

The oxidation and mechanical performance of HDPE geomembranes: a more practical durability parameter

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ABSTRACT: The mechanical durability of an HDPE geomembrane is assessed by measurements of oxidative induction time (OIT) and stress cracking resistance. The measurement of OIT is performed at 200°C so may not reflect the oxidation resistance at lower service temperatures. And in exposed environments the stress cracking process may only be initiated when all antioxidants have been consumed. An attempt has therefore been made to develop an oxidation resistance test at service temperatures then to combine oxidation resistance and stress cracking resistance to generate a single material durability factor (MDF).

1 BACKGROUND

Over the 15 years between 1980 and 1995 there were many stress cracking failures in high density polyethylene (HDPE) geomembranes, but since that time resins have been developed with more acceptable stress cracking resistances. However, recent experiences with cracking in and adjacent to welds, at point stresses, and at folds in HDPE geomembranes exposed for only eight years and less have identified a synergism between stress cracking resistance (SCR) and oxidation with respect to the mechanical durability of lining systems. This has occurred in HDPE geomembranes exceeding presently acceptable SCR and OIT parameters, 200 hr in the ASTM D5397 SCR-SP test and 100 min in the ASTM D3895 OIT test. This is of particular significance in exposed geomembranes and probably for primary liners in bioreactors. In bioreactors temperatures are higher and the settlement of the waste may induce higher stresses in the HDPE geomembranes. Stress cracking is accelerated at higher temperatures, as is oxidation.

The oxidation resistance of a geomembrane is usually defined by the oxidative induction time (OIT), which is a measure of the resistance to oxidation at 150°C (HP-OIT, ASTM D5885) or 200°C (standard OIT, ASTM D3895). OIT is often taken as being a measure of the mechanical lifetime of the geomembrane. However, if there is no stress on a geomembrane when all the antioxidant (AO) has been consumed, mechanical failure will not occur. If there is stress on the geomembrane its ultimate failure (break) time will then be a function of the basic SCR of the resin/geomembrane (the tie-molecule density). Therefore, a system that combines SCR and OIT, or some other measure of oxidation resistance, is proposed for a more practical assessment of the mechanical lifetime of an HDPE geomembrane. Thus, a material with a short OIT but high SCR could have a longer time to failure than a material with a long OIT but a lower SCR.

To protect an HDPE component from oxidation, the AO package consists of several components that protect the HDPE from oxidation over different temperature ranges. It has to be protected against the high extrusion temperatures, the cooling period after extrusion, during welding (twice where repairs are made), and during service where temperatures can be higher than 80°C. Therefore, measurements made at 150° and 200°C may not reflect the oxidation performance at lower service temperatures of, typically, 20° to 80°C. A material could have adequate resistance at elevated temperatures but poor resistance at service temperatures, and vice versa.

In service, oxidation of the surface layers obviously occurs first so cracking is initiated at flaws (scratches, notches) on the surface. However, the specimen for OIT measurement is taken through the full thickness of the specimen therefore averaging

the AO content throughout the full thickness of the geomembrane. Clearly, the surface layers could be fully oxidized but have very little impact on the overall OIT parameter. Consequently, it is more appropriate to measure the rate of oxidation of thin (surface) layers to effectively assess the potential practical start of the induction period for stress cracking.

Measured OIT values (at 200°C) in presently available commercial HDPE geomembranes vary by a factor of more than 3, from about 70 to 240 min. SCR-SP values vary by a factor of about 100 from 150 to 15,000 hr. Conversely, one of the conventional mechanical properties of HDPE geomembranes show differences exceeding a factor of about 1.25. Clearly the SCR and oxidation performance of an HDPE geomembrane primarily define its long-term mechanical performance, these being the only parameters that define the differences between HDPE geomembranes made with available resins. In recent installations the authors have seen liner failures in elevated temperature and oxidizing environments within 6 months to 8 years of installation due to selection of inappropriate materials. In the latter case the as-manufactured geomembrane displayed an SCR value of about 240 hr and an OIT of 102 min. However, after 9 years the OIT of exposed material was reduced to about 1.5 min, effectively zero. Evidently, while the AO package in the material demonstrated adequate OIT, the AO was rapidly consumed by exposure at service temperatures between about 15 and 85°C. Therefore, the relative oxidation performances of HDPE geomembranes at elevated test temperatures are not necessarily the same as they are at lower service temperatures.

