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Antioxidant Depletion from Textured Conductive and Non-conductive HDPE Geomembranes in Chlorinated Water

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ABSTRACT

This paper investigates the antioxidant depletion from two multilayered 2.0 mm thick double sided textured, white-surfaced (top side only) high density polyethylene (HDPE) geomembranes using jar immersion tests. Both geomembranes were produced by the same manufacturer from the same nominal resin, but one of the two geomembranes was manufactured with a conductive layer on its black side. The two textured geomembranes had smooth edges and the antioxidant depletion is examined for both the textured and the smooth edges of the rolls to investigate the effect of texturing and conductive layer on the rate of antioxidant depletion. Based on the five months incubation duration in chlorinated water at 85ºC, the preliminary results of standard oxidative induction time (Std-OIT) and high pressure oxidative induction time (HP-OIT) tests showed that the OIT depletion of the conductive geomembrane was faster than the non-conductive geomembrane. In addition, the Std-OIT depletion of the two textured geomembranes was faster than their smooth edges.

1. INTRODUCTION

High density polyethylene (HDPE) geomembranes (GMBs) are commonly used as part of the barrier systems in different geoenvironmental applications. Under long-term field exposure conditions, HDPE GMBs experience degradation that results in the loss of their mechanical properties with time (Hsuan and Koerner 1998; Rowe and Sangam 2002). Hsuan and Koerner (1998) showed that degradation of HDPE GMB involves three different stages including antioxidant depletion, induction time to the onset of polymer degradation, and polymer degradation resulting in change of a GMB property (e.g. tensile property per ASTM D6693; Melt index per ASTM D1238; stress crack resistance per ASTM D5397) to an arbitrary level; often to 50% of the initial value. The rate of the antioxidant depletion mainly depends on antioxidant package used in the GMB and exposure conditions such as service temperature and exposure media. However, even GMBs with the same antioxidant package may have different depletion rates when they are exposed to similar exposure conditions (Morsy and Rowe 2019). Other important factors that can affect the antioxidant depletion rate include manufacturing method, physical characteristics (e.g. thickness) or the percentage/type of carbon black used in the formulation of the GMB.

Texturing of HDPE GMBs is a technique used to increase the interface friction angle between the surface of GMB and adjacent materials. This contributes to higher shear stability on steep slopes and higher factor of safety against sliding of barrier system (Koerner 2005; Scheirs 2009). There are three common methods for texturing the GMBs including co-extrusion texturing, spray-on texturing, and patterning texturing (Müller 2007; Scheirs 2009). Each of these techniques could affect the GMB properties such as core thickness or mechanical properties (Müller 2007; Scheirs 2009; Morsy and Rowe 2019). For example, co-extrusion texturing with injection of blowing agent may cause some variability in the thickness of GMB and eventually lead to change the rate of antioxidant depletion (Morsy and Rowe 2019).

Morsy and Rowe (2019) examined the antioxidant depletion from a 1.5 mm black textured HDPE GMB manufactured using co-extrusion technique. The textured GMB roll had a 1.5 mm smooth edge (to allow welding of the sheets in the field) and thus they investigated the two parts of the roll to examine the effect of texturing. Their results showed that the antioxidant depletion time of the textured part was 40% faster for Std-OIT and 9% faster for HP-OIT compared to the smooth edge and hence concluded that texturing of the examined GMB affected the antioxidant depletion. Zafari and Abdelaal (2019) also compared the antioxidant depletion from a 2.0 mm single-sided to a 2.0 mm double-sided white HDPE co-extruded textured GMBs manufactured by the same GMB manufacturer. They showed that the double-sided textured GMB showed slightly faster Std-OIT depletion rate compared to the single-sided textured GMB after 6 months of incubation in a synthetic municipal solid waste (MSW) leachate and chlorinated water at 85ºC. Therefore, texturing may affect the rate of antioxidant depletion that eventually will affect the overall durability of the GMB.

Co-extruded HDPE GMBs can be produced with a white and conductive skin layers that can reduce the liner temperature for exposed GMBs and facilitate detecting leaks due to installation damage without the need of having conductive subgrade. However, there is a paucity of research investing the potential effects of the pigment/UV additives used in the white layer, or the electrically reactive carbon black used to enhance electrical conductivity, on the long-term performance of these GMBs. Thus, the objective of this paper is to examine the antioxidant depletion from a textured conductive and a textured non-conductive HDPE GMBs and their smooth edges to examine the potential effects of texturing and conductive layer on the antioxidant depletion stage.

