

Antioxidant Depletion from Single-sided and Double-sided Textured Geomembranes in Two Different Immersion Solutions

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ABSTRACT

Texturing of one or both sides of the geomembrane is a common technique to enhance the interface friction between the surface of the geomembrane liner and its overlying geosynthetic layer or the underlying subgrade. However, there is a paucity of the research investigating the effect of texturing on the performance of high density polyethylene (HDPE) geomembranes. This paper investigates the antioxidant depletion from a single-sided and double-sided textured HDPE geomembranes produced by the same manufacturer and from the same nominal resin incubated in a synthetic municipal solid waste leachate and chlorinated water at 85°C. These two incubation media were selected to speed up the antioxidant depletion stage to assess the performance of the two geomembranes in a short period of time. Based on a six-month incubation duration, results from the standard and high pressure oxidative induction time (OIT) tests from the two geomembranes showed very similar OIT depletion times for the two geomembranes in the two immersion solutions except for the high pressure OIT results in chlorine.

Keywords: textured geomembrane, municipal solid waste leachate, chlorine, antioxidant depletion

INTRODUCTION

Geomembrane (GMB) liners as part of the barrier systems in different geoenvironmental applications are used to contain liquids and gases to prevent their migration to the surrounding environment. GMB liners are usually combined with a low hydraulic conductivity layer (such as compacted clay or geosynthetic clay liner) and other geosynthetic layers to form the composite liner system. Although this combination improves the effectiveness of the composite barrier layer in minimizing the flow of contaminant into the underlying soil, the stability of the multilayered barrier system on steep slopes should be carefully considered (Ali et al. 2012). Sliding failures on steep slopes have been observed and reported for smooth GMBs due to their low surface roughness (Koerner and Soong 2000). To address this concern, textured GMBs are commonly used to minimize the risk of sliding of the barrier layers (Scheirs 2009).

Texturing is a technique used for increasing the interface friction between the surface of GMB liner and its overlying geosynthetic protection layer or the underlying subgrade. As a

result, the overall stability of the barrier system on slopes is improved. Texturing is applied either to a single side or both sides of the GMB based on composite liner design configuration. There are three major methods for texturing the GMBs that have been used by different GMB manufacturers: 1) co-extrusion texturing by blowing agent injection, 2) impingement or spray-on texturing, and 3) structured or embossed texturing (Müller 2007; Scheirs 2009; Morsy and Rowe 2017).

In the co-extrusion texturing method, one (for single-sided texturing) or two (for double-sided texturing) molten skin layers of nitrogen-infused GMB are co-extruded with the molten core layer through a multi-slot co-extrusion die (Müller 2007). Then, the nitrogen bubbles rupture and cool when the co-extruded GMB exit from the die, consequently, the texture surface is formed. While this method contributes to high interface friction values of the GMB, it results in non-uniform asperity heights and variable core thickness. This may also result in decreasing some of the mechanical properties of the GMB (Scheirs 2009).

Spray-on texturing involves a secondary process where texture particles (from a compatible material with the parent GMB but with lower melting point) are sprayed on the hot surface of GMB core layer and hence fusing into the surface to create the textured surface (Müller 2007; Scheirs 2009). While this method produces a textured GMB with consistent core thickness and homogenous structure (Scheirs 2009), the interface shear resistance is lower than that obtained from co-extrusion texturing (Ericson et al. 2008).

The third texturing method involves structuring the surface of the hot GMB sheet directly after extrusion from a flat die using embossed roller(s). This results in a consistent asperity and core thickness but more importantly, a textured surface from the same exact material of the core GMB (Scheirs 2009). Furthermore, double-sided textured GMB with two distinct patterns with different friction resistance can be produced from this method (Müller 2007).

Although all texturing methods can improve the interface friction angle of the GMB, texturing the surface can affect the GMB mechanical properties. For instance, due to the variation in thickness of textured GMBs, tensile properties at break can be reduced. This can be evidenced from the lower break strength/strains set as the minimum requirements by GRI-GM13 (2016) for textured GMBs compared to those required for their smooth counterparts.

