are listed below

2.4.1 Specimen modification

In the case of multi-layer geomembranes and specifically in conductive geomembranes some manufacturers require the outer conductive layer to be removed prior to testing as (Wong W and Hsuan Y, 2014) showed that the carbon black can interact with certain antioxidant packages.

2.4.2 Specimen homogenization

Note 4 in ASTM D5885 states the following If the sample requires homogenization prior to analysis, one of the procedures given in Appendix X1, Appendix X2, or Appendix X3 is recommended. Poor sample uniformity will adversely affect test precision. This is important when the specimens have been subjected to accelerated UV or oven aging where the outer layer of the geomembrane will have lost some of the antioxidants. This can create a rough temperature graph (Figure 4) which can affect the accuracy of the measurement, the homogenization process mixes the material thoroughly which produces a" clean" graph.

2.4.3 Specimen Compression molding

The standard requires sample preparation prior testing as the standard requires the specimen to be 250 ± 15µm. In order to reduce the specimen from typically 1 – 2mm down to the required thickness a larger specimen is compression molded (high temperature and high pressure) according to ASTM D4703. The potential issue here is the standard allows a range of temperatures to be applied and ASTM D5885 states "temperature can affect the results etc" but doesn't define the maximum allowable temperature or the maximum duration the specimen can be exposed for.

2.5 Material Type & Specimen Preparation

Several specimen preparation procedures were evaluated including; cutting a cross section of sheet material and trimming to mass (mass preparation only), molding (ASTM D 4976), adding the homogenization process (ASTM D 5885 annexure X2), and testing the material core only (ASTM D 5885 annexure X4). Table 2 shows the average of multiple tests in the same laboratory for the same material type with and without a conductive layer. The influence of specimen preparation process was more pronounced with the conductive material. The response to specimen preparation varied, a different material formulation also with a conductive layer produced higher test values when homogenized and plaqued than when only cut to mass.

Table 2- Results of laboratory test for conductive and non-conductive materials

Material	Homogenised and Plaqued	Mass Preparation Only	Difference
Non-Conductive	514	536	4.2%
	439	472	7.4%
Conductive	379	451	18.9%
	378	445	17.6%
Conductive, (Core material0-Annexure X4)	371	476	28.3%

2.6 Data Interpretation

The standard requires the interpretation of the heat plot produced by the digital scanning calorimeter, by placing a best fit line along the induction/exothermic phase of the test. The application of the "best fit line" is subjective and as such when presented with the same data results can vary between operators. This can become complex when oven aged specimens are tested and the outer layer which has had some depletion of the antioxidant package begins to react sooner than the core, this can produce a multi peak plot which complicates interpretation of the data. The standard was updated in 2017 to include a note on homogenization of the specimen which allows pulverizing of the sample, which essentially blends the sample and compression molding of the material in order to overcome multi peak issue.
Examples of curves are provided below Figure 3a, b, c :

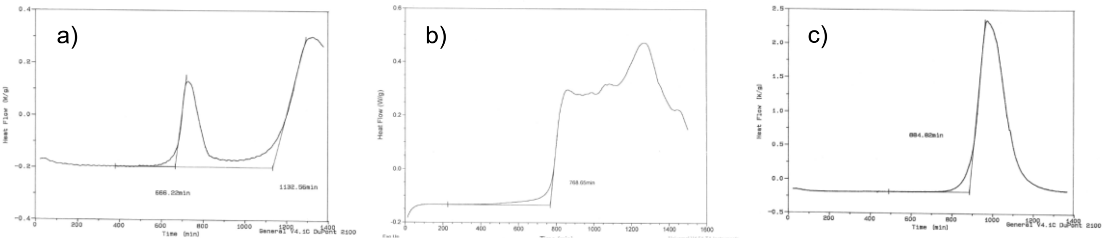

Figure 3 . a) Multi-Layer Geomembrane plot. b) Aged Non-homogenized plot. c) Aged and Homogenized plot

It can clearly be seen that homogenization will reduce the potential for inter and intra laboratory variation, without this process the inter laboratory will remain in the 25% range.

2.7 Precision Test Procedure

Factors which could contribute to test repeatability issues were considered and the specimen preparation process and test procedure revised to assess if a "precision" approach could reduce the test coefficient of variation (CoV). Specimens were extracted from a HDPE sample in close proximity and were homogenized and compression molded identically. Additional measures were taken to reduce variability. This approach would appear to have merit, Table 3 shows low values of CoV* were achieved.