2. EXPERIMENTAL INVESTIGATION

2.1 Examined GMBs and Index Testing

The examined GMBs are 2.0 mm HDPE GMBs manufactured from the same nominal resin by the same GMB manufacturer in 2017. The two GMBs were co-extruded with textured surfaces on both sides and a white layer on one side only. A conductive layer was applied to one of the two GMBs (GMB1) on its black side. Both GMBs were produced with smooth edges for the welding purposes in the field. The smooth edges for the two GMBs had different shades of colour from the textured part of the roll (changing from bright white for the textured part to a light grey at the smooth edge) implying that the thickness and the additives used in the skin layers of the smooth edges were essentially less than those in the textured part of the roll.

Different ASTM index tests methods were used to assess the initial properties of the GMBs for both the textured parts (Table 1) and smooth edges (Table 2) of the rolls 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 used to assess both the initial OIT values and the antioxidants depletion time for the aged GMB specimens. The Std-OIT test was conducted using a TA Instruments Q-2000 series differential scanning calorimeter (DSC) in which specimens were heated from ambient temperature to 200ºC at a rate of 20ºC/min in a nitrogen environment. The isothermal conditions were maintained for 5 min in nitrogen and then the gas was changed to oxygen at a pressure of 35 kPa (5.1 psi). Due to high test temperature, Std-OIT can only detect antioxidant with high effective temperatures such as phosphites and hindered phenols used to protect the GMB during the manufacturing stages and during the GMB service life. However, other antioxidants such as hindered amine light stabilizers (HALS) and thiosynergists may volatize at the Std-OIT test temperatures and, thus, cannot be detected in the Std-OIT test. To detect these antioxidants, HP-OIT tests were conducted using a TA Instruments Q20 at 150ºC but under a cell pressure of 3450 kPa (500 psi). Thus, the two tests were conducted in parallel to detect the effect of different antioxidants stabilizing the GMBs on the time to oxidation under the conditions examined in these index tests.

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

Property	Method	GMB 1	GMB 2
Conductivity	-	Conductive	Non-conductive
Std-OIT (min)	ASTM D3895	220 ± 35	285 ± 4.0
HP-OIT (min)	ASTM D5885	705 ± 50	960 ± 80

Table 2. Initial properties of the smooth edges of studied GMBs (mean ± standard deviation)

Property	Method	Smooth edge of GMB 1	Smooth edge of GMB 2
Std-OIT (min)	ASTM D3895	290 ± 20	285 ± 4.0
HP-OIT (min)	ASTM D5885	1460 ± 50	1430 ± 25

2.2 Accelerating Aging Method

The relative performance of the examined GMBs was investigated using jar immersion tests. In this method, GMB samples were cut into 190 x 100 mm coupons and placed in 4-liter glass containers. 5 mm diameter glass rods were placed as separators between coupons to ensure that leachate will be in contact with both surfaces of coupons. The solution was then added to jars and they were placed in a forced air oven at 85ºC. The GMBs were only incubated at 85ºC to assess their relative performance in a short period of time.

2.3 Incubation Solution

Immersion tests were conducted using chlorinated water. The solution was prepared by mixing 5 ml of sodium hypochlorite (NaOCl) in one liter of reverse osmosis (RO) water (Abdelaal and Rowe 2014a). For the effect of immersion solution on the GMB durability, Abdelaal and Rowe (2019) examined antioxidant depletion from a 1.5 mm HDPE GMB in three different solutions including RO water, MSW leachate, and chlorinated water. Their results 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 short duration and to provide a comparison of the antioxidant depletion from the two examined GMBs. To ensure that the solution strength remained relatively constant, the chlorinated water was replaced every week to prevent excessive evaporation of chlorine at 85ºC (Abdelaal and Rowe 2019).

3. RESULTS AND DISCUSSION

3.1 Initial OIT Values

The initial OIT values for the smooth edges of the examined GMBs were almost similar while the initial values for the textured parts were different (Tables 1 and 2). This implies that the two GMBs were manufactured using the same antioxidants stabilizing the core, but the different skin layers may have resulted in the variation in the OIT values between the textured parts of the two GMBs.

The non-conductive GMB (GMB 2) had similar initial Std-OIT value of 285 min for both the textured and the smooth edge while the initial HP-OIT value of the smooth edge (1430 min) was substantially higher (by a factor of 1.5) than the initial HP-OIT of the textured GMB (960 min). The difference in the HP-OIT can be attributed to the difference in the white layer between the smooth edge and the textured part that might have affected the initial HP-OIT of GMB 2.