For the effect of texturing on the GMB durability, Morsy and Rowe (2017) examined the antioxidant depletion from a 1.5 mm black textured GMB and its smooth edge of the roll (for welding purposes of the roll in the field). Their results showed that texturing of GMB slightly increased the rate of antioxidant depletion resulting in approximately 15% reduction of the antioxidant depletion time for their examined GMB. In general, there is a paucity of research examining the effect of texturing on the GMB durability. Thus, the objective of this paper is to investigate the antioxidant depletion from a single-sided textured and a double-sided textured high density polyethylene (HDPE) GMBs produced by the same manufacturer.

EXPERIMENTAL INVESTIGATION

Examined GMBs and Index Testing. The examined GMBs were 2.0 mm white HDPE GMBs manufactured from the same nominal resin by the same GMB manufacturer in 2017. The GMBs were textured using the co-extrusion method by injecting nitrogen on both sides (GMB 1) and one side (GMB 2) of the core layer. Different ASTM index tests were used to assess the initial properties of the GMBs (Table 1) and to monitor their aging with time. Standard oxidative induction time (Std-OIT; ASTM D3895) and high pressure oxidative induction time (HP-OIT;

ASTM D5885) tests were conducted using a differential scanning calorimeter (DSC) to measure the initial OIT values for the two GMBs in addition to assessing the antioxidants depletion time for the aged GMB specimens. In the Std-OIT tests, bore-cut specimens were heated from ambient temperature to 200°C at a rate of 20°C/min in a nitrogen environment. The isothermal conditions were maintained for 5 min in nitrogen and then the gas was replaced by oxygen at a pressure of 35 kPa. The Std-OIT test was used to detect antioxidants with high effective temperatures such as hindered phenols and phosphites. The HP-OIT tests were conducted at 150°C and cell pressure of 3450 kPa (500 psi) to detect antioxidants such as hindered amine light stabilizers (HALS) and thiosynergists with lower effective temperatures.

Table 1. Initial properties of studied GMBs (mean ± standard deviation).

Property	Method	Unit	GMB 1	GMB 2
Type	-	-	Double-sided textured HDPE	Single-sided textured HDPE
Color	-	-	One-side white	One-side white (textured side)
Std-OIT	ASTM D3895	minutes	285 ± 4.0	245 ± 25
HP-OIT	ASTM D5885	minutes	960 ± 80	715 ± 50

Accelerating Aging Method. The relative performance of the examined GMBs was investigated using jar immersion tests. In this method, 16 GMB coupons (190 x 100 mm) were incubated in 4-liter glass jars and separated by 5 mm glass rods to ensure that the leachate was in contact with the two surfaces of GMB. The solution was then added to jars and they were placed in a forced air oven at 85°C. The GMBs were only incubated at 85°C to assess their relative performance in a short period of time.

Incubation Solutions. Immersion tests were conducted using synthetic municipal solid waste (MSW) leachate and chlorinated water. The examined MSW leachate (Table 2) was reduced to simulate the shortage of oxygen at the bottom liners of MSW landfills. The chemistry of the MSW leachate was adopted from Rowe et al. (2008) based on their findings that the surfactant was the most aggressive chemical on the depletion of the antioxidants.

The chlorinated water solution examined was prepared by mixing 5 ml of sodium hypochlorite (NaOCl) in one liter of reverse osmosis (RO) water (Abdelaal and Rowe 2014a). Abdelaal and Rowe (2014a) examined antioxidant depletion from a 1.5 mm thick HDPE GMB in three different solutions including RO water, MSW leachate, and chlorinated water and showed that chlorinated water had significantly faster depletion rates than the other two solutions. Chlorinated water, therefore, was used in this study as an aggressive incubation media to reach the depletion time in a shorter duration and to provide a comparison of the antioxidant depletion from the two examined GMBs in another incubation media.

To ensure that the solutions strength remained relatively constant, the MSW leachate and chlorinated water were being replaced every 6 weeks and 1 week, respectively. The frequent change for the chlorine solutions was done to prevent excessive evaporation of chlorine at 85°C (Abdelaal and Rowe 2014a).