Table 3- HP-OIT Test & Coefficient of Variation

Test 1	Test 2	Test 3	Av	CoV*
375	374	370	373	0.8%
376	369	360	368	2.4%
347	353	344	348	1.4%
343	334	332	336	1.9%
461	484	458	468	3.3%

343	336	332	337	1.8%
		Average		1.9%

3. HP-OIT TESTING VARIABILITY AND 90 DAY OVEN AGING

3.1 Macro variability

The data in Tables 4 and 5 below are from geomembrane production sequences each of approx. 85 MT. Un-aged HP-OIT testing frequencies were approx. 8MT, compared with GRI GM13 testing frequency of one per 90MT. This increased testing frequency provides data to quantify macro variability of a production sequence. Geomembrane sheet material properties will not be completely uniform. The proportions of resin and anti-oxidant additive, carbon black, uniform mixing, thermal histories during material processing and difference in properties between resin and additive batches are some of the factors which will affect material properties. Sample preparation and testing was consistent with the “precision” processes referenced earlier in this paper. Material D has a coefficient of variation of 3.45% and material B and 5.93%. The contribution of material variability and test repeatability to the overall coefficient of variation is unknown. The data suggests that material variability can be a greater influence in macro variability than test repeatability when the test procedure is highly controlled.

Table 4. HP-OIT results, Material D

Roll #	HP-OIT (mins)
1	913
4	950
9	948
18	956
25	895
31	885
36	940
41	972
46	967
51	982
58	972
Average	944
CoV*	3.5%

Table 5. HP-OIT results, Material B

	HP-OIT (min)
1	476
9	437
16	458
28	429
31	432
36	400
41	442
46	410
52	473
60	428
Average	439
CoV*	5.8%

3.2 Alternative Approach to Characterizing Ageing

Data revealed that when degradation rates were low test repeatability was more significant than the underlying degradation characteristic of the geomembrane. Material F is an example of this, figure 6. A decay trend line is unreliable from this data which has a CoV of around 5%. The unaged result appears to be an unrepresentative outlier, although repeat tests provided similar values. Samples used to oven age geomembrane are typically 0.2m X 0.3m. Variations in geomembrane properties are likely to be small within this area. Variability in results are more likely to be attributable to test repeatability.

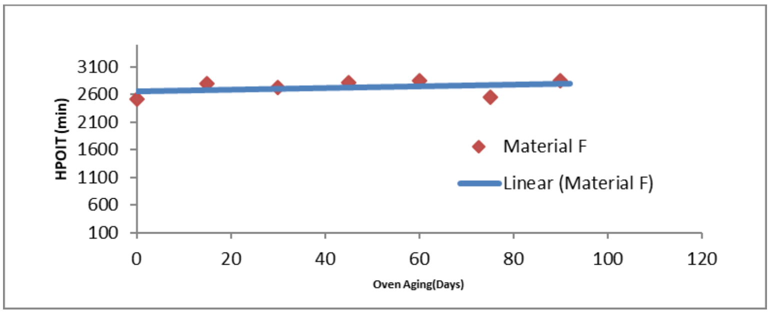

Figure 6. HP-OIT ageing test results of Material F

In published research HP-OIT ageing behavior is usually assessed until values reach a residual level where the antioxidants can still be measured but are no longer protecting the material (Rowe and Shoaib, 2017). Even under accelerated ageing conditions de-activation typically take years. A 1st order three parameter model (exponential decay) has provided a good fit to the HP-OIT decay characteristic in most studies (Hsuan and Koerner, 1998; Rowe et al. 2013), although four parameter models are sometimes appropriate (Abdelaal and Rowe, 2013; Zhang et. Al., 2018). Applying this model to the 90 days of test data has errors associated with commencing at the zero-day test point and modeling to residual values of zero (Ewais et al. 2014). However, over the initial degradation phase during 90-days of oven ageing it may prove useful. A linear regression model was considered as this model uses all data points with equal weighting and does not rely on the zero-day test result calculating the modeled zero-day result. In the table below material E and G were tested to typical industry test procedures and materials and have higher test repeatability than material D and C which were tested to the enhanced, precision test procedure. Measurements were taken every 15 days during oven ageing.

