



Contents lists available at ScienceDirect

Geotextiles and Geomembranes

journal homepage: www.elsevier.com/locate/geotexmem

Regular Paper

Degradation of HDPE, LLDPE, and blended polyethylene geomembranes in extremely low and high pH mining solutions at 85 °C

F.B. Abdelaal^a, R. Kerry Rowe^{b,*}, M.S. Morsy^c, R.A. e Silva^d^a GeoEngineering Centre at Queen's-RMC, Queen's University, Ellis Hall, Kingston, ON, K7L 3N6, Canada^b Barrington Batchelor Distinguished University Professor and Canada Research Chair in Geotechnical and Geoenvironmental Engineering, GeoEngineering Centre at Queen's-RMC, Queen's University, Ellis Hall, Kingston, ON, K7L 3N6, Canada^c Soil Mechanics and Foundation Engineering Unit, Structural Engineering Department, Faculty of Engineering, Ain Shams University, Cairo, 11535, Egypt^d GeoEngineering Centre at Queen's-RMC, Queen's University, Kingston, ON, K7L 3N6, Canada

ARTICLE INFO

Keywords:

Geosynthetics
Geomembranes
HDPE
LLDPE
Blended polyolefin
Degradation
Heap leach pads
Mining
Low pH
High pH
Stress crack resistance
Morphology
HALS

ABSTRACT

The durability of five 1.5-mm thick geomembranes (GMBs) is investigated in pH 0.5 and 13.5 synthetic mining solutions using immersion tests. Two high density polyethylene (HDPE), two linear low density polyethylene (LLDPE), and one blended polyethylene (BPO) GMBs are investigated at 85 °C for incubation durations of 4.5–6.5 years. It is shown that the degradation of all five GMBs in the high pH solution is faster than in the low pH solution. In the pH 0.5 solution, one of the HDPEs and the BPO GMBs exhibited polymer degradation before or at the time of the depletion of their antioxidants. In pH 13.5, four out of the five GMBs exhibited degradation and followed the conceptual three-stage degradation model until nominal failure. However, there is no correlation between the long-term performance of these GMBs and their resin type or their initial properties since one of the examined LLDPEs outperformed all the higher density/crystallinity GMBs with higher initial properties while the other LLDPE did not perform well. Thus, when selecting a GMB for a desired application, the relative performance of different candidate GMBs can be only assessed using immersion tests using the solutions expected in the field.

1. Introduction

Heap leaching is an economical hydrometallurgy ore beneficiation process for low grade ores (Thiel and Smith 2004; Smith 2008). In this process, crushed ores are piled over an engineered leach pad and irrigated with acidic (copper, uranium, and nickel bearing ores) or basic (silver and gold bearing ores) solution to dissolve the precious metal of interest (Lupo 2010; Abdelaal et al., 2011). The leached solution (pregnant leach solution “PLS”) is collected in a lined pond and then processed to extract the metals/minerals of interest. Geomembrane (GMB) liners are used as a part of the composite liner system in the pad under the ore (Abdelaal and Rowe 2017) and in the PLS and raffinate ponds (Thiel and Smith 2004; Rowe and Abdelaal 2016). The GMB is part of a heap leaching system in which its role (Rowe et al., 2013; Rowe 2011) is to preserve the minerals in the PLS (Christie and Smith 2013) and, together with the local hydrogeologic environment (Rowe 1988), to protect the environment from the corrosive PLS.

A survey for the type of GMBs used in 88 heap leach pad projects showed that high density polyethylene (HDPE), linear low density polyethylene (LLDPE), and polyvinyl chloride (PVC) GMBs were used in 75%, 22%, and 3%, respectively, of the surveyed projects (Rowe et al., 2013). Nevertheless, there is a growing interest in using LLDPE and blended polyolefin (BPO) GMBs as the primary liner material in barrier systems of high-stress applications such as heap leach pads due to their high stress crack resistance. However, there is a paucity of information about their long-term performance relative to HDPE GMBs under heap leaching exposure conditions.

PE GMBs are polyolefins produced by the polymerization of olefins or copolymerization of olefins with other co-monomers, where the olefins comprise at least 50% of the polymer mass (ASTM D883). HDPE is a predominantly linear PE with a density greater than or equal to 0.941 g/cm³ (ASTM D883), while LLDPE is a linear PE but with greater branching than HDPE resulting in a lower density of 0.919–0.925 g/cm³ (ASTM D883). Therefore, HDPE resins are assumed to have higher

* Corresponding author.

E-mail addresses: fady.abdelaal@queensu.ca (F.B. Abdelaal), kerry.rowe@queensu.ca (R.K. Rowe), mohamed.salah@eng.asu.edu.eg (M.S. Morsy), r.esilva@queensu.ca (R.A. e Silva).<https://doi.org/10.1016/j.geotexmem.2023.04.011>

Received 14 February 2023; Received in revised form 24 March 2023; Accepted 29 April 2023

0266-1144/© 2023 Published by Elsevier Ltd.

chemical resistance than LLDPE due to their higher crystallinity (Scheirs 2009). BPO resins are made of a blended resin that may be composed of different polyolefins such as PE and polypropylene (Martuscelli et al., 1980; Teh et al., 1994; Rachtanapun et al., 2004) or PE of different densities such as HDPE and LLDPE (Lee and Jho 1998; Schellenberg and Fienhold 1998; Munaro and Akcelrud 2008). Although there is little information about the degradation behaviour of BPOs, it is expected that their performance will depend on the polymer blends (type and ratio) used in the formulation of these resins. It is also expected that their performance will not be solely dependent on the chemistry of their base resin. This is because their morphology (configuration of macromolecules and chains' structure) and the additives (Földes et al., 1987; Gulmine et al., 2002) used in their formulations (e.g. antioxidants, carbon black) can affect their chemical durability. Thus, the relative long-term performance of PE GMBs with different formulations in a given application requires examining their degradation behaviour under the same long-term conditions.

Few studies have compared the relative performance of GMBs with different resin types to select the best GMB for a desired application. These studies were conducted using immersion tests to assess the durations of the GMB three degradation stages (Hsuan and Koerner 1998) that include: antioxidant depletion (Stage I), induction period Stage II (Stage II), and degradation to nominal failure to 50% of the initial value or a value specified by GRI-GM13 (2021) for a selected GMB property (Stage III). For example, Thiel and Smith (2004) compared the degradation of tensile strength of HDPE and LLDPE GMBs when immersed in a strong acidic solution at 50 °C for 4 months. It was shown that the tensile strength of the HDPE GMB slightly degraded by 3% while the LLDPE degraded by 10% and thus the HDPE GMB examined had better performance than the LLDPE. Morsy et al. (2020) compared 12 different GMBs including different LLDPEs, HDPEs, and BPOs in chlorinated water. They reported that one of the examined 1.5 mm LLDPE GMBs had the longest degradation stage compared to all other examined GMBs except for a 3.0 mm-thick HDPE GMB. However, this observation cannot be generalized to other incubation media since the degradation mechanism of GMBs exposed to chlorinated water (Abdelaal et al., 2019; Abdelaal et al., 2019; Morsy et al., 2020) is very different from their degradation behaviour in other incubation media such as municipal solid waste or mining solutions (Hsuan and Koerner 1998; Hsuan et al., 2008; Abdelaal et al., 2014; Rowe et al. 2003, 2009, 2014, 2020; Ewais et al., 2018; Morsy and Rowe 2020).

There is also a paucity of research examining the long-term performance of different PE GMBs in mining solutions. Previous studies involving GMBs immersed in mining solutions investigated the degradation of one HDPE GMB for three years (Rowe and Abdelaal 2016; Abdelaal and Rowe 2017, 2023) or the longevity of LLDPE and BPO GMBs in terms of antioxidant depletion time for few months (Abdelaal and Rowe 2014a; Morsy and Rowe 2017). Therefore, the objective of the current study is to investigate the relative performance of HDPE, LLDPE, and BPO GMBs with different formulations in terms of their antioxidant depletion time and nominal failure when exposed to acidic and basic synthetic heap leaching solutions for up to 6.5 years of incubation.

2. Experimental investigation

2.1. Accelerating ageing tests

Immersion tests were used to accelerate the ageing of the GMBs in which coupons (190 mm × 100 mm) were placed in 4-litre glass containers filled with incubation fluid. 5 mm-thick glass rods were used to separate the coupons to ensure their exposure to immersion solutions from both sides. Immersion tests were conducted at 85 °C only to allow for the comparison between the GMBs examined in a reasonable time (43–77 months).

The GMBs were incubated in two different heap leaching synthetic solutions (Table 1). These solutions were prepared by mixing de-ionized

Table 1

Laboratory analyzed composition of different solutions used in the current study (mg/L unless noted).

Component ^a	L1	L8
Nominal pH	0.5	13.5
Average pH ^b	0.53 ± 0.07	13.4 ± 0.2
Ag ⁺	<1.0	0.3
Al ³⁺	5000	<1.0
As ³⁺	<0.03	0.9
Ba ²⁺	<0.05	<0.05
Cd ²⁺	1.7	<0.025
Ca ²⁺	515	0.86
Co ²⁺	20	0.03
Cu ²⁺	87	9
Fe ²⁺	710	<0.05
Li ⁺	1000	<0.05
K ⁺	<0.2	198
Mg ²⁺	3300	0.13
Mo ⁶⁺	<0.05	0.74
Mn ²⁺	620	<0.05
Na ⁺	50	27,500
Ni ²⁺	7.6	<0.3
Pb ²⁺	1.4	<0.03
S ⁶⁺	2250	124
Zn ²⁺	62	0.02
Cl ⁻	5100	<0.5
O ^{2-c}	0	0.59
OH ^{-c}	0	20,410
SO ₄ ²⁻	68,000	300

98% concentrated sulfuric acid or 15 mol NaOH solution were used for pH adjustment.

^a Metal ions were analyzed using inductively coupled plasma-mass spectrometer (ICP-MS), while the anions were analyzed using Ion chromatography (IC).

^b Average pH (average of 18 values) measured at the times of incubation solution replacement every 2 months during the years of incubation.

^c Not measured directly.

water (pH ≈ 6.5) with different metal salts. Solution L1 (Rowe and Abdelaal 2016) had a pH of 0.5 that simulates the chemical composition and pH of copper pregnant leach solution (PLS), the solution below the ore, and the raffinate solution (Queja et al. 1995; Jergensen 1999). Solution L8 (Abdelaal and Rowe 2017) had a pH of 13.5 simulating the extremely high pH of the PLS for gold/silver heap leaching (without the cyanide for safety reasons). To achieve the nominal pHs, the metal solutions were titrated using 98% sulfuric acid (L1) and 15 mol sodium hydroxide (L8) (Table 2). The immersion fluids (L1 & L8) were replaced every 1.3 months to avoid the build-up of depleted antioxidants in the solution and to maintain a constant pH during the entire incubation duration (Rowe and Abdelaal 2016; Abdelaal and Rowe 2017).