Table 2. Chemistry of the MSW leachate used in this study (in mg/l except for pH).

Analyte	MSW leachate ¹
pH	6.9
Aluminum	<1.0
Ammonium	555
Boron	<1.0
Calcium	800
Cobalt	0.03
Iron	0.4
Potassium	320
Molybdenum	<0.05
Magnesium	400
Phosphorus	6.0
Chloride	2500
Sulphate	1330
Carbamide	695
Nitrate	<12.5
Bicarbonate	4260
Carbonate	140
Hydrogen phosphate	<50
Surfactant ²	5

¹Based on Rowe et al. (2008)

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RESULTS AND DISCUSSION

Immersion in MSW Leachate. Figures 1 and 2 show the change of the normalized OIT values (i.e. OIT at any given time divided by the initial OIT values) with the incubation for the two GMBs immersed in MSW leachate at 85°C. Normalized values were used to mitigate the differences in the initial OIT values to allow the comparison of the depletion rates of the two GMBs.

After 196 days of incubation in MSW leachate, GMB 1 reached 11 min (4% of its initial value) while GMB 2 reached 12 min (5% of its initial value) at 85°C (Figure 1). The OIT values for the two GMBs are still showing gradual decrease and full depletion of Std-OIT to residual values was not reached. However, there is a clear difference between the early-time and later-time depletion rates of the GMBs and hence the current data were modeled in terms of a four-parameter decay function (Abdelaal and Rowe 2014b), viz:

$$OIT_t = ae^{-s_1t} + be^{-s_2t} \quad (1)$$

where OIT_t (min) is the OIT value at time t , s_1 (day^{-1}) is the early (first) antioxidant depletion rate, s_2 (day^{-1}) is the late (second) antioxidant depletion rate (day^{-1}), t (day) is the incubation time, a and b are the exponential fit parameters where in this case a is the first rate (s_1) y-axis (OIT) intercept, b is the second rate (s_2) y-axis (OIT) intercept, and $a + b = OIT_o$.

Based on 196 days of incubation, the early Std-OIT depletion rates for GMB 1 and GMB 2 were 0.065 and 0.08 day^{-1} , respectively and the later depletion rates were 0.012 and 0.010 day^{-1}

(Table 3). The two GMBs had very similar depletion rates in MSW leachate and the predicted depletion time to a residual value of 1.5 min was around 360-380 days for both GMBs. Thus, the two GMBs showed similar Std-OIT depletion times despite the lower initial Std-OIT of the single sided textured GMB.

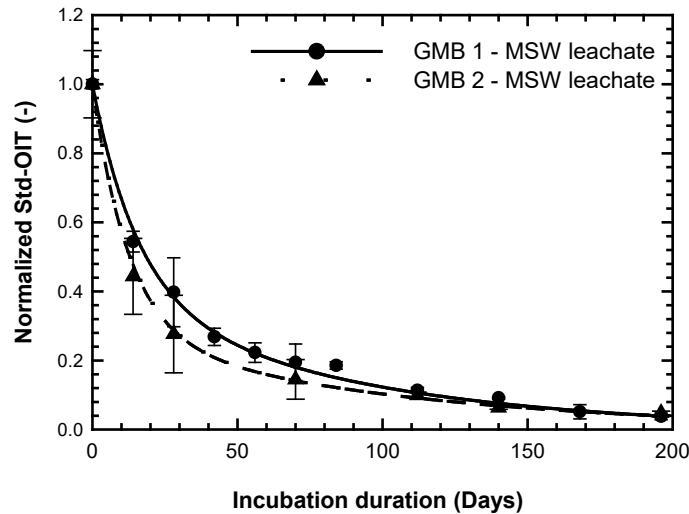


Figure 1. Variation of the normalized Std-OIT vs incubation time for immersion in MSW leachate at 85°C.