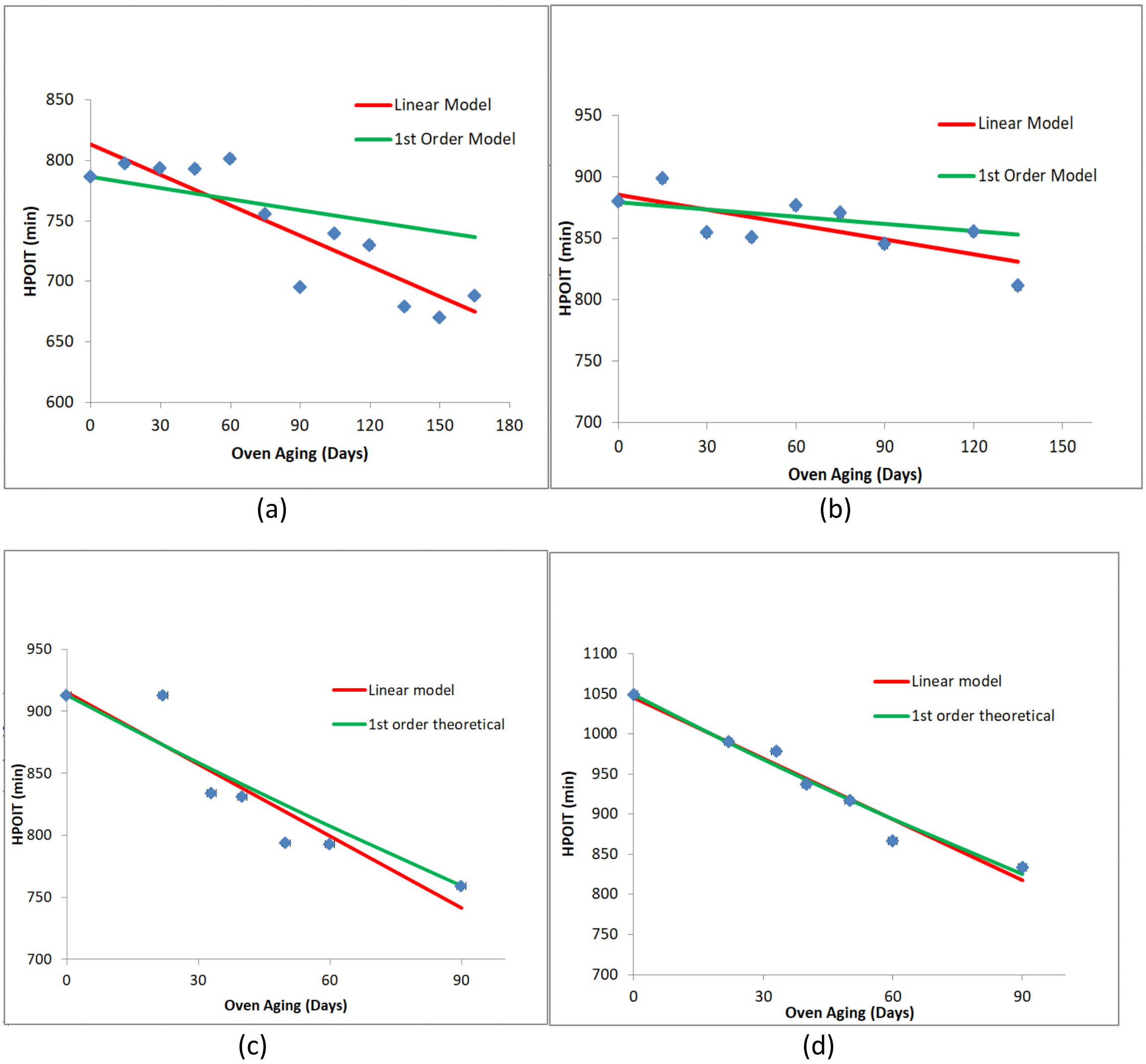

Figure 7 . HP-OIT ageing Test Results. a) Product E. b) Product G. c) Product D. d) Product C

Linear regression and first order exponential models from the graphs in figure 7 are compared in table 6, data having been normalized. Results for material G with a low degradation rate, (<95% at 90-days) had the lowest R^2 value and consistent with other findings for materials with low degradation rates the underling degradation characteristic is difficult to determine in this test period.