2.2. Index testing to monitor GMB degradation

Standard oxidative induction time (Std-OIT) (35 kPa/200 °C; ASTM D 3895) and high-pressure oxidative induction time (HP-OIT) (3500 kPa/150 °C; ASTM D 5885) were conducted simultaneously to monitor the depletion of the different antioxidant packages used in the formulation of the different GMBs examined. The OIT samples were prepared using the bore-cut method without any homogenization since four out of the five GMBs examined were single-layered black smooth GMBs. Sample homogenization was not used for the co-extruded GMB examined since at the beginning of this research between 2011 and 2014, it was an optional procedure in the ASTM test methods. Moreover, homogenization methods generally consume larger samples from the coupons and would thus limit the monitoring of properties after aging for many years.

Degradation in physical and mechanical properties was monitored using, (1) high-load melt flow index (HLMI) (21.6kg/190 °C; ASTM D1238), (2) notched constant tensile load stress crack resistance (SCR; ASTM D5397), and (3) tensile properties (Type V; ASTM D6693). The

Table 2
Geomembrane properties.

Property ^a	MxA15	MxC15	LxD15	LxE15	BzSW15
Resin Type based on ASTM D883	HDPE	HDPE	LLDPE	LLDPE	Blended
Resin type ^b	Pétromont (S-7000)	K306(Chevron)	K203 (chevron)	K203 (chevron)	Not Supplied
Production date	2005	2008	2011	2011	2014
Nominal thickness (mm)- (ASTM D5199)	1.5	1.5	1.5	1.5	1.5
Colour	Black	Black	Black	Black	White
GMB density ^b (g/cm ³)-(ASTM D1505)	0.947	0.946	0.924	Not supplied	0.932
Crystallinity (percentage)-(ASTM D3418)	56.1 ± 2.2	56 ± 2.0	38 ± 0.0	36 ± 1.3	43 ± 2.6
Std-OIT (min)- (ASTM D3895)	100 ± 2	160 ± 2	190 ± 5	155 ± 5	180 ± 26
HP-OIT (min)- (ASTM D5885)	260 ± 10	960 ± 17	350 ± 13	890 ± 25	3300 ± 220
Stabilized with HALS ^b	No	Yes	No, but may contain Traces	Yes	Yes
HLMI ^c (g/10min) -(21.6 kg) (ASTM D1238)	15.9 ± 0.30	13.9 ± 0.80	13.4 ± 0.80	14.7 ± 0.30	13.1 ± 0.27
LLMI ^d (g/10min) - (2.16 kg)	0.11 ± 0.01	0.12 ± 0.001	0.14 ± 0.001	0.153 ± 0.011	0.13 ± 0.001
Melt flow ratio (HLMI/LLMI)	151	120.5	94	90	103
SCR ₀ ^b (hours) -(ASTM D5397)	720±130 ^c	800 ± 90	19,000 ± 5500	18,500	26,000
Tensile break properties (ASTM D6693)	Cross-machine direction				
Break strength (kN/m) Type (IV)	47 ± 2	51 ± 2	55 ± 2	53 ± 3.8	52 ± 3
Break Strain (%)	874 ± 46	857 ± 23	980 ± 34	980 ± 92	1012 ± 111
Break strength (kN/m) Type (V)	57 ± 3	56 ± 2	57 ± 2	56 ± 2.5	58 ± 6
Break Strain (%)	816 ± 9	800 ± 17	840 ± 40	800 ± 28.3	760 ± 40

^a GMB initial properties are subjected to small changes with time due to storage of the roll at room temperature for long period, variability of the material within the same roll (e.g., distribution of additives; resin imperfections), and periodic calibration of the testing equipment.

^b Information provided by GMB manufacturers.

^c High load Melt Index.

^d Low load Melt Index.

HLMI test was mainly used to assess the time at which the degradation initiates (i.e., Stage II) and the potential degradation mechanism (i.e., cross-linking or chain scission). However, since these degradation mechanisms can occur simultaneously causing a simultaneous increase and decrease in the values (Abdelaal and Rowe 2014b), the HLMI was not used to assess the duration of Stage III (and, hence, the time to nominal failure). Due to the substantially high initial SCR of the examined LLDPE and BPO GMBs, degradation in SCR was only assessed for the HDPE GMBs and only one LLDPE GMB.

2.3. Tested GMBs

Five 1.5 mm-thick smooth blown film polyethylene GMBs manufactured by two different manufacturers were investigated in the current study (Table 2). According to their resin type, the five GMBs were: two HDPEs, two LLDPEs, and one BPO designated as MxA15, MxC15, LxD15, LxE15, and BzSW15. These designations are used to identify the different GMB information including:

- Resin Type: M = MDPE, L = LLDPE, and B = BPO.
- GMB manufacture: x = Manufacturer 1 and z = Manufacturer 2.
- Formulation: A, C, D, E, and S designates the specific GMB, each with either a different resin lot and/or antioxidant package.
- Colour: unless otherwise noted a GMB is Black. "W" indicates a single surface white coated GMB
- Thickness: 15 = 1.5 mm

The two HDPE GMBs MxA15 and MxC15 were produced by the same manufacturer with a three-year production time difference. While the two GMBs had similar initial SCR and tensile break properties, they had different resins from two different resin suppliers with different melt flow rates (Table 2). Another notable difference between MxA15 and MxC15 was their initial HP-OIT. The relatively high initial HP-OIT value of MxC15 (>400 min) implies that hindered amine light stabilizers (HALS) were part of the antioxidant/stabilizer package of MxC15 only (Scheirs 2009).

The two LLDPE GMBs LxD15 and LxE15 were both produced by the same manufacturer and were produced in the same year. According to the GMB manufacturer, the two GMBs were manufactured from the same resin and with the same type of carbon black. The main difference

between these two GMBs was that LxE15 had a boosted OIT package with high molecular weight antioxidants that increased the initial HP-OIT value by a factor of 3 ($HP-OIT_0 = 890$ min) but reduced the initial Std-OIT from 190 min to 155 min. Such a decrease in Std-OIT could be attributed to some possible antagonistic mechanisms of the HALS consuming the hindered phenols representing the bigger portion of the Std-OIT package stabilizing the GMB (Barret et al. 2002).

BzSW15, produced by Manufacturer 2, was the only blended and single-sided coated white GMB examined. According to the GMB manufacturer, the blend consisted of 90% LLDPE resin and 10% HDPE resin, which resulted in the relatively high initial SCR (26000 h) and GMB density and crystallinity that were within the range of the values obtained for the examined HDPE and LLDPE GMBs (Table 2). BzSW15 had also the highest initial HP-OIT ($HP-OIT_0 = 3300$ min) that was an order magnitude higher than the GMBs without HALS (MxA15 and LxD15) and three times higher than the initial HP-OIT of the examined MxC15 and LxE15 with HALS.

3. Results and discussion

3.1. Degradation of GMBs in extreme pH environment

3.1.1. HDPE GMBs

For the Std-OIT depletion in L1 with pH 0.5, MxA15 had a relatively fast early depletion rate over the first 14 months followed by a very slow depletion rate to reach 3 min ($\approx 3\%$ Std-OIT₀) at 77 months (Fig. 1). MxC15 also exhibited depletion at different rates to reach 10 min (6% Std-OIT₀) at 76 months. Hence, MxC15 had longer Stage I in pH 0.5 attributed to slower early and second stage depletion rates than MxA15.

For the HP-OIT, MxA15 without HALS had a HP-OIT depletion that was consistent with the Std-OIT depletion over the first 33 months but then stabilized at approximately 95 min (36% HP-OIT₀) until 77 months. MxC15 with HALS had a gradual depletion of the HP-OIT to reach 310 min ($\approx 32\%$ HP-OIT₀) after 44 months and then stabilized at that residual value until the end of incubation. While the two GMBs exhibited the same % drop in HP-OIT (to 32–36% HP-OIT₀), the residual HP-OIT reached at the end of incubation of MxC15 was higher than the initial HP-OIT of MxA15. This implies that for both GMBs, most of the low molecular weight antioxidants (representing MxA's antioxidant package and part of MxC's package) were readily depleted in L1 given the

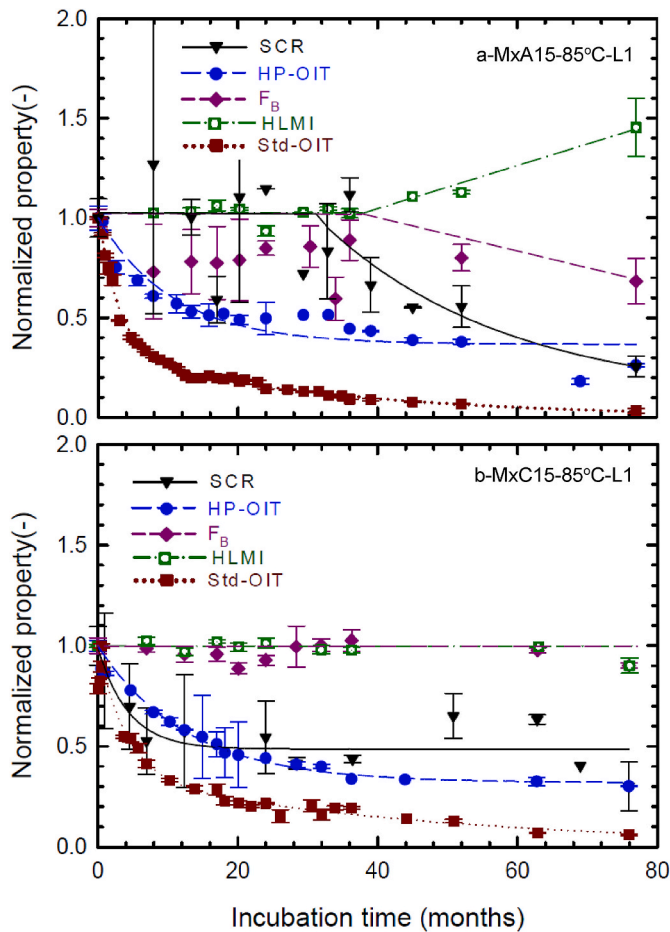


Fig. 1. Variation of different index properties in L1 (pH 0.5) at 85 °C for the HDPE GMBs: (a) MxA15 (without HALS) & (b) MxC15 (with HALS; modified from Abdelaal and Rowe 2023).

relatively low residual HP-OIT value of MxA that was only stabilized with low molecular weight antioxidants. This also implies that some of the high molecular weight antioxidants present as part of MxC15’s HP-OIT package were not depleted in L1 and could still be detected by the HP-OIT test as a high residual HP-OIT after 76 months.

At 85 °C and during the 6.3-year immersion in the pH 0.5 solution, MxC15 did not encounter any change in its physical and mechanical properties except a gradual reduction in the SCR (Fig. 1b) related to physical ageing (Ewais and Rowe 2014; Rowe et al., 2019).

MxA15 started degradation in SCR and break strength (F_B) after 30 and 38 months, respectively, from the start of incubation to reach 25% SCR_o and 70% F_{Bo} at 77 months. For the HLMI, the values were retained at $HLMI_o$ for 38 months, then showed an increase to reach 145% $HLMI_o$ after 77 months implying the domination of chain-scission oxidative reactions. These results show the superior performance of MxC15 in the low pH media relative to MxA15 which exhibited degradation before the full depletion of its Std-OIT.