For GMB 1 with both conductive and white layers, the initial Std-OIT value decreased from 290 min at the smooth edge to 220 min for the textured part. Likewise, the initial HP-OIT decreased from 1460 min at the smooth edge to 705 min at the textured part of the roll. Thus, the change in the conductive and the white layers between the textured and smooth edge of GMB 1 may be responsible for such reduction in the initial OIT values from smooth edge to textured part.

3.2 OIT Depletion of the textured parts

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 chlorinated water at 85ºC. 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.

For both GMBs, there was a clear difference between the early-time and the later-time Std-OIT depletion rates (Figure 1). GMB 2 showed a gradual decrease in Std-OIT over the 165 days to reach 5 min at the end of incubation and hence the current data was modeled using a four-parameter decay function (Abdelaal and Rowe 2014b) viz:

$$OIT_t = \mathrm{a}e^{-s_1 t} + \mathrm{b}e^{-s_2 t} \qquad [1]$$

GMB1 reached a residual Std-OIT value of 4 min after 70 days of incubation and the Std-OIT values stabilized at this value for the remaining 95 days of incubation. In this case, a five-parameter decay function (Eq. 2) was used to model the Std-OIT depletion of GMB1, viz:.

$$OIT_t = \mathrm{a}e^{-s_1 t} + \mathrm{b}e^{-s_2 t} + OIT_r \qquad [2]$$

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, 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, OIT_r (min) is the residual OIT value (i.e., $OIT_t \rightarrow OIT_r$ as $t \rightarrow \infty$), and $a + b + OIT_r = OIT_o$.

The early Std-OIT depletion rates for GMB 1 and GMB 2 were 0.3 and 0.072 day^{-1}, respectively and the later depletion rates were 0.057 and 0.02 day^{-1} (Table 3). Thus, after 165 days of incubation there was faster depletion of Std-OIT of GMB1 than GMB2. Thus, the current results highlight the effect of the conductive layer that resulted in faster Std-OIT depletion time of GMB1 compared to the non-conductive GMB (GMB 2).

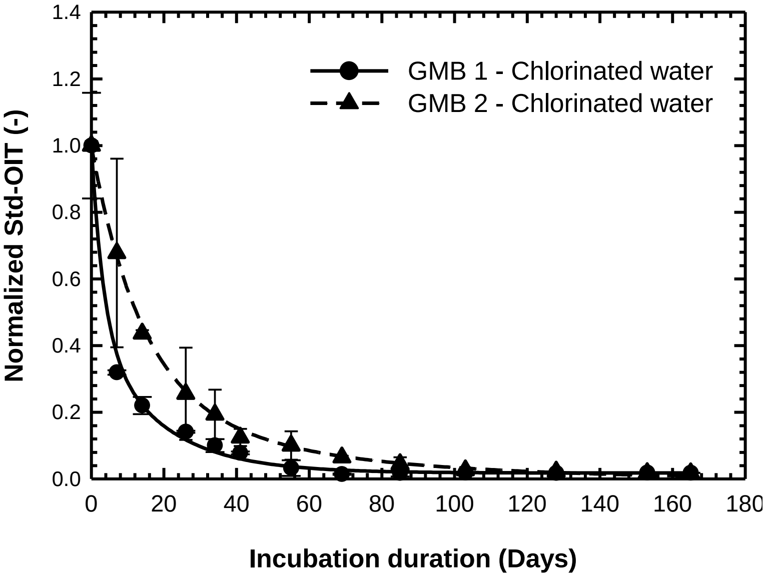

Figure 1. Variation of the normalized Std-OIT vs incubation time for immersion in chlorinated water at 85°C

Table 3. Std-OIT depletion rates and the exponential fit parameters after 165 days of incubation in chlorinated water

GMB	s_1	s_2	a	b	OIT_r
GMB 1	0.3	0.057	121	95	4
GMB 2	0.072	0.02	214	71	-

For the HP-OIT, based on the 165 days of incubation, GMB 1 had a faster depletion rate until reaching a residual value of around 240 min (i.e., 34% of its initial) close to the end of the incubation duration (Figure 2). GMB 2 had slower depletion than GMB1 and was still showing a decrease in the HP-OIT values at the end of the 165 days without reaching a residual value. The current results show that the HP-OIT depletion of GMB 1 was faster than GMB 2 similar to Std-OIT depletion. However, more data is needed to establish the depletion rates and residual OIT values for the two GMBs.