Therefore, it might be practical to express the mechanical durability of any given HDPE geomembrane in a single term that is a combination of the SCR and the resistance to oxidation under service conditions. This performance characteristic should be determined at 80° or 85°C, which is the highest temperature that the average geomembrane will experience in service, be it exposed, or be it in the most aggressive bioreactor landfill.

The carbonyl group content (CC) of the HDPE provides a measure of the degree of oxidation. Based on past unpublished research work by one co-author (Thomas), it was expected that CC could be expressed on an absorbance unit scale from 0.05 to 1.0, with 1.0 being fully oxidized and zero being unoxidized. Then a single durability factor (MDF) could be expressed as a ratio of SCR/CC, with durability increasing as the MDF increases. Thus, an HDPE with a 200 hr SCR would have an MDF between 4000 (CC=0.05) and 200 (CC=1.0) while an HDPE with a 5000 hr SCR would have an MDF between 100,000 and 5000. Thus, MDF's could vary over a wide range between 200 and 100,000 approximately.

It would then become possible to identify say four different classes of HDPE geomembrane with MDFs between 200 and

1000, 1000 and 5000, 5000 and 25,000, and over 25,000, that would be suitable for different types of applications according to the criticality of the application. For instance, golf course ponds would typically require a low MDF liner, MSW landfills a moderate MDF liner, and hazardous liquid ponds a high MDF liner. It does not make sense for a golf course pond to potentially have the same durability liner as a hazardous waste pond nor would the hazardous waste pond owner be comfortable knowing he had the same durability liner that was used in a golf course pond.

2 EXPERIMENTAL OBSERVATIONS

Three production geomembranes, Samples 1, 2, and 3, manufactured and supplied for liner projects within the past three years were selected for oxidation testing. They had SCR/OIT times of: (1) 60 hr/140 min; (2) >4000hr/140 min; and (3) 284 hr/140 min.

Instead of using OIT as the measure of oxidation resistance, a melted and pressed thin film (approximately 6 μm in thickness) was mounted in a standard FTIR specimen holder, the carbonyl content measured in the FTIR spectrometer, then the specimen was heated in an air oven for different times up to 900 hr at 85°C. It would be preferred to use an unheated, original-microstructure microtomed section of the actual geomembrane but microsections with a sufficiently large area are impractical to obtain from a thin geomembrane. After heating in air (oxidation) the specimen was re-placed in the FTIR spectrometer to measure the change in carbonyl content (CC) – a measure of the degree of oxidation.

Three spectra from the same as-received (unheated) specimen of each sample are shown in Figure 1. Figures 2, 3, and 4 show spectra from Samples 1, 2, and 3 respectively after heating for up to 900 hr. The spectra are normalized to the peak at 1370 cm^{-1} at an absorbance of 0.5 units, and changes in the height of the carbonyl peak at 1740 cm^{-1} were examined as a function of time to give the relative degree of oxidation (CC). Unfortunately, as noted in Figure 2 to 4, no significant progressive differences could be seen - it was not even necessary to measure the peak heights.

The spectra of Sample 1 do show small bumps at 1740 cm^{-1} that indicate a little oxidation had occurred in the material prior to testing. There are significant peaks in the spectra of Sample 2 indicating a higher degree of oxidation than in Sample 1. However in Sample 3 there is essentially no prior oxidation. More significant changes in peak height were expected from the oxidation tests. Since all samples were recently manufactured this pre-test oxidation probably occurred during the manufacturing process or during melting and pressing the thin film.

