Physical and mechanical performance of a HDPE Geomembrane in ten mining solutions with different pHs

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ABSTRACT

The degradation in physical and mechanical properties of a 1.5 mm-thick HDPE geomembrane immersed in seven different low pH and three high pH simulated mining solutions is examined at temperatures between 95 and 40°C for 3 years. The solutions with pH between 0.5 and 13.5 encompass solutions found in copper, nickel, uranium, gold, and silver heap leach pads. The geomembrane did not exhibit any chemical degradation during the 3 years of incubation in all the low pH solutions. However, in the solutions with pH 9.5, 11.5, and 13.5, some of the geomembrane's physical and mechanical properties are shown to reach nominal failure at 95 and 85°C. While the geomembrane examined shows superior performance in the acidic environments than in the basic solutions examined, its performance in such extremely basic environments is still better than in neutral reduced municipal solid waste leachate. Using Arrhenius modelling the predicted times for the antioxidant depletion stage of the geomembrane examined in composite liner configuration range between 31 years in pH 13.5 to 51 years in pH 0.5 for pad liners at 50°C exceeding a typical leaching period of the ore of around 20 years in different heap leaching operations.

KEYWORDS: Geosynthetics, Geomembranes, HDPE, Degradation, Heap leach pads, Mining, Low pH, High pH, Stress crack resistance, HALS.

1. INTRODUCTION

Heap leaching is a mining process in which ores are leached with various solvents (acidic or basic) to extract valuable metals. Relative to other mineral extraction technologies, heap leaching enables cost-effective metallurgical recovery from very low-grade ores (Christie and Smith 2013). It is used to recover copper, uranium, gold, and silver at a very large commercial scale whereas nickel is recovered at limited commercial production (Abdelaal et al. 2011; Christie and Smith 2013). Heap leach operations rely on different geosynthetic products to provide efficient solution recovery and environmental containment (Thiel and Smith 2004). A key geosynthetic product is the pad geomembrane (GMB) liner that allows the collection of the leach solutions after passage through the ore (often called the pregnant leach solution; PLS) for recovery of the valuable metals and prevents migration of the contaminants to the surrounding environment. Under the field conditions, the GMB is exposed to extreme pH in addition to high vertical pressures from the large stacking heights of the ore on top of the pad (Lupo 2010) and together these represent one of the most aggressive service environments for GMB liners (Scheirs 2009). In addition, under some circumstances pyrite rich tailings may have a low pH while red mud may have a high pH pore water in contact with a liner or cover.

Under long-term exposure to such site conditions, polyolefin GMBs may undergo degradation in their physical, mechanical, and chemical properties that can affect their hydraulic barrier role in the pad. GMB degradation is often divided into three distinct stages (Hsuan and Koerner 1998, Rowe and Sangam 2002). It conceptually starts with the loss of antioxidants in Stage I due to chemical consumption or physical extraction. Stage II is the induction time with no change in the GMB mechanical properties. In Stage III, the GMB starts to exhibit degradation in its mechanical and physical properties until nominal failure is reached when the properties of the GMB either decrease to (i) 50 % of the initial value (Hsuan and Koerner 1998) or (ii) 50 % of the value specified in GRI-GM13 (2021) (Rowe et al. 2009) or (iii) 50 % of the stabilized stress crack resistance (SCR_m; Rowe 2020;

Rowe et al. 2020). Stains that cause stress cracking may be induced in numerous ways (Tognon et al. 2000; Abdelaal et al. 2014; Ewais et al. 2014; Rowe et al. 2019; Rowe and Yu 2019) and considering is needed to assessing Stage I considering the likely thermal history of the facility (e.g., Yoshida and Rowe 2003; Rowe and Islam 2009; Jafari et al. 2014), and to design in the context of minimizing stain and considering the overall system including the hydrogeologic environment (e.g., Rowe and Booker 1995; Rowe 1988, 1998, 2005, 2011, 2012, 2020; Rowe et al. 2003; Rowe et al. 2004; Rowe and Jefferis 2022).