The degradation behaviour observed for the two HDPEs in the low pH solution was slower than any of the published data for these two GMBs in other incubation media (Table 3). For instance, at 85 °C MxA15 experienced degradation in mechanical properties (e.g., F_B) after 6 months in DI water, 8.5 months in synthetic municipal solid waste (MSW) leachate (with surfactant), and 22 months of incubation in air, compared to 38 months in L1. Time to nominal failure (t_{NF}) of MxA15 assessed based on a reduction in F_B to 50% of the initial value was reached after 24 months in DI water, 30 months in MSW leachate, and around 40 months in air compared to > 77 months in L1. Likewise, MxC15 showed much slower degradation in L1 than MSW leachate with

Table 3

Length of the degradation stages in months of MxA15 and MxC15 in different incubation media.

Degradation Stages(months)	MxA15 ^a				MxC15 ^c	
	DI Water	MSW Leachate	Air	L1	MSW Leachate	L1
Stage I based on Std-OIT	35	4.5	>30	77	2.2	>76
Stage II*	No Stage II	4.0	No Stage II	No Stage II	22.8	UD
Stage III*	18	21.5	18	65*	4.0	UD
Time to nominal Failure (t_{NF})*	24	30	40	103*	29	>76

N/A = Not applicable-UD=Undefined based on the current incubation duration.

*Values based on cross-machine F_B

^bEwais et al. (2014).

^a Abdelaal and Rowe (2014b).

a Stage I based on Std-OIT of only 2.2 months and time to nominal failure to 50% of the initial F_B of 29 months at 85 °C in MSW leachate (Ewais et al., 2014) compared to a Stage I > 76 months in L1. This implies that antioxidant/stabilizer packages and resins of the two HDPE GMBs had high resistance to the combined effect of the examined chemistry and acidic conditions in L1.

In L8 with pH 13.5 (Fig. 2), the two HDPE GMBs showed degradation in their properties during the incubation time considered herein,

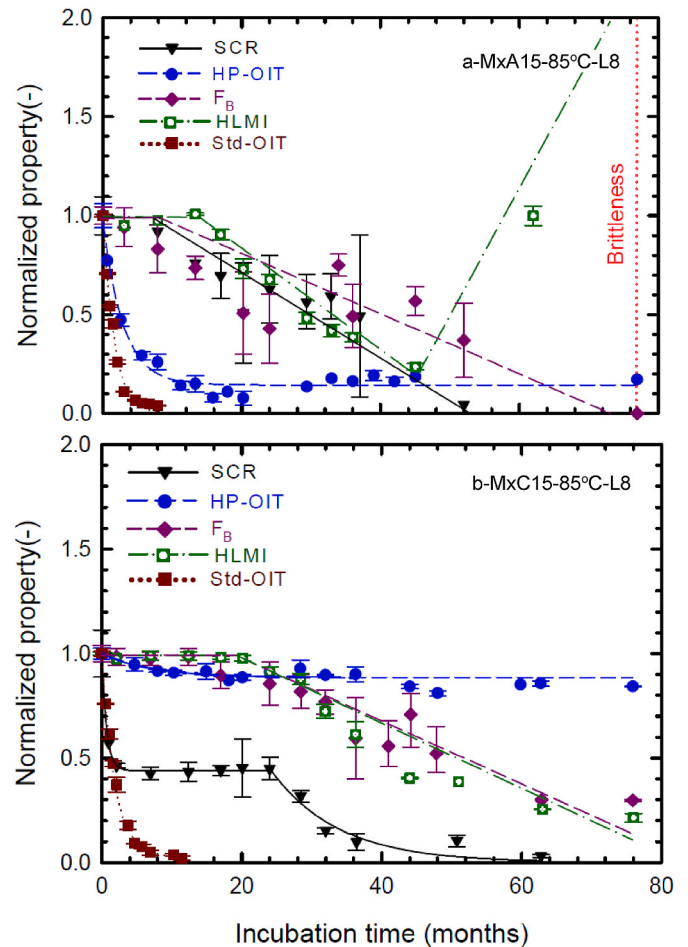


Fig. 2. Variation of different index properties in L8 (pH 13.5) at 85 °C for the HDPE GMBs: (a) MxA15 (without HALS) & (b) MxC15 (with HALS; modified from Abdelaal and Rowe, 2023).

indicating lower resistance to degradation in the high pH media than in the low pH. The Std-OIT and HP-OIT of MxA15 (without HALS) were fully depleted to residual values of 3 min ($\approx 3\%$ Std-OIT₀) and 35 min (13% HP-OIT₀), respectively, after 7.8 months from the start of incubation (Fig. 2a). MxC15 (with HALS; Fig. 2b) had a two-rate Std-OIT depletion pattern to reach 3 min ($\approx 2\%$ Std-OIT₀) after 11.6 months while its HP-OIT depleted to 850 min ($\approx 90\%$ HP-OIT₀) after 12.3 months and stabilized at this residual value until the end of the incubation time (Abdelaal and Rowe 2017). This shows that the antioxidants stabilizing MxC15 had better resistance to depletion in L8 than those stabilizing MxA15.

For the degradation in the mechanical properties, MxA15 started degradation in SCR and F_B after 8 months from the start of incubation. The HLMI was retained for 12 months, then showed a reduction to $\sim 20\%$ HLMI₀ after 45 months implying the domination of cross-linking oxidative reactions. However, there was a steep increase in values to reach 170% HLMI₀ at 77 months implying degradation by chain-scission, after which the GMB became brittle. The t_{NF} based on 50% of the initial values for F_B and SCR was reached after 40 and 30 months, respectively, from the onset of incubation. Thus, unlike the degradation in L1, MxA15 followed the traditional 3-stage degradation model (Hsuan and Koerner 1998) in which the degradation of mechanical properties in L8 was observed after the depletion of antioxidant/stabilizer to a residual value.

While the HP-OIT of MxC15 was retained at 90% HP-OIT₀ after the slight depletion obtained during the first 12.3 months of incubation in L8, degradation in HLMI and F_B started after 8.4 months from the Std-OIT depletion to residual values. For SCR, after an early-time 55% reduction over the first 2 months of incubation, the SCR values were stabilized at this value for the following 22 months then further decreased to reach 3% SCR₀ over the next 40 months of incubation. The early reduction of SCR is not attributed to chemical degradation but primarily to physical ageing altering the polymer from the off-the-roll state (SCR₀) to a more stable state (SCR_m; Rowe et al., 2019). Hence, t_{NF} based on SCR due to chemical degradation was assessed as 50% of SCR_m (Morsy and Rowe 2020). In this case, the t_{NF} of MxC15 based on SCR reaching 50% of SCR_m was 31 months from the start of incubation while t_{NF} based on F_B was 52 months. These results show that the degradation in the different mechanical properties of the GMB can change based on the sensitivity of its different properties to the physical and chemical changes introduced during ageing.

Aside from the relatively short Stage III of MxC15 based on SCR (mainly due to its low SCR_m relative to MxA15), MxC15 had longer Stage I and t_{NF} than MxA15. What is notable about these two GMBs was the remarkably longer Stage II for MxC15 when assessed based on the different properties. For instance, MxA15 that had a slightly shorter Std-OIT depletion stage (7.8 months), showed chemical degradation in SCR after 8 months from the start of incubation (i.e., after 0.2 months from the Std-OIT depletion) while MxC15 showed similar degradation after 12.4 months from its Std-OIT depletion time. The longer lag period between the Std-OIT depletion and the initiation of degradation (i.e., Stage II duration) for MxC15 than in MxA15 may imply that MxC's resin was more resistant to degradation in pH 13.5, even without effective antioxidant (inferred from the complete depletion of Std-OIT and retention of HP-OIT at high residual values), than MxA's resin. However, when Abdelaal and Rowe (2023) compared the degradation of MxC15 in pHs 9.5, 11.5, and 13.5, they showed longer Stage II in pH 13.5 (with the lowest depletion of HP-OIT) than the other two high pH solutions despite having the shortest Stages I and III relative to pH 9.5 and pH 11.5. Based on this, it was hypothesized that beyond the fast Std-OIT depletion, the antioxidants detected by the high residual HP-OIT may have a role in delaying the start of polymer degradation during Stage II in pH 13.5. However, the role of these residual antioxidants cannot be verified with certainty from the comparison between MxA15 and MxC15 given the differences in resin between the two GMBs.

3.1.2. LLDPE GMBs

The Std-OIT depletion patterns in L1 (pH 0.5) were very different between the two LLDPEs. While LxD15 displayed a single-rate depletion over the 60 months of incubation, LxE15 had a fast early depletion rate during the first five months followed by a slower rate of depletion until the end of incubation (Fig. 3). The Std-OIT values reached at the end of incubation were 25 min for LxD15 (13% Std-OIT₀) and 19 min for LxE15 (12% Std-OIT₀). Thus, LxE15 with the lower initial Std-OIT value had faster Std-OIT depletion than LxD15 in the low pH. Notwithstanding, the antioxidants detected by Std-OIT of both LLDPEs seem to have good resistance to extraction (chemically or physically) in the low pH media and their Stage I based on Std-OIT exceeded the 60-month incubation duration.

For the HP-OIT, although the two GMBs had a substantial difference in their initial values, both GMBs showed the same depletion pattern. However, the HP-OIT of LxE15 (with HALS and HP-OIT₀ = 890 min) reached a residual value of 40% HP-OIT₀ after only 8 months while LxD15 (without HALS and HP-OIT₀ = 350 min) showed gradual depletion over the first 18 months and stabilized at 43% HP-OIT₀. Thus, similar to the examined HDPE GMBs, the high residual HP-OIT of LxE15 (355 min) implies that some of its high molecular weight antioxidants were not depleted in L1 and most of the HP-OIT depletion was due to the depletion of the low molecular weight antioxidants similar to LxD15. Also similar to MxC15, both LLDPE GMBs did not exhibit degradation in tensile properties or HLMI during the 60 months of incubation at 85 °C in low pH (Fig. 3).

In L8 (pH 13.5), LxD15 had a two-rate Std-OIT depletion pattern over the first 18 months reaching residual values of 5 min but depletion of

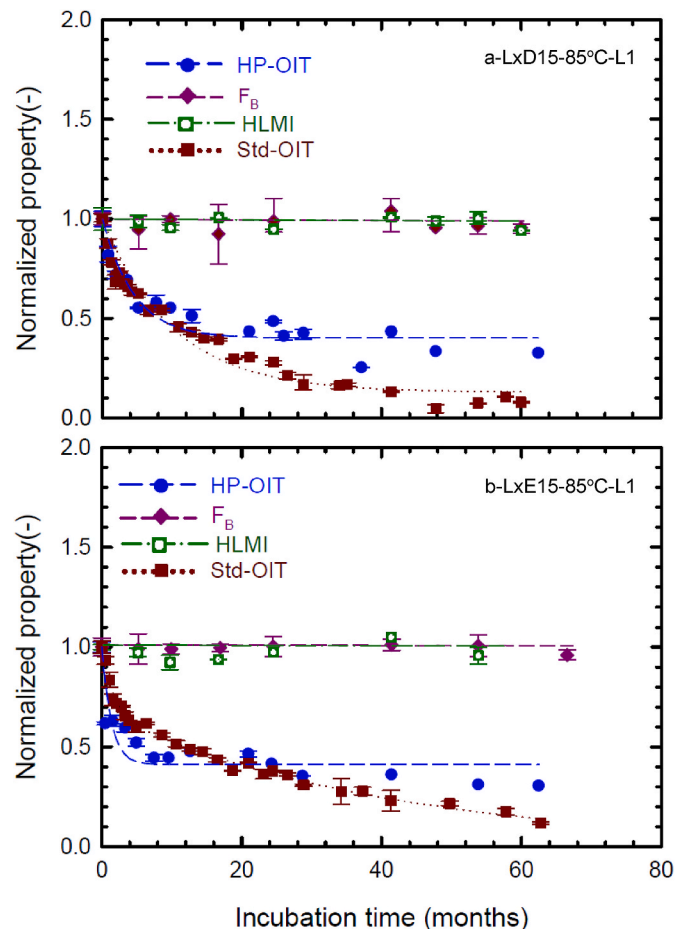


Fig. 3. Variation of different index properties in L1 (pH 0.5) at 85 °C for the LLDPE GMBs: (a) LxD15 (without HALS) & (b) LxE15 (with HALS).