It is interesting to note that Sample 2 showed the most pre-test oxidation – oxidation that likely occurred just over the melting temperature of about 125°C – even though Sample 3 had the lowest OIT and would be considered to have the lowest oxidation resistance. Both Samples 1 and 2 had OITs of 140 min, so would conventionally be expected to have very similar oxidation resistances. While confirmatory testing would need to be done, this may be an indicator that relative oxidation rates at lower temperatures are indeed different to those at higher temperatures.

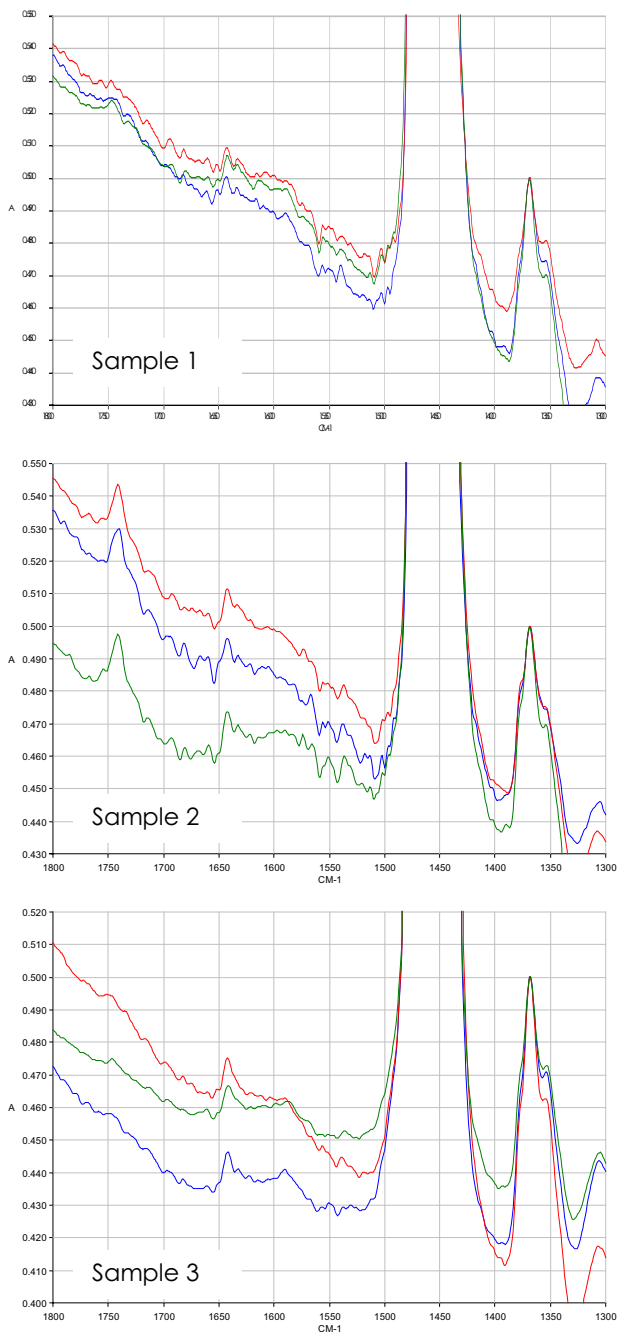
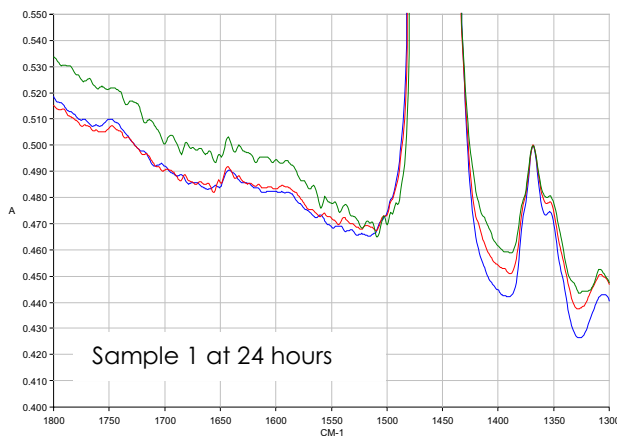