Previous studies (e.g., Gulec et al 2004; Jeon et al. 2008; Rowe and Abdelaal 2016; Abdelaal and Rowe 2017; Zhang et al. 2018) examined the effect of high and/or low pH on the antioxidant depletion (i.e., Stage I) of GMBs in mining solutions. However, there is a paucity of published information regarding the performance of polyolefin GMBs after their oxidative induction time (OIT) has depleted to a constant residual value in simulated heap leach extraction solutions at extreme pHs. Thus, the objective of this paper is to investigate the degradation of a high density polyethylene (HDPE) GMB in ten simulated mining solutions with pH between $0 \leq \text{pH} \leq 2$ and $9.5 \leq \text{pH} \leq 13.5$.

2. BACKGROUND

Rowe and Abdelaal (2016) and Abdelaal and Rowe (2017) investigated the antioxidant depletion from a HDPE GMB (Table 1) for three years at five different temperatures (40-95^{o}C) in different low and high pH solutions, respectively, with the range of pH and chemistries likely to encompass those found in different heap leach applications (Table 2). Where there had been sufficient time (at higher temperatures) to deplete the antioxidants to reach a residual value, these residual values tended to be relatively high (Fig. 1; Table 3). For example, at 85^{o}C, residual standard oxidative induction time (Std-OIT; ASTM D8117) was reached after approximately 27.6 months of incubation with residual Std-OIT values of 0.19 Std-OIT$_o$ at pH 0.5, 0.14 Std-OIT$_o$ at pH 1.25, and, 0.16 Std-OIT$_o$ at pH 2.0. For the high pressure oxidative induction time (HP-OIT; ASTM D5885), in the pH = 1.25 solution the highest residual of 0.70 HP-OIT$_o$ was reached in the shortest time (i.e., after 2.4 months). A residual of 0.61 HP-OIT$_o$ was reached after 2.9 months in the pH =2 solution while the lowest residual of 0.37 HP-OIT$_o$ was reached after 37 months in the pH =0.5 solution.

Immersing the same GMB in solutions with pH 9.5, 11.5, and 13.5 (denoted as Solutions L6, L7, and L8, respectively, in Table 2), Abdelaal and Rowe (2017) showed that the depletion time at 85^{o}C of 12 months was the fastest in the pH=13.5 solution, followed by 23 months in the pH=11.5 solution, and 28 months in the pH= 9.5 solution. A residual Std-OIT of 0.02 Std-OIT$_o$ was reached in all high pH solutions (Fig. 1). For the HP-OIT, the depletion times followed the same depletion trends of Std-OIT giving a depletion time of 12 months to reach 0.9 HP-OIT$_o$ at pH 13.5. In the pH =11.5 and 9.5 solutions, the estimated HP-OIT depletion times were 54 months to reach 0.62 HP-OIT$_o$ and 97 months to reach 0.083 HP-OIT$_o$, respectively.

Similar trends were observed at other temperatures (Table 3). Predictions of time to antioxidant depletion using Arrhenius modelling based on both OIT tests were longer for pH = 0.5 than at pH = 1.25 or 2.0. For example, at 40 °C, Std-OIT depletion was predicted to take 28 years at pH = 0.5 and 25 years at pH = 1.25 and 2.0 while HP-OIT was predicted to take around 45 years at pH = 0.5 compared to 5 years for pH = 1.25 and 9 years for pH = 2.0. For the high pH solutions, at 40°C Std-OIT depletion was predicted to take 24 years for pH 9.5, 21 years for pH 11.5, and 17 years for pH 13.5 while the HP-OIT was predicted to reach the residual values after 26, 11, and 2.4 years for pH 9.5, 11.5, and 13.5, respectively.