HP-OIT took 36 months to reach 70 min. Although the antioxidant package of LxD15 did not contain HALS, it seems that the antioxidants and stabilizers remaining after manufacturing were mostly ones that were only detected by the HP-OIT test. Following the Std-OIT depletion, LxD15 retained its HLMI for 24 months before exhibiting a notable increase that implies degradation by chain scission. Between 42 and 48 months from the start of incubation, HLMI increased by a factor of two then cross-linking became the dominant degradation mechanism, leading to a decrease in HLMI. At 60 months, complete brittleness was observed in LxD15 and samples broke upon bending and clogged inside the melt index machine. For F_B , the values were retained for 37 months but beyond this time, the GMB started to encounter fast degradation to reach 50% of the initial F_B after only 3 months from the time interpreted as the initiation of degradation (Fig. 4a). From the limited SCR data collected, the results suggest that LxD15 encountered physical ageing that led to a 70% drop over the first 8 months of incubation. This value was retained for the next 36 months ($SCR_m \approx 30\% SCR_o$) before it decreased to less than 1% SCR_o at the end of the incubation time considered (Fig. 4a). In this case, t_{NP} to 50% SCR_m was estimated to be reached after 45 months. Overall and similar to the HDPE GMBs, LxD15 showed degradation in the high pH media implying lower resistance to basic solution compared to the acidic solutions.

LxE15 (Fig. 4b) showed a very different degradation trend in L8 when compared to any other GMB examined in this study. First, and perhaps most notably, LxE15 did not show any degradation in its HLMI or F_B over the entire incubation duration of 52 months that was longer than the time at which degradation started in LxD15, MxA15 and

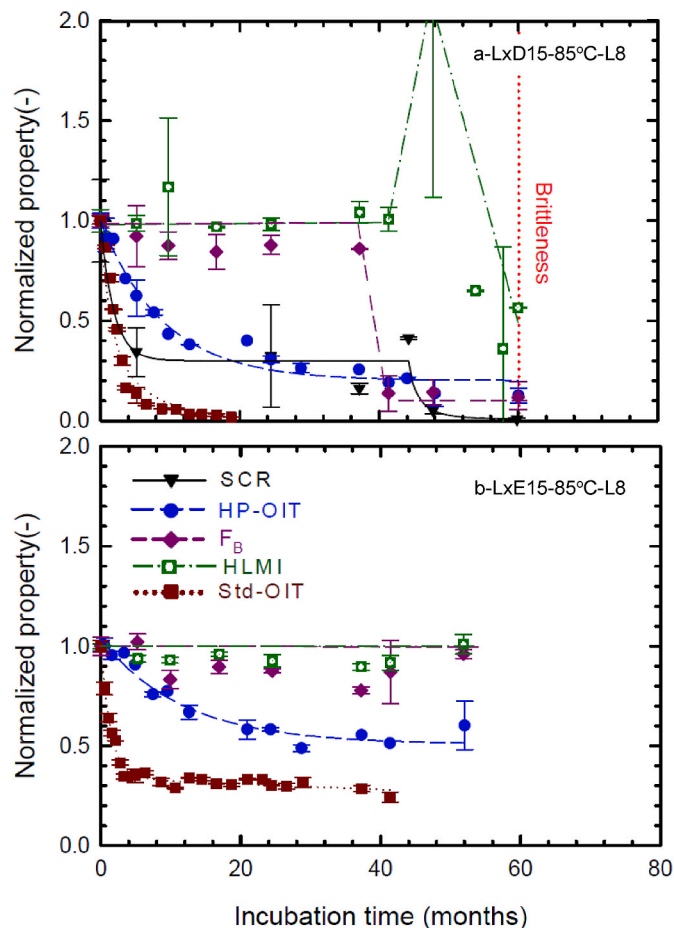


Fig. 4. Variation of different index properties in L8 (pH 13.5) at 85 °C for the LLDPE GMBs: (a) LxD15 (without HALS) & (b) LxE15 (with HALS). Note: regression line for the degradation of SCR for LxD15 was established to give the most conservative (i.e., shortest) durations of Stages II and III.

MxC15. Although it was stabilized with HALS, unlike MxC15 it showed a gradual decrease in its HP-OIT reaching 50% $HP-OIT_o$ at the end of incubation. This suggests that different HP-OIT packages (even those giving similar initial values such as those in MxC15 and LxE15) may interact differently with high pH media and this could be related to the nature and chemical composition of the HALS used in stabilizing both GMBs. For the depletion of Std-OIT, LxE15 showed a fast rate (0.73 month^{-1}) over the first four months followed by a second rate that was slower by about two orders of magnitude (0.005 month^{-1}) during the following 36 months of incubation. With these rates, the Std-OIT of LxE15 was depleted to 25% of its initial value with most of this depletion taking place during the first four months of incubation. This suggests that the antioxidant/stabilizer package of LxE15 had high resistance to depletion in both L1 and L8 and this could be the main reason for its better longevity (relative to all the other examined GMBs).

3.1.3. Blended GMB

The blended GMB, BzSW15, showed signs of degradation when immersed in L1 (pH = 0.5) during the 60-month incubation time unlike the two LLDPE GMBs examined (Fig. 5). For antioxidants detected by Std-OIT, there was a fast early-time depletion rate (0.7 month^{-1}) followed by a much slower rate (0.06 month^{-1}) to a residual value of 5 min ($\approx 3\% \text{ Std-OIT}_o$) that was reached after 46 months of immersion. HP-OIT depleted to a residual value of 1700 min (51% $HP-OIT_o$) over the first 12 months and stabilized at this value until 60 months. Both HLMI and F_B started to decrease at 46 months (i.e., at the time of Std-OIT depletion), implying dominating cross linking oxidative reactions.

Similar to the HDPE and LLDPE GMBs, the depletion of antioxidants of BzSW15 when immersed in L8 (pH = 13.5) was faster than in L1. The Std-OIT depleted to a low residual value of 5 min (3% $Std-OIT_o$) after 4 months, while the HP-OIT depleted to a residual value of 2500 min (76% $HP-OIT_o$) that was first reached after the same time (i.e., 4 months; Fig. 6). Following the depletion of both Std-OIT and HP-OIT, a measurable reduction in HLMI was observed after 14 months of incubation (i.e., 10 months after Std- and HP-OIT depletion to a residual value). After 28 months of incubation, F_B started to decrease (i.e., 14 months after the start of degradation in HLMI) and nominal failure was observed after 30 months from the onset of incubation.

Unlike the degradation trends observed in any of the GMBs examined or those typically reported for PE GMBs in previous studies, the HLMI and F_B for BzSW15 were retained at 30 and 50% of the initial values, respectively, following the initial degradation observed for both properties (Fig. 6). To explore this unusual behaviour of BzSW15, unaged samples as well as samples aged for 34 months (Stage III) were strained

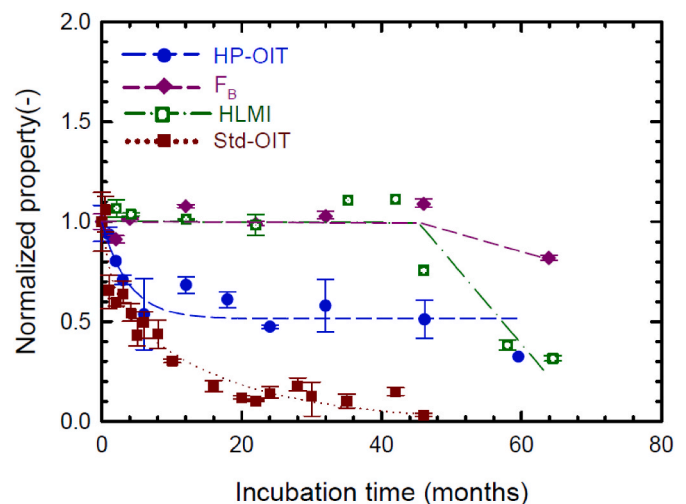


Fig. 5. Variation of different index properties in L1 (pH = 0.5) at 85 °C for the blended polyolefin GMB BzSW15.

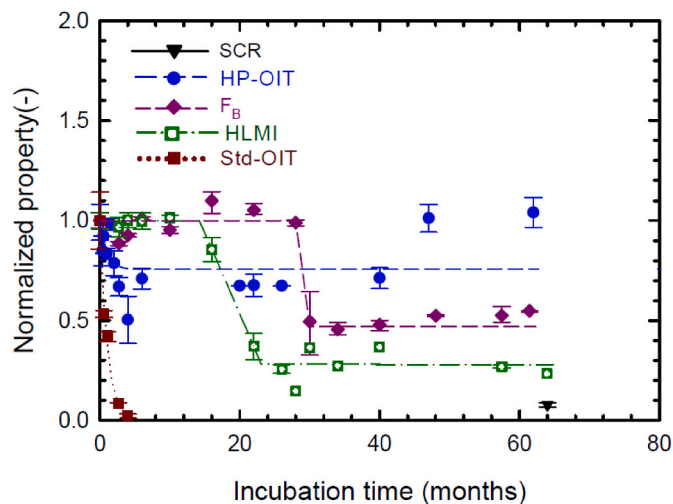


Fig. 6. Variation of different index properties in L8 (pH 13.5) at 85 °C for the blended polyolefin GMB BzSW15.

under tension and examined under an optical microscope to explore the formation of any surface cracks in the various layers of the aged GMB relative to the unaged sample. While the unaged sample did not show any signs of cracks in any of its layers until the breakpoint (Fig. 7a), the 34 month-aged sample had a set of parallel surface cracks (perpendicular to the loading direction) on both the white and the black skin layers (Fig. 7b). However, the cracks observed in the black skin were more severe than those detected in the white skin presumably due to the different formulations between these layers. With such cracks in both surfaces of the GMB, the core of the GMB was still elongating beyond the

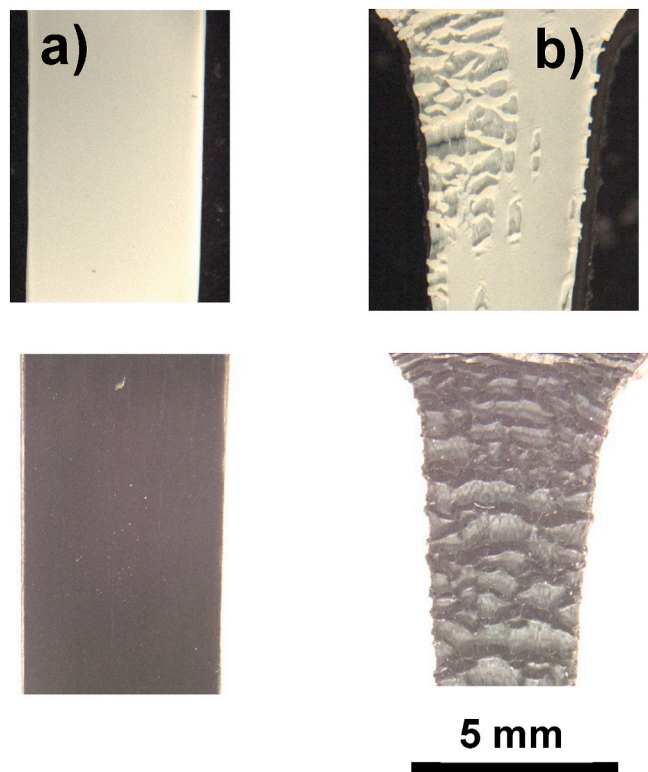


Fig. 7. Strained specimens of BzSW15 during the tensile tests incubated in pH 13.5 at 85 °C for (a) 0 months; and (b) 34 months. The top pictures show the white surface and the bottom pictures show the black surface. Images were obtained using an optical microscope.

point of the onset of these surface cracks until the complete rupture of the sample to give the obtained F_B at the residual value (50% of the initial tensile break strength).