In terms of HP-OIT, after 196 days of incubation, the HP-OIT values of GMB 1 decreased to reach 34% its initial values while GMB 2 reached 40% of its initial values (Figure 2). The HP-OIT values are still decreasing with time in MSW leachate at 85°C without reaching the residual values at the end of incubation. Similar to Std-OIT, the two GMBs exhibited very similar HP-OIT depletion rates in MSW leachate despite the differences in their initial values.

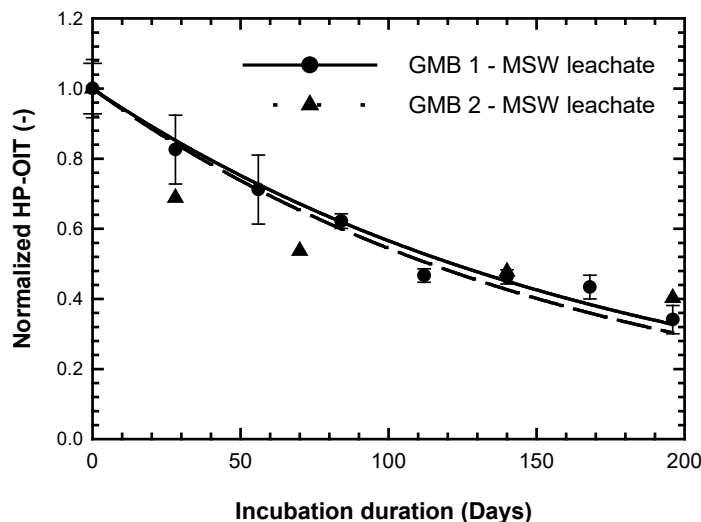


Figure 2. Variation of the normalized HP-OIT with incubation time for immersion in MSW leachate at 85°C.

Immersion in Chlorinated Water. The Std-OIT depletion pattern for immersion in the chlorinated water was similar to that observed in MSW leachate since the GMBs exhibited a clear difference in the early-time and later-time depletion rates (Figure 3). Thus, the Std-OIT data in chlorine was fitted using a 4-parameter exponential equation (Equation 1).

Both GMBs reached around 2% of their initial Std-OIT values after 165 days of incubation in chlorinated water at 85°C. While both GMBs showed similar later-time depletion rates ($s_2 \approx 0.02$), GMB2 had faster early depletion rate ($s_1=0.2$) than GMB1 ($s_1=0.072$). However, since the later-time depletion rates have more effect on the depletion times, both GMBs reached the same Std-OIT values at the end of incubation. Assuming a residual value of 1.5 min at depletion, the predicted time to Std-OIT depletion of the two GMBs was around 190 days. Thus, similar to incubation in MSW leachate, the two GMB showed similar Std-OIT depletion times in chlorinated water.

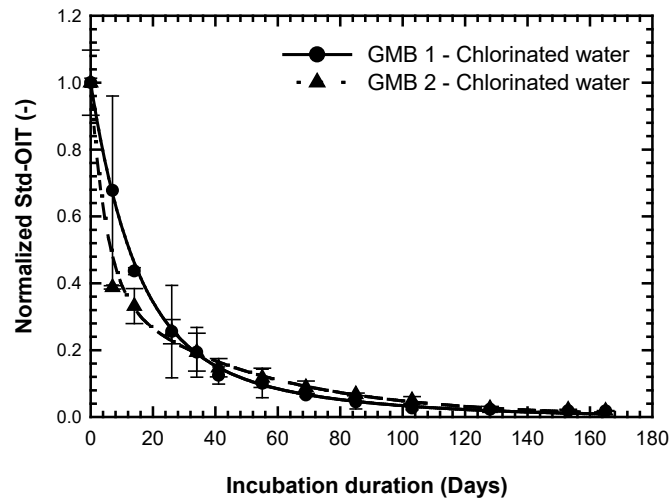


Figure 3. Variation of the normalized Std-OIT with incubation time for immersion in chlorinated water at 85°C.

Table 3. Std-OIT depletion rates after 196 days of incubation in MSW leachate and 165 days of incubation in chlorinated water at 85°C.