Rowe and Abdelaal (2016) and Abdelaal and Rowe (2017) hypothesized two possible scenarios to explain the high residual OIT values (the high residual Std-OIT for the low pH solutions and the high HP-OIT values for all solutions). Scenario 1 envisaged that the residual antioxidants detected by either of the OIT tests continued to protect the GMB resin from degradation (i.e., the GMB was still in Stage

I). Scenario 2 envisaged that the residual antioxidants were inactive and were not protecting the GMB and hence the GMB was in Stage II once the residuals had been reached and should, in time, experience degradation of the mechanical/physical properties when the GMB entered Stage III. However, the validity of these two scenarios and, hence the duration of Stage I could be only explored by monitoring the changes in the physical and mechanical properties of the GMB.

If the traditional 3-stage model proposed by Hsuan and Koerner (1998) is followed, then there should be no degradation of the GMB before the antioxidants are fully depleted to a residual value. However, previous studies (e.g., Abdelaal and Rowe 2014; Rowe and Shoaib 2017) have shown that polymer degradation (i.e., Stage III) can begin before the OIT depletes to residual values. In this case, the traditional three-stage degradation conceptual model may still apply at a given point in the GMB but does not apply to the entire thickness of the GMB and the predicted length of Stage I (antioxidant depletion based on time to residual OIT; Table 3) may exceed the time at which Stage III (degradation in physical properties) begins. Hence, the length of Stage I cannot always be assessed based on OIT depletion only. This raises the question of whether the high residual OIT values measured at the end of the incubation in both Rowe and Abdelaal (2016) and Abdelaal and Rowe (2017) were protecting the GMB from degradation. This question is investigated in the rest of this paper by examining the changes in the mechanical and physical properties of the GMB examined by Rowe and Abdelaal (2016) and Abdelaal and Rowe (2017) in the same solutions with pH ranging from 0.5 to 13.5.

3. EXPERIMENTAL INVESTIGATION

3.1 Immersion Solutions

The ten different synthetic mining solutions were prepared by mixing de-ionized water (pH ≈ 6.5) with the different metal salts to give the different concentrations of the cations and anions presented in Table 2. To adjust the pH, either concentrated H_2SO_4 (98 %) or 15 mol NaOH solutions were titrated to the solutions until the target pHs were achieved. To ensure a constant pH and prevent the build-up of antioxidant concentrations in the solution, the solutions were changed about every 1.3 months during the 36 months (3 years) of incubation. The pH of each fresh solution was checked and was in good agreement with the target pH (Table 2).

Solutions L1, L2, and L3 (Rowe and Abdelaal 2016) are the main low pH solutions investigated in the current study with pHs= 0.5, 1.25, and 2.0, respectively. These solutions generally address the chemical composition and pH range relevant to copper PLS, solution below the ore, and raffinate solution (Queja et al. 1995; Jergensen, 1999). Solution L4 was prepared with an acid content of 100 g/l of H_2SO_4 (pH ~ 0) and the GMB is incubated in this solution for two weeks before being removed and incubated in the Solution L2 (pH= 1.25) for ten weeks to simulate cyclic exposure to concentrated acids. This incubation cycle is repeated every three months to simulate precuring the ore with a high acid concentration in dynamic leach pads (Rowe and Abdelaal 2016). Solution L1-S (pH=0.5+surfactant) is the same as Solution L1 except that it also contains 5 mg/L of IGEPAL Ca-720 (Table 2) and was investigated to address the combined effect of surfactant (that could be added to the leach solution to enhance the permeability of the ore) and low pH. Solution L2-Cl is similar to solution L2 with a pH of 1.25 but with a chloride concentration boosted 15 times to investigate the combined effect of low pH and extremely high salt concentration. Solution water with pH = 0.5 (Table 2) was used as a control test to isolate the effect of the metals in copper PLS from the low pH on the degradation of the physical and mechanical properties of the GMB examined when compared to Solution L1 also at pH = 0.5 but with the high metal concentration.