Table 6 . 90 days aged test results

Comparison - 90 day % retained					
	Linear		1st Order		0 v 90
	%	R^2	%	R^2	
Material E	90.7%	0.79	96.5%	0.79	88.4%
Material G	95.9%	0.56	98.0%	0.55	96.1%
Material D	78.2%	0.96	78.7%	0.97	79.5%
Material C	81.0%	0.86	83.2%	0.87	83.2%

The R^2 values for the remaining materials (E, D and C) are very similar for both models with values indicating reasonable model fit. For materials C & D the both models correlate with the unaged HP-OIT and 90-day aged results, while there are differences between models with material E. The material E data indicates increasing HP-OIT levels over the first 45 days, which is improbable and more likely reflective of test repeatability factors. The first order model being reliant on the unaged HP-OIT result is predicting a low degradation rate at 90 days while the linear regression model predicts a more reliable unaged HP-OIT result. The 90-day HP-OIT result appears to be an outlier. The linear regression 90-day result of 90.7% is probably a better characterization of the materials ageing characteristic than the comparison of measured values when un-aged and after 90-days of ageing (88.4%).

3.3 Multiple Time-Based Data Points

When testing to approve project materials there is usually insufficient time to extend the test duration beyond the GM-13 nominated 90 days. Figure 8 shows results from material samples tested to current industry practice with a test interval of 15 days oven ageing. The data shows why comparing a singular un-aged HP-OIT result with a 90-day aged result can be unreliable. A benefit of assessing oven ageing performance with multiple tests and short time intervals between tests is that the degradation characteristic is revealed. Unusual results, outliers, which do not fit the regression model well become apparent as do multi-component decay characteristics. It is therefore suggested that testing more specimens over a shorter time interval and fitting data into a linear model can enhance the accuracy of the degradation prediction, while testing a similar number of samples at limited age points will not provide an insight into the materials performance as the observed changes in data can simply be due to variation in test results, and not a true indication of materials behavior.

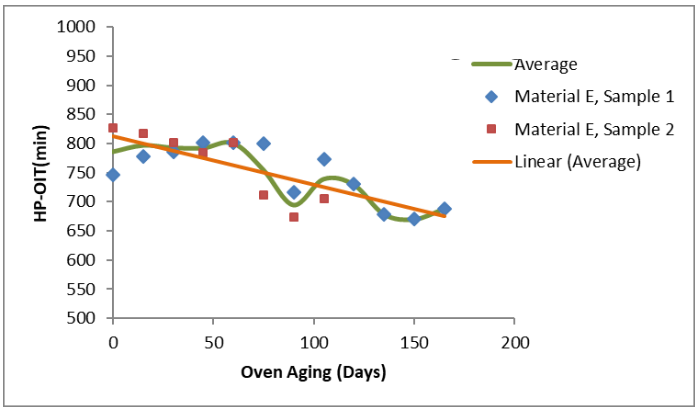

Figure 8. Oven ageing test results of material E, samples (1,2)

3.4 Predicting 90 Day Retained Performance

Further investigations were performed to determine whether a reduced testing period could predict the 90-day result. This would offer a significant advantage in product supply and acceptance testing. The data in figure 9 was to the “precision” process minimizing test repeatability.

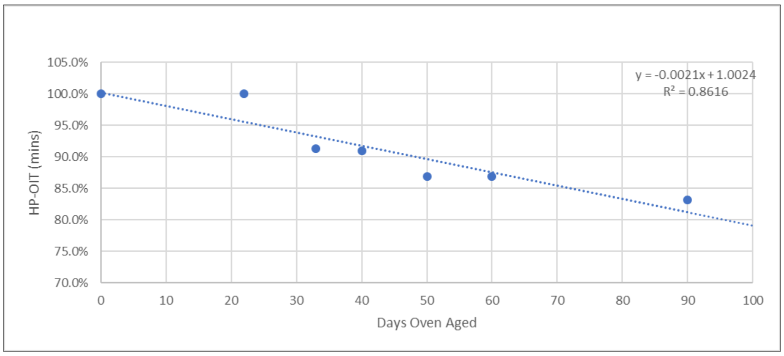

Figure 9. Oven aged HP-OIT results of material C

A linear model was used to predict the 90-day result based on data up to 50 days, up to 60 days and all the data to 90 days as shown in table 7. The 90-day result based on comparing unaged HP-OIT and 90-day aged HP- OIT test results and the linear model using all data were similar. With precision testing and an increased testing frequency linear model prediction at 50 days and 60 days are similar to values obtained at 90 days.