Figure 1 As received IR Spectra



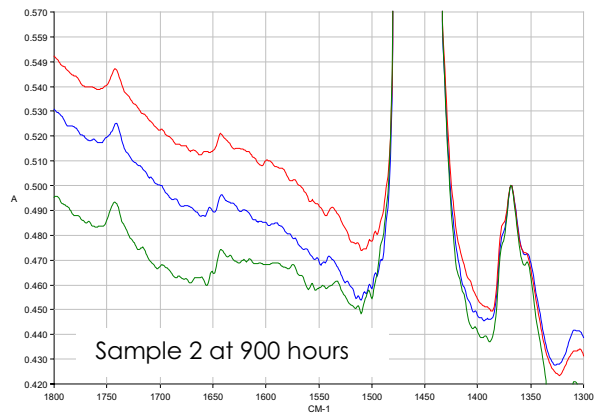
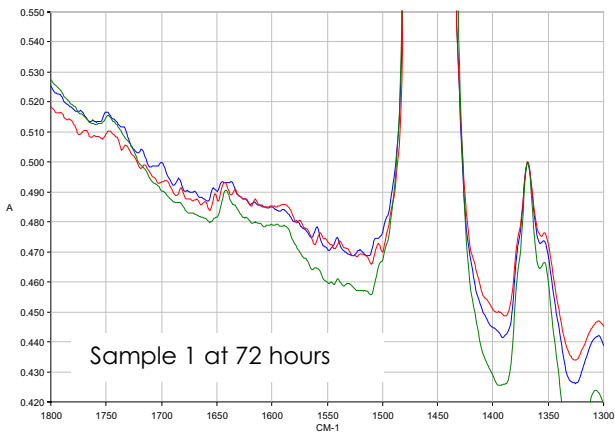