Although there is limited information available on the difference in formulation between the skin layers and the core of this GMB, the surface cracks developed in the skin layers only (Fig. 7) imply that the core layer exhibited less degradation in L8 than the two skin layers. This could be due to a highly resistant carrier resin in the core and/or the presence of residual antioxidants detected by HP-OIT delaying the degradation (similar to MxC15's behaviour in L8). Regardless of the reason, this resulted in a measurable resistance of the GMB beyond the nominal failure and the early decrease in Stage III could be mainly attributed to the degradation in the skin layers. These results show that BzSW15 did not follow the traditional degradation trend reported by Hsuan and Koerner (1998) and this was mainly due to the co-extrusion of different layers with different formulations.

3.2. Discussion of the relative performance of the five GMBs

3.2.1. L1 (pH = 0.5)

The HDPE GMB with HALS (i.e., MxC15) as well as the LLDPE GMBs with and without HALS (i.e., LxD15 and LxE15, respectively) all showed resistance to degradation in L1 (pH 0.5) media at 85 °C for more than 60 months, despite their different formulations, resin type and densities. This high resistance was essentially demonstrated in the slow depletion of their Std-OIT packages with time. This is because MxC15, LxD15, and LxE15 were still showing relatively high values that varied between 19 min for LxE15 to 10 min for MxC15 at the end of incubation (Table 4). For the HP-OIT, MxC15 reached residual values after 44 months while LxD15 and LxE15 reached the residual values after 18 and 8 months, respectively (Table 4). Thus, MxC15, LxD15, and LxE15 were still in Stage I and, therefore, they were not expected to exhibit any degradation following Hsuan and Koerner's degradation model.

For MxA15, depletion to a residual Std-OIT of 3 min was reached at the end of the 77-month incubation duration. While this may imply the GMB was still protected by the antioxidants (similar to MxC15, LxD15, and LxE15), changes in SCR, F_B , and HLMI were observed before the full depletion of antioxidants detected by Std-OIT. For example, the decrease in SCR and F_B started when Std-OIT was 13 min ($\approx 13\%$ Std-OIT₀), and 9 min ($\approx 9\%$ Std-OIT₀), respectively. HLMI increased concomitantly with the decrease in F_B . Likewise, the Std-OIT of BzSW15 depleted to a residual value of 5 min ($\approx 3\%$ Std-OIT₀) after 46 months of incubation and degradation in HLMI and F_B started at the same time. Thus, for MxA15 and BzSW15, the degradation was initiated before or just at the depletion of Std-OIT without the induction period (Stage II) in L1.

Comparing the degradation behaviour of the highly resistant GMBs (i.e., MxC15, LxD15, and LxE15) in L1 to those exhibited degradation (i.e., MxA15 and BzSW15), one may attribute their relative performance to (i) the slow depletion of Std-OIT, or (ii) the HP-OIT package, or (iii) the high resistance of PE resins to low pH environments, or (iv) a combination of these three factors.

For the role of the HP-OIT package, degradation in BzSW15 with the highest initial HP-OIT (3300 min) and residual value ($HP-OIT_r = 1700$ min $\approx 51\%$ $HP-OIT_0$) was observed in L1 while LxD15 without HALS ($HP-OIT_0 = 350$ min) did not encounter any degradation during the similar period. This implies that the HP-OIT package boosted with the high molecular weight HALS as well as the high residual value did not aid the protection of BzSW15 in the low pH media examined herein.

For the role of the depletion of Std-OIT, the degradation observed for MxA15 and BzSW15 before or at the Std-OIT depletion times, implies that while the antioxidants detected by Std-OIT may delay the initiation of degradation, their resins exhibited degradation once the efficacy of these antioxidants was partially or completely reduced (i.e., no Stage II). However for the resin used in MxC15, even when Abdelaal and Rowe (2023) added 5 ml/l of surfactant to L1 solution to deplete its Std-OIT after 4.3 months to a residual value of 3 min (relative to 10 min at 76

Table 4

Comparison of the performance of the tested GMB at 85 °C.

Property	units	pH 0.5					pH 13.5					
		MxA15	MxC15	LxD15	LxE15	BzSW15	MxA15	MxC15	LxD15	LxE15	BzSW15	
Length of Stage I	Std-OIT*	month	77	>76	>60	>60	46	7.8	11.6	18	>43	4
	HP-OIT		33	44	18	8	12	7.8	12.3	36	>43	4
	Std-OIT _r	min.	3	10	25***	19***	5	3	3	5	38***	5
	HP-OIT _r		95	310	150	355	1700	35	850	70	445	2500
Length of Stage II****	HLMI	month	no Stage II	UD	UD	UD	0	4.2	8.4	24	UD	10
	F _B (XD)		no Stage II	UD	UD	UD	0	0.2	8.4	19	UD	24
	SCR		no Stage II	UD	NI	NI	NI	0.2	12.4	26	NI	NI
Length of Stage III	F _B (XD) ^a	month	65**	UD	UD	UD	49**	32	32	3	UD	2
	SCR ^b		22	UD	NI	NI	NI	22	7	1	NI	NI
Time to nominal Failure (t _{NF})	F _B (XD) ^a	month	103** ^c	>76	>60	>60	95**	40	52	40	>52	30
	SCR ^b		52	>76	NI	NI	NI	30	31	45	NI	NI

NR= Not reached-NI= Not investigated-UD= Undefined based on the current incubation duration.

*Std-OIT_r = 3 min for MxA15 and MxC15; = 5 min for LxD15 and LxE15; = 6 min for BzSW15.

**Predicted based on current data.

***OIT value recorded at the end of the incubation.

****The length of Stage II is assessed based on the time from the Std-OIT depletion until the initiation of degradation.

^a t_{NF} when defined based on the property reducing to 50% of the initial value.^b t_{NF} when defined based on SCR being reduced to 50% of the stabilized SCR (SCR_m). For cases that did not show physical aging, t_{NF} when defined based on SCR being reduced to 50% SCR_o.^c Degradation initiated before Std-OIT depleted to residual and hence Stage I + Stage III ≠ t_{NF}.

months in L1 without surfactant), the GMB did not show any degradation for up to 36 months of incubation. This shows that even after the full depletion of the Std-OIT, the unprotected GMB resin of MxC15 maintained a high resistance to degradation at pH 0.5 for about 32 months at 85 °C. Thus, among the different factors that may contribute to the resistance to degradation in low pH, it seems that the longer retention of the properties for MxC15, LxD15 and LxE15 in the low pH solution could be attributed to the high resistance of their specific resins to pH 0.5 than the two different resins used for MxA15 and BzSW15. This resistance seems to be unrelated to the crystallinity (and density) of the resin given that the two lower crystallinity LLDPE GMBs outperformed the higher crystallinity MxA15 and BzSW15.

3.2.2. L8 (pH = 13.5)

The depletion of Std-OIT in L8 (pH 13.5) solution was substantially faster than in low pH for all the examined GMBs except for LxE15 that did not show full depletion of Std-OIT in either solution (Table 4). Full depletion of Std-OIT was obtained in L8 after 18, 11.6, 7.8, and 4 months for LxD15, MxC15, MxA15, and BzSW15, respectively, showing the least resistance to depletion in the high pH media for the blended BzSW15. In terms of the Std-OIT depletion patterns, only MxA15 and BzSW15 showed a single rate depletion to the residual values while MxC15, LxD15 and LxE15 had a two-rate depletion pattern. The two-rate depletion pattern was also observed by other investigators and may be due to the carbon black interaction with antioxidants (e.g., Müller and Jakob 2003; Wong 2011; and Abdelaal and Rowe 2014b) and/or may be due to the different antioxidant groups stabilizing the GMB and detected by Std-OIT (e.g., Abdelaal and Rowe 2014b; Abdelaal and Rowe 2017). Abdelaal and Rowe (2017) suggested that the early fast rate was related to the depletion of phosphites while the second slower rate was mainly reflecting the depletion of the higher molecular weight hindered phenols. Despite the susceptibility of the hindered phenols to base-catalyzed hydrolysis when exposed to strong caustic solutions (Schiers, 2009), it seems for MxC15, LxD15, and LxE15 that their hindered phenols were much more resistant to depletion relative to their phosphites group. However, it seems that LxE's phenolic antioxidants were very different from those of MxC15 and LxD15 given their substantial difference in the second stage depletion rates (0.005 month⁻¹ for LxE15 vs. 0.15 and 0.17 month⁻¹ for MxC15 and LxD15, respectively) although they had very close early rates (0.73, 0.8, 0.6 month⁻¹ for LxE15, LxD15, and MxC15, respectively). This implies that LxE15 may be stabilized with specially

modified phenolic antioxidants and/or there was a synergistic effect of the group of the stabilizers used in its formulation that showed remarkable resistance to extraction in the high pH environment.

For the HP-OIT, the relative depletion to residual values of the five GMBs was similar to their relative Std-OIT depletion times (i.e., LxE15>LxD15>MxC15>MxA15>BzSW15; Table 4). The two GMBs without HALS (i.e., MxA15 and LxD15) had residual values of 13% and 20% HP-OIT_o, respectively, while for MxC15, BzSW15, and LxE15 stabilized with HALS, the residual values were 88, 76, 50% HP-OIT_o, respectively. While it is expected for GMBs without HALS to have similar HP-OIT and Std-OIT depletion times, MxC15 and BzSW15 with HALS had similar HP-OIT and Std-OIT depletion times but to high residual values. Given the limited depletion of HALS in pH 13.5 (Abdelaal and Rowe 2017), the Std-OIT and HP-OIT tests were both essentially reflecting the depletion of the hindered phenols and hence the two OIT tests are expected to show the same depletion times (i.e., time to reach the residual values) but with different rates and to different residual values. This hypothesis applies also to LxE15 since its Std- and HP-OIT were both depleting over the entire incubation duration suggesting that the HP-OIT depletion was also reflecting the depletion of hindered phenols following the early limited depletion of the HALS. The only GMB with inconsistent Std-OIT and HP-OIT depletions times was LxD15 without HALS. This implies that this GMB was stabilized with antioxidants that can only be detected by HP-OIT other than the HALS given its low initial HP-OIT values.