Table 7. Prediction for Retained HP-OIT @ 90 days – Material C

Oven Ageing (days)	Regression coefficients M	C	R^2	Retained HP-OIT (%)	Measured HP-OIT (%)
50	-0.0025	1.002	0.823	77.7%	
60	-0.0023	1.007	0.855	80.2%	
90	-0.0024	0.997	0.860	78.1%	79.50%

4. CONCLUSION

Materials acceptance testing has been largely based on GRI GM13 testing requirements. Increasingly durability testing of project materials is required and typically durability is determined by the materials OIT response to ageing in air at 85 deg C for 90 days. Repeatability and reproducibility, and the time required to undertake ageing tests can make the interpretation of results problematic.

Having tested statistically significant sample sizes variability of HP-OIT measurements are shown to be significant arising from test repeatability and material consistency. Variability in results should be considered when assessing short duration, (90 day) ageing characteristics where individual data points are often used to determine performance, unlike long term testing where data can be averaged and smoothed in exponential models. The accuracy of durability characteristics determined over 90 days by comparing two ageing points compounds repeatability characteristics.

Sample preparation can have a significant effect on the measured HP-OIT result. Multi-layer materials can respond differently to specimen preparation depending on the material formulation. A precision specimen preparation procedure and test procedure has been developed which has reduced the test CoV. This has assisting in the ability to more accurately determine material durability characteristics over short test periods. The study did not define a universally best specimen preparation procedure.

Durability performance was best characterized by increasing the frequency of tests and using a precision test procedure and applying a linear regression model to the data. This approach assisted with identifying outlier test points and revealing if a multi-component decay characteristic was present.

With the testing approach developed it was possible to predict with reasonable accuracy 90-day degradation levels of materials after 60 days of testing.

REFERENCES

ASTM D 4703. Standard Practice for Compression Molding Thermoplastic Materials into Test Specimens, Plaques or Sheets, ASTM International, West Conshohocken, PA.

ASTM D 4976. Standard Specification for Polyethylene Plastic Molding and Extrusion Materials, ASTM International, West Conshohocken, PA.

ASTM D5721, Standard Practice for Air-Oven Aging of Polyolefin Geomembranes, ASTM International, West Conshohocken, PA.

ASTM D 5885. Standard Test Method for Oxidative Induction Time of Polyolefin Geosynthetics by High-Pressure Differential Scanning Calorimetry, ASTM International, West Conshohocken, PA.

EPA Victoria publication 788.3, Best Practice Environmental Management – Siting, Design, Operation and Rehabilitation of Landfills Victorian Government Gazette on 12 August 2015).

Ewais, A.M.R. Rowe, R.K. and Scheirs, J. (2014), *Degradation behavior of HDPE geomembrane with high and low initial high-pressure oxidative induction time*, Geotetiles and Geomembranes, 42 (2014) 111-26.
Hsuan, Y.G. Koerner, R.M. (1998), Antioxidant depletion lifetime in high density polythelyne geomembranes, J. Geotech. Geoenviron. Eng. 125 (6), 532-541.

Koerner, G. R. (2016), Geosynthetics Institute's Laboratory Accreditation Program: A Twenty (20) Year Review, GeoAmericas 2016, Miami Beach, USA.

Muller, W (2007). *HDPE Geomembranes in Geotechnics*, Springer-Verlag Berlin Heidelberg, Germany.

Rowe, R.K. Abdelaal, F.B. Brachman, R.W.I. *(2013), Antioxidant depletion from an HDPER geomembrane with a sand protection layer,* Geosynthetics Institute. 20 (2), 73-89.

Rowe, R. K. and Shoaib, M. (2017), Effect of brine on long-term performance of four HDPE geomembranes, Geosynthetics International vol 24 No. 5.

Wong, W. and Hsuan, Y. (2014), Interaction of anti-oxidants with carbon black in polyethylene using oxidative induction time methods, Geotextiles & Geomembranes Vol 42, 641-647.

Zhang, L. Bouazza, A. Rowe, R. K. and Scheirs, J. (2018), Effects of a very low pH solution on the properties of an HDPE geomembrane, Geosynthetics International, 25, No. 2.