Solutions L6, L7, and L8 (Abdelaal and Rowe 2017) are the high pH solutions investigated in the current study with pHs= 9.5, 11.5, and 13.5 (Table 2), respectively, simulating extremely high pH of the PLS for gold/silver heap leaching and some low-level radioactive waste leachates (Tian et al.

2017). For safety reasons, the cyanide found in gold and silver PLS was excluded from the extremely high pH solutions simulated in the current study.

3.2 GMB Examined

The 1.5 mm thick black smooth HDPE GMB (manufactured by Solmax International, Varennes, Quebec in 2008; Table 1) had an initial HP-OIT$_o$ (ASTM D5885) of 960 min that implies the presence of hindered amine light stabilizers (HALS) as part of the antioxidant package of this GMB (Scheirs 2009). The GMB had a medium density, high molecular weight hexene copolymer resin with a density of 0.936 g/cc (ASTM D1505). The GMB met all minimum requirements specified by GRI-GM13 (2021) with an initial notched constant tensile load stress crack resistance test (NCTL-SCR; ASTM D1238 appendix) of 800 h, machine direction break strength of 50 kN/m and break strain of 820 % (ASTM D6693), and a high load melt index (HLMI; ASTM D1238) of 12.9 g/10min (Table 2).

3.3 Accelerating ageing and index testing

Table 4 presents the testing matrix for the current study showing the immersion solutions and the testing temperatures. GMB coupons (190 mm x 100 mm) were placed in 4-litre glass containers that were separated using 5 mm glass rods to ensure that the immersion solution is in contact with all surfaces of the coupons. Jars filled with solutions L1, L2, L3, L6, L7, and L8 were incubated at 40, 65, 75, 85, and 95^{o}C. GMB coupons immersed in Solution L1-S were incubated at 65, 75, 85, and 95^{o}C. The other low pH immersion solutions were only incubated at elevated temperature(s) to correlate the degradation of the GMB in these solutions to the three main low pH solutions L1, L2, and L3. This paper mainly focuses on the degradation at elevated temperatures during the 3-year study since degradation at temperatures below 85^{o}C could take several years to occur and hence requires longer incubation than the 3 years presented herein.

Std-OIT and HP-OIT tests were used in parallel to monitor antioxidant depletion and detailed results were reported in Abdelaal and Rowe (2017) and Rowe and Abdelaal (2016). HLMI, SCR, and tensile properties were monitored at different incubation times over the 3 years of the study to quantify degradation in physical and mechanical properties.

4. RESULTS AND DISCUSSION

4.1 Degradation in low pH environment

4.1.1 Effect of decreasing the pH

With the high residual Std-OIT and insignificant effect of decreasing the pH from 2.0 to 0.5 on the Std-OIT depletion, there was no change in MI or tensile break properties (stress and strain) in either the machine and cross machine directions at any temperature between 95°C and 40°C in Solutions L1, L2, and L3 (Figs. 2 and 3). The only change in the GMB properties was measured for the SCR (Fig. 4). In the three low pH solutions, the SCR decreased within the first 10 months of incubation to a stabilized SCR_m value of 55 % of the initial SCR value (to about 440 hours) and was retained at this value until the end of the incubation period reported herein. A similar decrease in SCR was observed at lower temperatures but to lower SCR_m values (e.g., 42 % of the initial SCR value at 65°C). The retention of the MI and tensile properties during the 36 months of incubation duration suggests that the decrease in the SCR encountered by the GMB was either attributed to physical ageing (Ewais and Rowe 2014; Rowe et al. 2019) and/or slight surface degradation in the exposed polymer skin affecting the SCR (Abdelaal and Rowe 2014) only but not the other physical and mechanical properties.