In Solution L8 and except for LxE15 which did not show any degradation and hence outperformed all the other GMBs, the length of Stage II based on F_B for BzSW15, LxD15, MxC15, and MxA15 was 24, 19, 8.4, and 0.2 months, respectively after their Std-OIT depletion (Table 4). This may indicate that the examined LLDPE and blended resins were more resistant than the HDPE resins to initiate the degradation beyond the full Std-OIT depletion. However, considering the HP-OIT depletion time of LxD15 of 36 months (i.e., the time at which the HP-OIT reached a residual value of 70 min), the duration of Stage II is reduced to 1 month only (8 and 6 months based on SCR and HLMI, respectively). In this case, the retention time beyond the full depletion of effective antioxidants (either those detected by Std- or HP-OIT) was the longest for BzSW15 then MxC15 then LxD15 and the shortest Stage II was still for MxA15. With the high resistance of HALS to depletion in pH 13.5 (Schiers 2009), it seems that the presence of these high molecular weight antioxidants within the GMB could be one of the reasons responsible for the longer

retention of the physical and mechanical properties of MxC15 relative to MxA15 in L8. This can be also seen for BzSW15 which had the longest retention of its F_B (Stage II) relative to all the other GMBs despite its shortest Stage I duration. However, this hypothesis cannot be confirmed for the LLDPE GMBs since LxE15 is still in its antioxidant depletion stage. Further incubation is needed to explore the residual HP-OIT values at the onset of polymer degradation of LxE15.

For Stage III, the longest duration based on F_B , was for MxC15 and MxA15 (32 months), followed by LxD15 and BzSW15 with Stage III of only 3 and 2 months, respectively. This shows that once the degradation was initiated in the LLDPE and the blended resins, it propagated substantially faster than the examined HDPE resins. Similar behaviour was seen in L1 in which Stage III was shorter for the blended GMB than the HDPE MxA15.

Considering HLMI and SCR, the relative performance of the five GMBs was similar to their relative performance assessed based on F_B . The only exception was for the duration of Stage III for MxC15 based on SCR that was significantly shorter than MxA15 but still longer than LxD15. This big difference between MxC15 and MxA15 can be attributed to the physical ageing of MxC15 that resulted in an early decrease of SCR to $45\%SCR_o$ (i.e., SCR_m) in the first 2 months of incubation. Hence, the degradation to $50\%SCR_m$ (i.e., from $45\%SCR_o$ to $22.5\%SCR_o$) took a shorter time than Stage III of MxA15 with its Stage III being assessed as a 50% drop from its SCR_o . This shows that interpretation of the degradation stages should involve a holistic evaluation of the different index properties of the GMB not to rely on a single property that may be influenced by factors other than the chemical degradation (e.g., physical ageing in SCR).

Based on the foregoing discussion, adding the durations of the three different stages gives t_{NF} based on F_B of >60 months for LxE15, followed by 52 months for MxC15 then 40 months for LxD15 and MxA15 and finally, the shortest time to nominal failure was for BzSW15 of 30 months. If t_{NF} was assessed based on the currently available SCR data, LxD15 gives longer t_{NF} than MxA15 and MxC15 (Table 4). The comparison of the t_{NF} of the five different GMBs in L8 shows that the relative performance of these GMBs did not follow the expected behaviour from their resin densities and/or crystallinities. This is because the best performance was for a lower crystallinity/density LLDPE GMB (LxE15) and this was mainly attributed to its effective stabilizer package that delayed degradation in the aggressive basic media. Additionally, the durations of Stage I + Stage II of the other four GMBs were 37, 28, 20, and 8 months for LxD15, BzSW15, MxC15, and MxA15 based on F_B showing that the other LLDPE and the blended GMBs had longer retention of their properties than the two HDPE GMBs. However, once degradation was initiated, it appears that the crystallinity of the GMB plays an important

role in the rate of degradation and hence the length of Stage III as shown in the current study. This shows that with the difference in formulations of the examined GMBs, it was not possible to predict their relative performance based on their initial properties or their resin type. Thus, immersion tests simulating the chemistry and characteristics of the solutions in the field should be used to compare between the degradation behaviour under the expected field conditions to select the best GMB for the desired application.

3.3. Morphology of brittle failure surface after SCR testing

The SCR of PE GMBs is one of the primary factors controlling their service life in the field (Seeger and Muller, 2003; Abdelaal et al., 2014; Zha et al., 2022). Incidentally, among the big differences between HDPE, LLDPE, and BPO GMBs is their initial SCR. Thus, the failure surfaces of the aged SCR specimens from MxC15, LxD15 and BzSw15 were analyzed using both optical and scanning electron microscopy (SEM) to compare their SCR behaviour (e.g., failure time and the failure surface morphology). Fig. 8 shows SEM micrographs of the failure surface of the SCR samples after aging in L8 for a 5-year incubation duration at 85°C . The aged MxC15 specimen ($SCR_{5\text{years}} = 30\text{ h}$; $<1\%SCR_o$) had generally a three-phase morphology from bottom to top (Fig. 8a). The vicinity of the notch and the zone up to one-third of the fracture plane displayed very short thick fibres as a characteristic of brittle rupture (Chen 2014; Lu et al., 1991; Lustiger 1985). Crack growth then entered a transition zone of relatively more elongated fibres as the intact cross-sectional area of the specimen was increasingly reduced, which then led to larger stresses and ultimately to failure in a ductile manner in the third zone of the fracture surface.

For the LLDPE with an initial SCR of 19,000 h, the same ageing time resulted in the embrittlement of the polymer ($SCR_{5\text{years}} = 26\text{ h}$; $<0.2\%SCR_o$) and fracture did not initiate from the notch but rather from a surface crack at the left side of the specimen (Fig. 8b). SCR morphology was marked by a non-uniform long-fibrous detachment where the crack was initiated and mostly by a smooth brittle surface with much shorter fibres relative to MxC15.

The fractured plane of BzSw15 ($SCR_{5\text{years}} = 1750\text{ h}$; $\approx 7\%SCR_o$) was completely different from its HDPE and LLDPE counterparts (Fig. 8c). The first, and perhaps the most notable morphological feature was that the ductile failure did not occur towards the end of the crack growth path but at the middle of the specimen cross-section. This was because after 5 years of incubation surface degradation on the black skin (i.e., the unnotched side) was severe enough to induce cracks along its surface upon loading, and hence these cracks propagated through the thickness of the GMB during the SCR test (Fig. 9). The region of the brittle failure

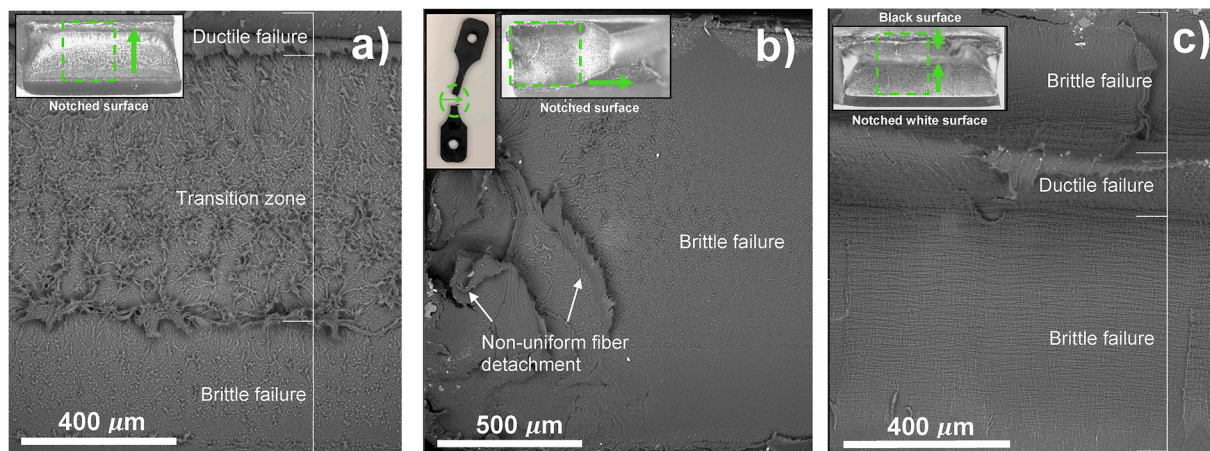


Fig. 8. SEM micrographs of the fracture surface from: (a) MxC15 ($SCR_{5\text{years}} = 30\text{ h}$; $<1\%SCR_o$); (b) LxD15 ($SCR_{5\text{years}} = 26\text{ h}$; $<0.2\%SCR_o$); and (c) BzSw15 ($SCR_{5\text{years}} = 1750\text{ h}$; $7\%SCR_o$). GMBs were immersed in L8 (pH 13.5) at 85°C . The notched side is at the bottom of the photographs.

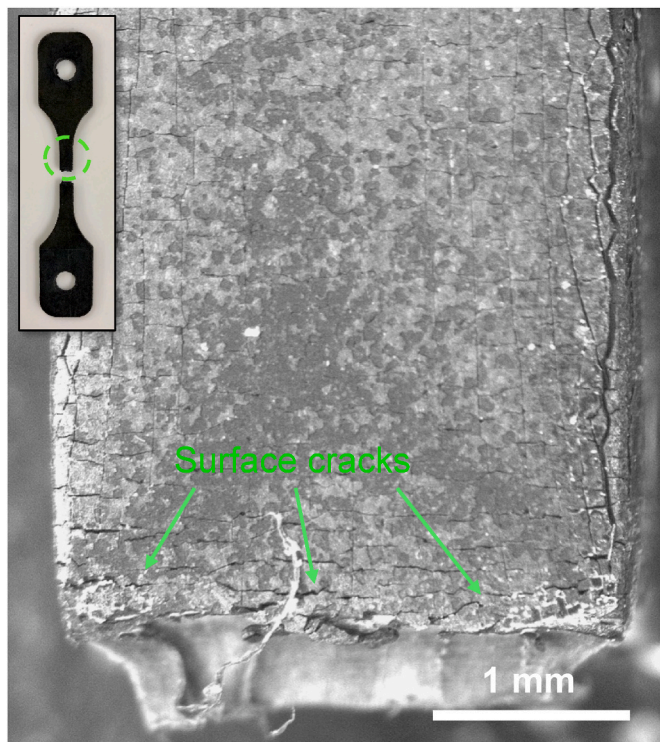


Fig. 9. Elevation of the SCR specimen of BzSw15 after failure showing severe surface degradation on the black skin (crack propagation is in the direction perpendicular to the page). Image obtained using an optical microscope.

was characterized by several short, thin fibres uniformly distributed and of somewhat uniform length and orientation. This was the predominant morphology for both crack paths, and unlike the HDPE GMB (MxC15), there was no gradual transition between brittle and ductile behaviour.