Figure 3. Spectra of Sample 2 heated up to 900 hr

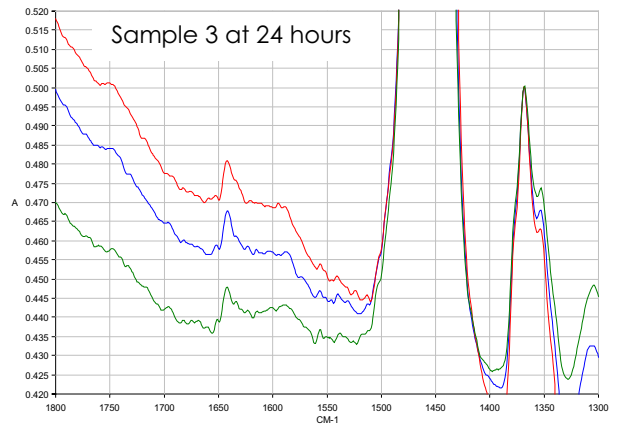
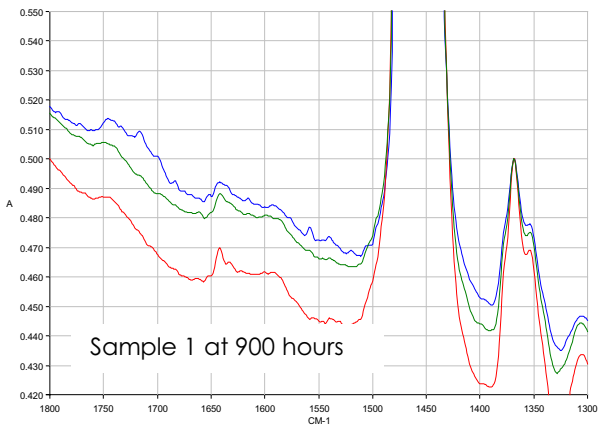
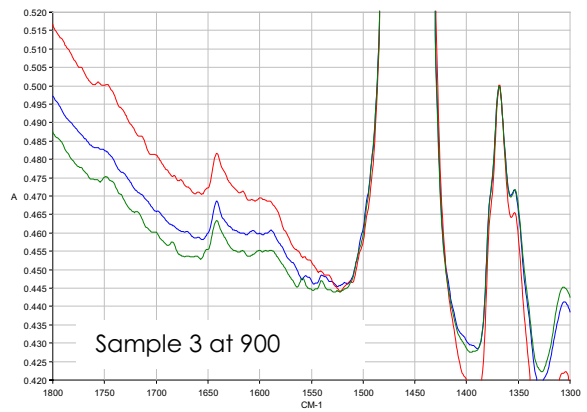
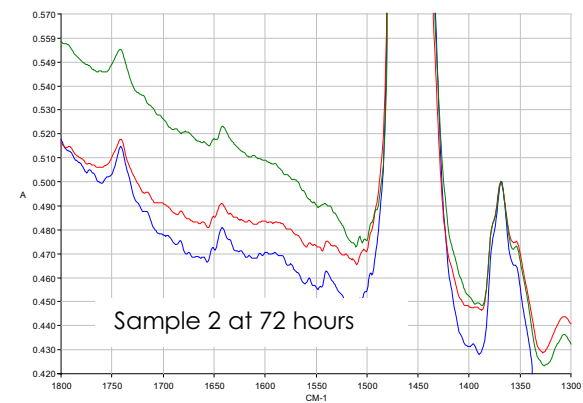
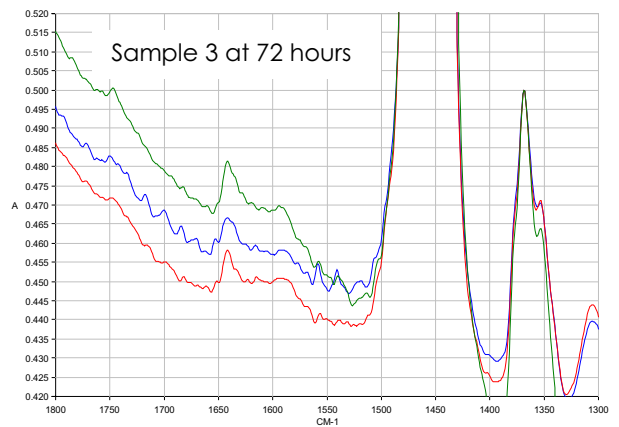
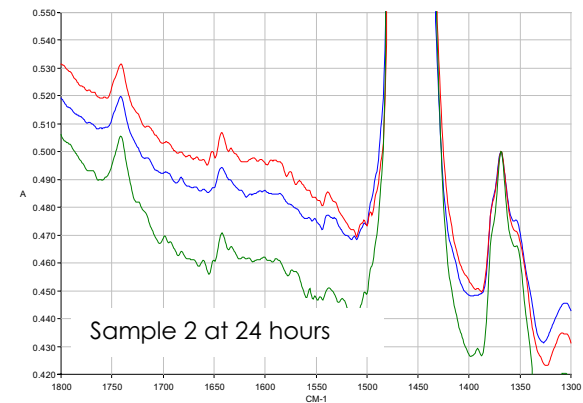