Immersion solution	Std-OIT depletion rates for GMB 1 (Day ⁻¹)	Std-OIT depletion rates for GMB 2 (Day ⁻¹)
MSW leachate	$s_1=0.065, s_2=0.012,$ $a=171, b=114$	$s_1=0.08, s_2=0.01,$ $a=176, b=69$
Chlorinated water	$s_1=0.072, s_2=0.02,$ $a=214, b=71$	$s_1=0.2, s_2=0.021,$ $a=150, b=95$

For the HP-OIT in chlorinated water, GMB 1 and GMB 2 reached 56% and 38% of their initial HP-OIT values, respectively, after 165 days of incubation. While the HP-OIT data is still

decreasing and residuals values were not reached, the current results showed that the HP-OIT depletion of GMB 2 was faster than GMB 1.

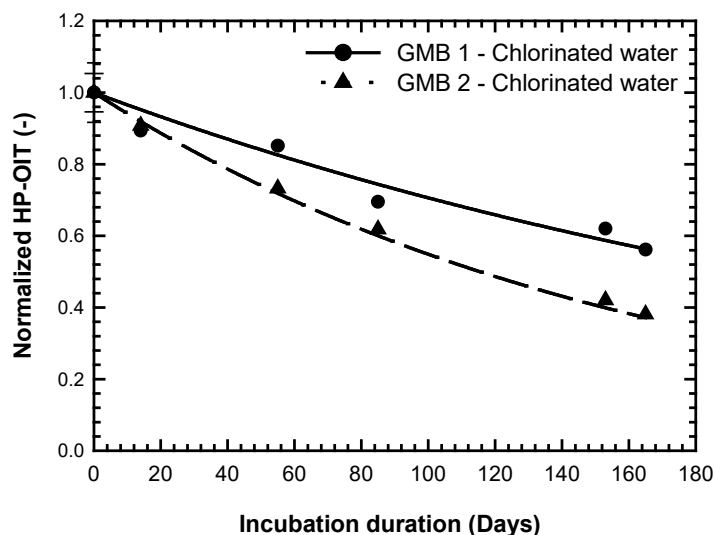


Figure 4. Variation of the normalized HP-OIT with incubation time for immersion in chlorinated water at 85°C.

SUMMARY AND CONCLUSION

The performance of a double-sided textured (GMB 1; $\text{Std-OIT}_0/\text{HP-OIT}_0 = 285/960$) and a single-sided textured (GMB 2; $\text{Std-OIT}_0/\text{HP-OIT}_0 = 245/715$) HDPE GMBs from the same nominal resin was evaluated based on antioxidant depletion by immersion tests. The tests were conducted at 85°C using synthetic MSW leachate and chlorinated water for 196 and 165 days, respectively. Based on the reported results, the following preliminary conclusions were reached:

- Both GMBs showed similar Std-OIT depletion times in MSW leachate and chlorinated water. However, since the double sided textured GMB had higher initial Std-OIT, thus, its antioxidants depleted at a faster rate than the single sided textured GMB.
- While the HP-OIT data in both immersion solutions at 85°C were still decreasing during the incubation duration presented in this study, the two GMBs had similar depletion rates in MSW leachate whereas in chlorinated water, GMB 2 exhibited faster HP-OIT depletion rate than GMB 1. This could be attributed to the difference in the HP-OIT packages used in the formulation of the two GMB and their resistance to depletion in chlorine.
- For the two GMBs examined, the antioxidant depletion in chlorinated water was significantly faster than in MSW leachate.

This paper focused on the relative performance of the two examined GMBs immersed in two different solutions based on the antioxidant depletion detected by the Std-OIT and HP-OIT tests. The results presented in the current study only apply to the specific GMBs tested in the immersion solutions presented. Further incubation is needed to assess the antioxidant depletion to the residual values at 85°C and at lower temperatures for better of understanding of the performance of these GMBs. In addition, monitoring the changes of the physical properties will allow assessment of the degradation behaviour of the examined textured GMBs. The full set of

results will be published in a subsequent paper when they have been run for a sufficient time to draw clear conclusions.

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