The micrographs presented in Fig. 8 show that the SCR failure behaviour can significantly vary among HDPE, LLDPE and BPO GMBs when aged under the same exposure conditions for the same time. For instance, while MxC15 and LxD15 were aged to reach the same SCR (~30 h), only LxD15 reached brittleness. For BzSW15, although it reached nominal failure faster than MxC15 and LxD15, its SCR after 5 years of ageing in L8 was twice the initial SCR of the unaged MxC15. Thus, the relatively short t_{NF} of BzSW15 obtained using the immersion tests does not necessarily mean a short service life of this GMB in the field. This is due to the retention of its properties beyond the nominal failure ($SCR_{5years} = 1750$ h and $F_{B5years} = 50\% F_{B0}$) at higher values than the other GMBs examined, making it less susceptible to stress-cracking. With such unusual behaviour of BzSW15, further investigation is required to examine BzSW15 under simulated field conditions (specifically field stresses) to assess its service life since this cannot be explored using immersion tests (Rowe et al., 2010). Although the arbitrary definition of t_{NF} to 50% of the initial values used in the current study was useful in comparing the relative chemical durability of the different GMBs (i.e., their resistance to degradation), it does not necessarily reflect how long these GMBs can last in the field under simulated conditions.

4. Conclusions

Using immersion tests at 85 °C in two different solutions simulating both low (pH = 0.5) and high (pH = 13.5) pH mining applications, the degradation behaviour of the following five GMBs with different resins and antioxidant/stabilizer packages was examined:

- MxA15 (HDPE, $Std-OIT_o = 100$ min, $HP-OIT_o = 260$ min, and $SCR_o = 720$ h),
- MxC15 (HDPE, $Std-OIT_o = 160$ min, $HP-OIT_o = 960$ min, and $SCR_o = 800$ h),
- LxD15 (LLDPE, $Std-OIT_o = 190$ min, $HP-OIT_o = 350$ min, and $SCR_o = 19,000$ h)
- LxE15 (LLDPE, $Std-OIT_o = 155$ min, $HP-OIT_o = 890$ min, and $SCR_o > 18,500$ h)
- BzSW15 (BPO, $Std-OIT_o = 180$ min, $HP-OIT_o = 3300$ min, and $SCR_o = 26,000$ h)

For the GMBs and test conditions (e.g., temperature, solution chemistry, and pH) investigated herein, the following conclusions were reached:

1. The relative performance of the five GMBs and their chemical compatibility with the solutions expected in the field could not be predicted based on their initial properties or their resin type.
2. The best long-term performance in both the low and high pH solutions was obtained for one of the LLDPE GMBs (LxE15) with the lowest crystallinity/density and with moderate $Std-OIT_o$, $HP-OIT_o$, and SCR_o relative to the other four GMBs, however, this is likely due to a better antioxidant-stabilizer package rather than the resin itself.
3. While most of the GMBs examined followed the conceptual three-stage degradation model in the L8-pH 13.5 solution, in L1-pH 0.5, two GMBs exhibited polymer degradation before or at the time of the depletion of the antioxidants detected by Std-OIT. In this case, the traditional three-stage degradation conceptual model may still apply at a given point in the GMB but not to the entire thickness of the GMB and the length of Stage I can exceed the time at which Stage III starts.
4. Over an incubation period of 4.5–6.5 years at 85 °C, of the five GMBs examined, four showed degradation in their mechanical and physical properties in L8-pH 13.5 while only two showed degradation in L1-pH 0.5. Thus, except for LxE15 that did not exhibit degradation in either solution, the pH 13.5 solution examined was more aggressive than the pH 0.5 solution. For the GMBs where comparison can be made to other incubation media, the degradation in the pH 0.5 solution was slower than in neutral de-ionized water.
5. While the slow depletion of the antioxidants detected by Std-OIT had a role in delaying the initiation of degradation in L1-pH 0.5, the retention of the GMB properties (i.e., in Stage II) can be attributed to the resistance of the GMB resin to the degradation in the low pH media. This resistance seemed to be unrelated to the resin's crystallinity/density but mainly to the resin chemistry and chain structure, given that the two lower crystallinity/density LLDPE GMBs outperformed one of the HDPE GMBs and the blended GMB with higher crystallinities.
6. In pH 13.5, the antioxidants stabilizing the GMBs had an important role in their longevity and hence their relative performance. The duration of Stage I was dependent on the resistance of the antioxidants to base-catalyzed hydrolysis when exposed to the strong caustic solution. Beyond the full depletion of effective antioxidants (either those detected by Std- or HP-OIT) to residual values, the presence of the high molecular weight antioxidants detected as the high residual HP-OIT values may be related to the longer retention of the GMB properties. For example, Stage II based on F_B was 24 months for BzSW15 ($HP-OIT_r = 2500$ min), 8.4 months for MxC15 ($HP-OIT_r = 850$ min), 1 month for LxD15 ($HP-OIT_r = 70$ min), and 0.2 months for MxA15 ($HP-OIT_r = 35$ min). Overall, it is hypothesized that the duration of Stage I+II in pH 13.5 was more dependent on the stabilizer package than the resin type since a longer retention period was obtained for the LLDPE and the blended GMBs than the two HDPE GMBs.
7. In L8-pH 13.5, the crystallinity and density of the resin had an important effect on the degradation rates beyond Stages I and II (i.e., in Stage III). When the polymer degradation was initiated, the LLDPE

and BPO GMBs with lower crystallinity and density had shorter Stage III than the HDPE GMBs when immersed in the pH 13.5 solution. This shows the different effects of crystallinity and density of the resin on the different stages of the GMB degradation given that they did not have a clear effect on the length of Stage II in L1-pH 0.5.

- The co-extruded BPO GMB exhibited unusual retention of its HLMI and F_B at 30 and 50% of the initial values, respectively, after reaching nominal failure and until the end of the incubation duration reported in this study. This behaviour was attributed to the faster degradation of the co-extruded skin layers than the core layer during exposure to the pH 13.5 solution.
- The failure surface of the SCR samples from MxC15, LxD15, and BzSW15 showed different morphology after ageing for 5 years in pH 13.5. Although the blended GMB had the shortest time to nominal failure, its SCR after 5 years was higher than the initial SCR of MxC15. Thus, while immersion tests can reveal information about the efficiency of the stabilizer package and the resin in resisting degradation, the assessment of the long-term performance of GMBs with different resin types (especially those having high initial SCR) should also consider their resistance to failure under field stresses.

This paper presented the relative performance of HDPE, LLDPE, and BPO GMBs when immersed in low and high pH solutions for an incubation period of up to 6.5 years at 85 °C. The results are relevant to the particular GMBs, and conditions examined. Given the difference in formulation and properties between the GMBs, their relative performance can be only assessed using accelerated immersion testing similar to those described in this study. Further testing is required to investigate the behaviour of the blended GMB to assess how long it will retain its properties beyond nominal failure and the effect of this behaviour on its service life in the field. Additionally, incubation at lower temperatures is needed to explore the relative performance of the GMBs at different temperatures and to predict their nominal failure at field temperatures.

Data

Some or all data used are available from the corresponding author by request.

Declaration of competing interest

The authors declare there are no competing interests.

Data availability

Data will be made available on request.

Acknowledgements

The research presented in this paper was funded by the Natural Science and Engineering Research Council of Canada (NSERC) through the strategic partnership grant (STPGP 521237), and used equipment provided by funding from the Canada Foundation for Innovation (CFI) and the Ontario Ministry of Research and Innovation. The authors are grateful to their industrial partners, Solmax, Terrafix Geosynthetics Inc., Layfield, Wood, Golder Associates Ltd., Knight-Piesold, Titan Environmental Containment, SNC-Lavalin, Klohn Crippen Berger and the CTT group for their participation in, and contributions to, the overarching project. The authors also acknowledge the contribution from the Coordination for the Improvement of Higher Education Personnel (CAPES, Brazil) for partially funding Mr. E Silva. However, the opinions expressed in this paper are solely those of the authors.