Figure 2 Spectra of Sample 1 heated for up to 900 hr



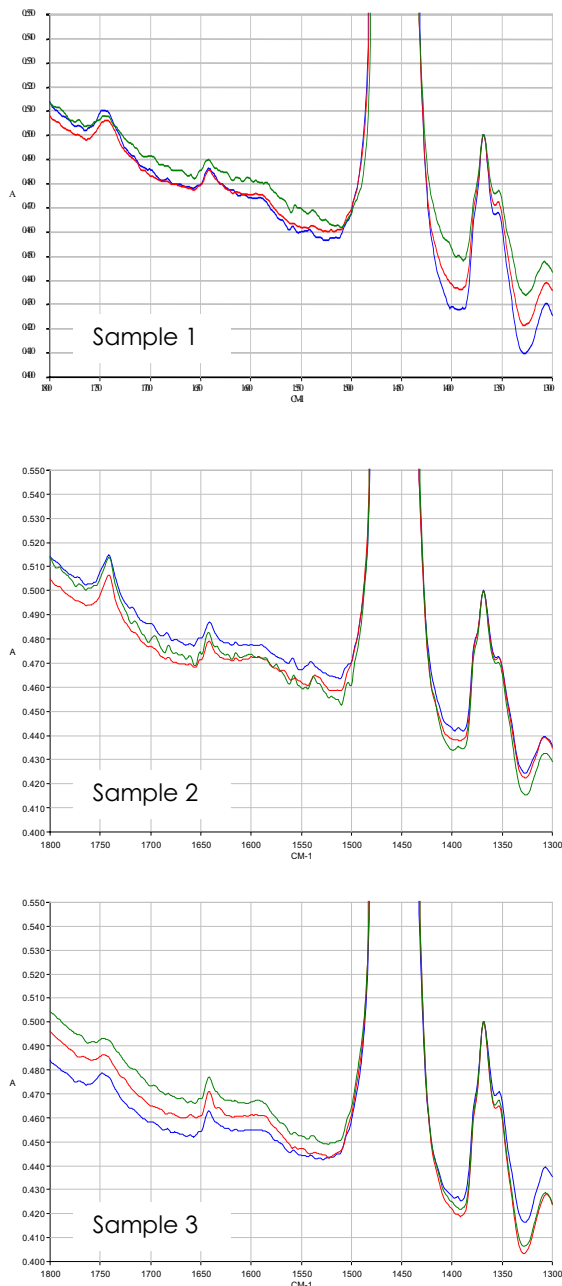


Figure 5. IR spectra after 24 hours in oxygenated atmosphere

The results unfortunately show that at an oxidation temperature of 85°C there is no significant increase in carbonyl content in any of the specimens. Therefore this is not a meaningful test and will not achieve the desired objective. This perhaps demonstrates the difficulty of performing real-time oxidation tests. However, the heating, while not performed in a stagnant air oven, was not performed in a forced air oven. Significant improvements in oxidation rate might be achieved by heating in a forced air oven, in an oxygenated atmosphere, or even in a pressurized oxygen atmosphere similar to the ASTM D5885 OIT test.

At the time of writing this paper, heating in an oxygenated atmosphere (unpressurized) had just commenced. Figure 5, shows that after only 24 hr (at 90°C) a more significant carbonyl group peak was apparent in Samples 1 and 3, indicative of more oxidation. Testing is continuing. Thus there is potential for achieving the objective of the test by using an enriched oxygen atmosphere. Whether a pressurized atmosphere is required re-

mains to be determined. In any case, the testing time should not exceed about 200 hr. Clearly, the test is a performance test to evaluate the performance of different resins and different additive packages, so would not be performed frequently as a quality control or quality assurance test.

If an oxygen atmosphere test does not generate measurable differences in the carbonyl content one could revert to using the OIT time, normalized to 100 min, for the oxidation factor (OF), bearing in mind the possibility that OIT can be varied without any influence on the oxidation resistance at service temperatures. The opposite is also true. The OF would vary between 0.75 and about 2.5.

Since an OIT-based oxidation factor (OF) is high for high oxidation resistance the MDF would be $SCR \times OF$ and would vary between 75 and 45,000. Thus low criticality applications might require MDFs between 75 and 400, moderate criticality applications between 400 and 1000, and critical applications above 1000. However, the primary influence of the SCR on the MDF must clearly be recognized.

3 SUMMARY

It is impractical to measure the oxidation resistance of an HDPE geomembrane by heating in normal air at 85°C then by measuring the carbonyl group content. The use of an enhanced oxygen environment shows some promise and is being further investigated.

The Material Durability Factor (MDF), which is SCR/CC when evaluating oxidation resistance by carbonyl group content, and $SCR \times OF$ when using normalized OIT, provides a single-parameter measure of the long-term mechanical durability of HDPE geomembranes.

Only OIT, SCR, and consequently MDF identify the long-term performance differences between the commercially available HDPE geomembranes – all the other conventional mechanical properties are essentially identical.

OIT does not necessarily reflect the oxidation resistance of HDPE geomembranes at lower service temperatures.

MDF provides a basis for the classification of HDPE geomembranes from commodity through specialty applications having different degrees of criticality.

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