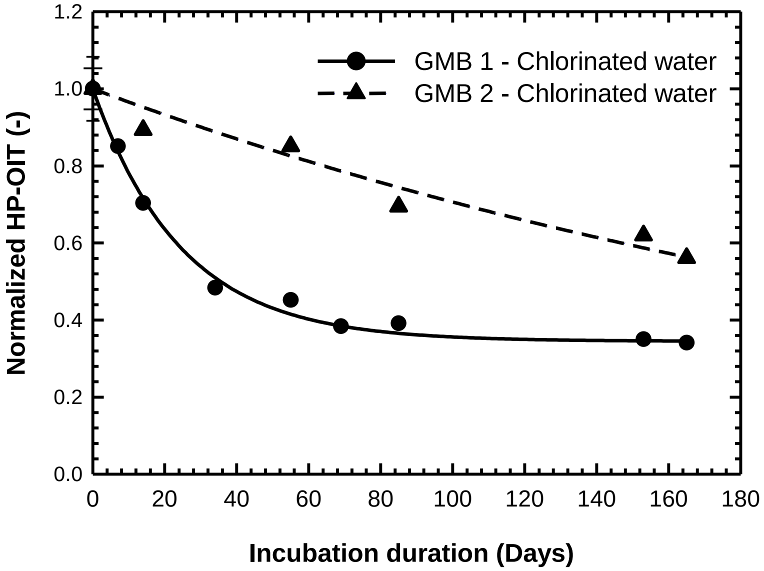

Figure 2. Variation of the normalized HP-OIT vs incubation time for immersion in chlorinated water at 85°C

3.3 OIT Depletion of the Smooth Edges

After 165 days, the Std-OIT values of the smooth edge of GMB 1 decreased to reach 14% (41 min) of its initial value while the smooth edge of GMB 2 reached 6% (18 min) of its initial value (Figure 3). Similar to the textured parts, both GMBs showed a clear difference between the early-time and the later-time depletion rates of Std-OIT and hence the current data were modeled using Eq. 1 (Table 4). Although both GMBs had similar early Std-OIT depletion rates (0.035 day^{-1}), the later depletion rate for the smooth edge of GMB 2 (0.012 day^{-1}) was slightly faster than GMB 1 (0.008 day^{-1}). The current results show that the Std-OIT depletion for the two textured GMBs was faster than their smooth edges. These results highlight the effect of the skin layers available in the textured parts on the Std-OIT depletion of the two examined GMBs.

Unlike the textured parts of the rolls that showed faster depletion in Std-OIT for the conductive GMB, the Std-OIT depletion of the smooth edge of the non-conductive GMB 2 was slightly faster than the smooth edge of GMB 1. However, the very small difference in depletion rates between the smooth edges of the two GMBs together with similarity in their depletion pattern (i.e., both were modelled using Eq.1) implies that the difference in the Std-OIT of the textured rolls between the two GMBs was essentially due to the skin layers (mainly the conductive layer) and their potential effects on the Std-OIT depletion of the textured parts of the rolls. However, the smooth edges of the two GMBs did not reach residual values during the 165 days and hence further incubation is needed to better assess their depletion behaviour.

Table 4. Std-OIT depletion rates and the exponential fit parameters for smooth edges of examined GMBs after 165 days of incubation in chlorinated water

GMB	s_1	s_2	a	b
Smooth edge of GMB 1	0.035	0.008	140	150
Smooth edge of GMB 2	0.035	0.012	140	145

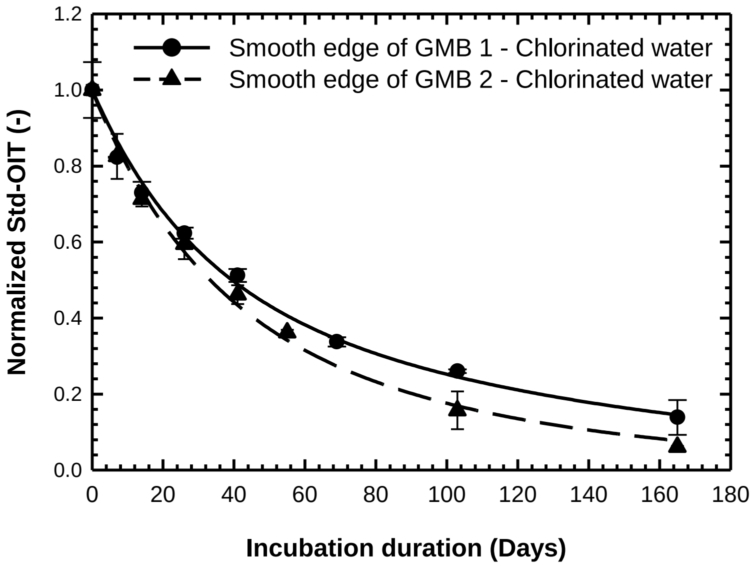

Figure 3. Variation of the normalized Std-OIT for the smooth edges of examined GMBs vs incubation time for immersion in chlorinated water at 85ºC