References

- Abdelaal, F.B., Rowe, R.K., 2014a. Antioxidant depletion from a LLDPE geomembrane in an extremely high pH solution. In: *Proceedings of Conference of Geosynthetics Mining Solutions*. Canada, Vancouver.
- Abdelaal, F.B., Rowe, R.K., 2014b. Effect of high temperatures on antioxidant depletion from different HDPE geomembranes. *Geotext. Geomembranes* 42 (4), 284–301. <https://doi.org/10.1016/j.geotexmem.2014.05.002>.
- Abdelaal, F.B., Rowe, R.K., 2017. Effect of high pH found in low-level radioactive waste leachates on the antioxidant depletion of a HDPE geomembrane. *J. Hazard., Toxic, Radioact. Waste* 21 (1), D4015001. [https://doi.org/10.1061/\(ASCE\)HZ.2153-5515.0000262](https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000262).
- Abdelaal, F.B., Rowe, R.K., 2023. Degradation of physical and mechanical properties of a HDPE geomembrane with HALS in ten different low and high pH mining environments. *Can. Geotech. J.* <https://doi.org/10.1139/cgj-2022-041> (in press).
- Abdelaal, F.B., Rowe, R.K., Islam, M.Z., 2014. Effect of leachate composition on the long-term performance of a HDPE geomembrane. *Geotext. Geomembranes* 42 (4), 348–362. <https://doi.org/10.1016/j.geotexmem.2014.06.001>.
- Abdelaal, F.B., Morsy, M.S., Rowe, R.K., 2019. Long-term performance of a HDPE geomembrane stabilized with HALS in chlorinated water. *Geotext. Geomembranes* 47 (6), 815–830. <https://doi.org/10.1016/j.geotexmem.2019.103497>.
- ASTM D1238. Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer. American Society for Testing and Materials, West Conshohocken, PA.
- ASTM D1505. Standard Test Method for Density of Plastics by the Density-Gradient Technique. American Society for Testing and Materials, West Conshohocken, PA.
- ASTM D3418. Standard Test Method for Melting and Crystallisation Temperatures by Thermal Analysis. American Society for Testing and Materials, West Conshohocken, PA.
- ASTM D3895. Standard Test Method for Oxidative Induction Time of Polyolefins by Differential Scanning Calorimetry. American Society for Testing and Materials, West Conshohocken, PA.
- ASTM D5199. Standard Method for Measuring the Nominal Thickness of Geosynthetics. American Society for Testing and Materials, West Conshohocken, PA.
- ASTM D5397. Standard Test Method for Evaluation of Stress Crack Resistance of Polyolefin Geomembranes Using Notched Constant Tensile Load Test. American Society for Testing and Materials D5397, West Conshohocken, PA.
- ASTM D5885. Standard Test Method for Oxidative Induction Time of Polyolefin Geosynthetics by High Pressure Differential Scanning Calorimetry. American Society for Testing and Materials D5885, West Conshohocken, PA.
- ASTM D6693. Standard Test Method for Determining Tensile Properties of Non-reinforced Polyethylene and Nonreinforced Flexible Polypropylene Geomembranes. American Society for Testing and Materials, West Conshohocken, PA.
- Barret, J., Gijsman, P., Swagten, J., Lange, R.F.M., 2002. A molecular study towards the interaction of phenolic anti-oxidants, aromatic amines and HALS stabilizers in a thermo-oxidative ageing process. *Polym. Degrad. Stab.* 76 (3), 441–448. [https://doi.org/10.1016/S0141-3910\(02\)00047-2](https://doi.org/10.1016/S0141-3910(02)00047-2).
- Chen, Y., 2014. Investigations of environmental stress cracking resistance of HDPE/EVA and LDPE/EVA blends. *J. Appl. Polym. Sci.* 131, 39880 <https://doi.org/10.1002/app.39880>.
- Christie, M.A., Smith, M.E., 2013. A brief history of heap leaching. In: *Proceedings of Geosynthetics 2013 Conference*, Industrial Fabrics Association International. CA, USA, pp. 265–287.
- Ewais, A.M.R., Rowe, R.K., 2014. Effect of aging on the stress crack resistance of an HDPE geomembrane. *Polym. Degrad. Stab.* 109, 194–208. <https://doi.org/10.1016/j.polymdegradstab.2014.06.013>.
- Ewais, A.M.R., Rowe, R.K., Scheirs, J., 2014. Degradation behaviour of HDPE geomembranes with high and low initial high pressure oxidative induction time. *Geotext. Geomembranes* 42 (2), 111–126. <https://doi.org/10.1016/j.geotexmem.2014.01.004>.
- Ewais, A.M.R., Rowe, R.K., Rimal, S., Sangam, H.P., 2018. 17-year elevated temperature study of HDPE geomembrane longevity in air, water and leachate. *Geosynth. Int.* 25 (5), 525–544. <https://doi.org/10.1680/jgein.18.00016>.
- Földes, E., Iring, M., Tüdös, F., 1987. Degradation of HDPE and LLDPE in closed mixing chamber: a comparison. *Polym. Bull.* 18 (6), 525–532. <https://doi.org/10.1007/BF00255337>.
- GRI (Geosynthetic Research Institute), 2021. *Standard Specification For Test Methods, Test Properties, and Testing Frequency For High Density Polyethylene (HDPE) Smooth And Textured Geomembranes: GRI Test Method Geomembrane 13*. Geosynthetic Research Institute, Folsom, PA, USA.
- Gulmine, J.V., Janissek, P.R., Heise, H.M., Akcelrud, L., 2002. Polyethylene characterization by FTIR. *Polym. Test.* 21 (5), 557–563. [https://doi.org/10.1016/S0142-9418\(01\)00124-6](https://doi.org/10.1016/S0142-9418(01)00124-6).
- Hsuan, Y.G., Koerner, R.M., 1998. Antioxidant depletion lifetime in high density polyethylene geomembranes. *J. Geotech. Geoenviron. Eng.* 124 (6), 532–541. [https://doi.org/10.1061/\(ASCE\)1090-0241\(1998\)124:6\(532\)](https://doi.org/10.1061/(ASCE)1090-0241(1998)124:6(532)).
- Hsuan, Y.G., Schroeder, H.F., Rowe, R.K., Müller, W., Greenwood, J., Cazzuffi, D., Koerner, R.M., 2008. Long-term Performance and Lifetime Prediction of Geosynthetics. 4th European Conference on Geosynthetics, Edinburgh, UK, September.
- Jergensen, G.V., 1999. Copper leaching, solvent extraction, and electrowinning technology. Society for mining, metallurgy and exploration, inc. SME Symposium proceedings.
- Lee, S.Y., Jho, J.Y., 1998. Effect of comonomer sequence distribution of LLDPE on miscibility of HDPE/LLDPE blends in the melt state. *J. Ind. Eng. Chem.* 4 (2), 170–176.

- Lu, X., Qian, R., Brown, N., 1991. Discontinuous crack growth in polyethylene under a constant load. *J. Mater. Sci.* 26 (4), 917–924. <https://doi.org/10.1007/BF00576768>.
- Lupo, J.F., 2010. Liner system design for heap leach pads. *Geotext. Geomembranes* 28 (2), 163–173. <https://doi.org/10.1016/j.geotexmem.2009.10.006>.
- Lustiger, A., 1985. *The Molecular Mechanisms of Slow Crack Growth in Polyethylene*. PhD Thesis. Drexel University.
- Martuscelli, E., Pracella, M., Avella, M., Greco, R., Ragosta, G., 1980. Properties of polyethylene-polypropylene blends: crystallization behavior. *Makromol. Chem.: Macromol. Chem. Phys.* 181 (4), 957–967. <https://doi.org/10.1002/macp.1980.021810417>.
- Morsy, M.S., Rowe, R.K., 2017. Performance of blended polyolefin geomembrane in various incubation media based on Std-OIT. *Geotech. Front.* 2017, 1–10. <https://ascelibrary.org/doi/abs/10.1061/9780784480434.001>.
- Morsy, M.S., Rowe, R.K., 2020. Effect of texturing on the longevity of high-density polyethylene (HDPE) geomembranes in municipal solid waste landfills. *Can. Geotech. J.* 57 (1), 61–72. <https://doi.org/10.1139/cgj-2019-0047>.
- Morsy, M.S., Rowe, R.K., Abdelaal, F.B., 2020. Longevity of twelve geomembranes in chlorinated water. *Can. Geotech. J.* 58 (4), 479–495. <https://doi.org/10.1139/cgj-2019-0520>.
- Müller, W., Jakob, I., 2003. Oxidative resistance of high density polyethylene geomembranes. *Polym. Degrad. Stab.* 79 (1), 161–172. [https://doi.org/10.1016/S0141-3910\(02\)00269-0](https://doi.org/10.1016/S0141-3910(02)00269-0).
- Munaro, M., Akcelrud, L., 2008. Polyethylene blends: a correlation study between morphology and environmental resistance. *Polym. Degrad. Stab.* 93 (1), 43–49. <https://doi.org/10.1016/j.polymdegradstab.2007.10.017>.
- Queja, C.B., Orman, M.E., Hlinko, M.J., 1995. *Flexible Membrane Liner Compatibility Involving Copper Leachate Solutions*. Society for mining, metallurgy, and Exploration, Inc. for presentation at the SME annual meeting, Denver, Colorado.
- Rachtanapun, P., Selke, S.E.M., Matuana, L.M., 2004. Effect of the high-density polyethylene melt index on the microcellular foaming of high-density polyethylene/polypropylene blends. *J. Appl. Polym. Sci.* 93 (1), 364–371. <https://doi.org/10.1002/app.20428>.
- Rowe, R.K., 1988. Contaminant migration through groundwater: the role of modelling in the design of barriers. *Can. Geotech. J.* 25 (4), 778–798.
- Rowe, R.K., 2011. Systems engineering: the design and operations of municipal solid waste landfills to minimize leakage of contaminants to groundwater. *Geosynth. Int.* 16 (6), 391–404.
- Rowe, R.K., Abdelaal, F.B., 2016. Antioxidant depletion in HDPE geomembrane with HALS in low pH heap leach environment. *Can. Geotech. J.* 53 (10), 1612–1627. <https://doi.org/10.1139/cgj-2016-0026>.
- Rowe, R.K., Sangam, H.P., Lake, C.B., 2003. Evaluation of an HDPE geomembrane after 14 years as a leachate lagoon liner. *Can. Geotech. J.* 40 (3), 536–550.
- Rowe, R.K., Rimal, S., Sangam, H., 2009. Ageing of HDPE geomembrane exposed to air, water and leachate at different temperatures. *Geotext. Geomembranes* 27 (2), 137–151. <https://doi.org/10.1016/j.geotexmem.2008.09.007>.
- Rowe, R.K., Islam, M.Z., Brachman, R.W.I., Arnepalli, D.N., Ewais, A.R., 2010. Antioxidant depletion from an HDPE geomembrane under simulated landfill conditions. *ASCE J. Geotech. Geoenviron.* 136 (7), 930–939.
- Rowe, R.K., Brachman, R.W.I., Irfan, H., Smith, M.I., Thiel, R., 2013. Effect of underliner on geomembrane strains in heap leach pad applications. *Geotext. Geomembranes* 40, 37–47. <https://doi.org/10.1016/j.geotexmem.2013.07.009>.
- Rowe, R.K., Abdelaal, F.B., Islam, M.Z., 2014. Aging of HDPE geomembrane of three different thicknesses. *Journal of Geotechnical and Geoenvironmental Engineering*. ASCE 140 (5), 1–11. [https://doi.org/10.1061/\(ASCE\)GT.1943-5606.0001090](https://doi.org/10.1061/(ASCE)GT.1943-5606.0001090).
- Rowe, R.K., Morsy, M.S., Ewais, A.M.R., 2019. Representative stress crack resistance of polyolefin geomembranes used in waste management. *Waste Manag.* 100, 18–27. <https://doi.org/10.1016/j.wasman.2019.08.028>.
- Rowe, R.K., Abdelaal, F.B., Zafari, M., Morsy, M.S., Priyanto, D., 2020. An approach to HDPE geomembrane selection for challenging design requirements. *Can. Geotech. J.* 57 (10), 1550–1565. <https://doi.org/10.1139/cgj-2019-0572>.
- Scheirs, J., 2009. *A Guide to Polymeric Geomembranes: a Practical Approach*. John Wiley and Sons.
- Schellenberg, J., Fienhold, G., 1998. Environmental stress cracking resistance of blends of high-density polyethylene with other polyethylenes. *Polym. Eng. Sci.* 38 (9), 1413–1419. <https://doi.org/10.1002/pen.10311>.
- Seeger, S., Muller, W., 2003. Theoretical approach to designing protection: selecting a geomembrane strain criterion. In: *Geosynthetics: Protecting the Environment: Proceedings of the 1st IGS UK Chapter National Geosynthetics Symposium*, pp. 137–151.
- Smith, M.E., 2008. Emerging issues in heap leaching technology. In: *The Proceedings of the 4th Euro Geo Conference, Paper No. 270, Edinburgh, Scotland, UK*.
- Teh, J.W., Rudin, A., Keung, J.C., 1994. A review of polyethylene–polypropylene blends and their compatibilization. *Adv. Polym. Technol.: J. Polym. Proc. Inst.* 13 (1), 1–23. <https://doi.org/10.1002/adv.1994.060130101>.
- Thiel, R., Smith, M.E., 2004. State of the practice review of heap leach pad design issues. *Geotext. Geomembranes* 22 (6), 555–568. <https://doi.org/10.1016/j.geotexmem.2004.05.002>.
- Wong, W.K., 2011. *Evaluation of the oxidative degradation mechanism of corrugated high density polyethylene pipe and the pipe resin* (PhD Thesis). Drexel University, Philadelphia, United States.
- Zha, S., Lan, H.Q., Huang, H., 2022. Review on lifetime predictions of polyethylene pipes: limitations and trends. *Int. J. Pres. Ves. Pip.* 198, 104663 <https://doi.org/10.1016/j.ijpvp.2022.104663>.
- Abdelaal, F.B., Rowe, R.K., Smith, M.E., Thiel, R., 2011. OIT Depletion in HDPE GMBs used in contact with solutions having very high and low pH. In: *Pan-Am CGS Geotechnical Conference*. Toronto, ON, Canada.