The HP-OIT values for the smooth edges of GMB 1 and GMB 2 decreased after 165 days to 40% (580 min) and 42% (600 min) of their initial values, respectively (Figure 4). Based on available data, it appears that both GMBs reached the HP-OIT residual values at the end of incubation. The current results show that the HP-OIT depletion of the smooth edges of these GMBs was fairly similar to each other unlike the textured parts that showed significant difference between GMB1 and GMB2. Again, this could be attributed to the reduction in the thickness of the skin layers at the smooth edges of these GMBs and hence the HP-OIT depletion was governed by the depletion of antioxidant from the core of the two GMBs that was essentially the same.

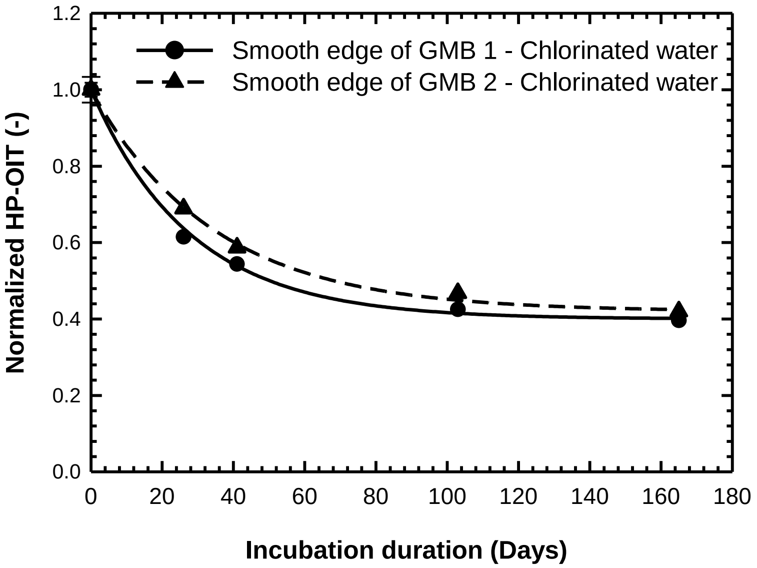

Figure 4. Variation of the normalized HP-OIT for the smooth edges of examined GMBs vs incubation time for immersion in chlorinated water at 85ºC

4. SUMMARY AND CONCLUSION

The performance of a conductive textured (GMB 1; Std-OIT_o/HP-OIT_o = 220/705) and a non-conductive textured (GMB 2; Std-OIT_o/HP-OIT_o = 285/960) HDPE GMBs produced by the same manufacturer from the same nominal resin was evaluated based on antioxidant depletion by using immersion tests in chlorinated water during 165 days at 85ºC. The effect of texturing was also investigated by comparing the OIT values of the examined GMBs to their smooth edges. Based on the reported results, the following **preliminary** conclusions were reached:

- Both examined GMBs had identical initial OIT (Std and HP) values at the smooth edge of the rolls implying that they were initially formulated with the same antioxidant package. However, the two GMBs had different initial OIT values for the textured parts that can be attributed to the conductive layer introduced in GMB 1 only.
- The initial OIT values of the smooth edges were higher than initial OIT values of the textured parts of the roll for the two examined GMBs. This can be attributed to the variation in the white layer and/or the conductive layer between the smooth edge and the textured parts affecting the initial OIT values of these GMBs.
- The conductive GMB (GMB 1) exhibited faster depletion rates in chlorinated water than non-conductive GMB (GMB 2) for both Std-OIT and HP-OIT.
- The smooth edges of the two GMBs showed slower depletion of OIT than the textured parts highlighting the effects of the skin layers on both the Std-OIT and HP-OIT depletion of textured parts.
- Comparing the depletion of the smooth edges of the two GMBs, the current results showed very similar depletion rates and depletion patterns for the two GMBs unlike the textured parts of the rolls. This implies that the depletion of OIT at the smooth edges was dominated by the core layer due to lower thickness of the skin layers at the smooth edges.

This study focused on the relative performance of the two examined GMBs immersed in chlorinated water 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 solution presented. Further incubation is needed to assess the antioxidant depletion to the residual values at 85ºC and at lower temperatures for better 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 multilayered 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 conclusion.

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