The foregoing results provided no insight into the question as to whether this performance of the GMB in low pH was attributed to the high residual Std-OIT that was retained at the end of incubation (implying that the GMB is still in Stage I) or the good resistance of the GMB resin to the low pH solutions examined (implying that the GMB is in Stage II). It is also unclear to what extent the range of pH (i.e., 0.5 to 2.0) and the high salt concentrations in solutions L1, L2, and L3 affected GMB performance. The answers to these questions are explored below.

4.1.2 Effect of precuring and high chloride content

To explore the effect of lower pH than those examined in L1, L2, and L3, the degradation behaviour of the GMB was investigated in Solution L4. Rowe and Abdelaal (2016) showed that there was a small difference in Std-OIT depletion in both the depletion rate and the residual OIT values in Solution L4 when compared to Solution L2 (Fig. 5a) due to the short period of immersion in the very high acid concentration for L4. The depletion of HP-OIT was also slightly faster in L4 than in L2 (Fig. 5b) indicating a slight effect of the high acid concentration on the OIT depletion. Even with such high acid content in L4, the GMB did not encounter any chemical degradation similar to L2 (Fig. 6). This implies that the two weeks spike every 12 weeks (total duration of 6.5 months over the 36 months of incubation) in the acid content simulated in L4 did not affect the degradation of the GMB compared to Solution L2 with a constant pH of 1.25.

For the effect of high salt content in an acidic solution, L2-Cl with the high chloride content had a slower Std-OIT depletion rate but a slightly faster HP-OIT depletion rate relative to Solution L2 with the similar pH (Rowe and Abdelaal 2016). This implies that the salts in L2-CL had a beneficial effect on the depletion of the antioxidant detected by the Std-OIT since Stage I was longer in L2-CL than L2 (Fig. 5). Additionally, the high salt concentration in L2-Cl did not affect the GMB degradation since MI and tensile properties were retained at the initial values while SCR was retained at the SCR_m similar to L2 (Fig. 6). Such a beneficial effect of the salts can be also observed when comparing the degradation behaviour in L1 to Solution water at pH=0.5 without any salts. The GMB showed faster OIT depletion in water at pH=0.5 than Solutions L1 or any other low pH solution with salts (Fig. 7). Despite such faster depletion of the Std-OIT, chemical degradation was not initiated in water with pH=0.5 (Fig. 8) during the remainder of the 3 years of testing after the antioxidants stabilized at lower residual values.

The foregoing results indicate that increasing/decreasing the salt content or decreasing the pH in a range of solutions with low pH (≤ 2.0) did not affect the chemical degradation of the GMB during the three years of incubation. In all these low pH solutions, both the Std-OIT and HP-OIT depleted to relatively high residual values. However, with the data discussed so far, it is still not possible to conclude with absolute certainty whether the GMB was in Stage I or Stage II due to such high residual Std-OIT ranging from 10 min in water with pH=0.5 to 25 min in L1 (pH=0.5) at 85°C.

4.1.3 Effect of surfactant

Surfactants have been shown to significantly affect the depletion of antioxidants, especially those detected by Std-OIT (e.g., Rowe et al. 2008; 2014; Abdelaal et al. 2014; Abdelaal and Rowe 2014; 2015). Thus, in Solution L1-S, the Std-OIT followed a single depletion rate to a low residual value of about 3 min after only 4.3 months at 85°C (Fig. 7a). Additionally, the depletion rate of HP-OIT in L1-S was almost an order of magnitude greater than L1 (1.0 vs. 0.094 month^{-1}) but to a higher residual value (0.75HP-OIT$_o$ vs. 0.37 HP-OIT$_o$; Fig. 7b). These results indicate that the GMB had a Stage I of 4.3 months based on Std-OIT and, hence, the GMB started the induction period (Stage II). Beyond Stage I of 4.3 months and up to 36 months, MI and tensile properties were retained at the initial values while SCR was retained at the SCR_m value in Solution L1-S (Fig. 8). Thus, despite the short Stage I in L1-S and the low residual Std-OIT reached at 4.3 months, chemical degradation was not initiated and Stage II was longer than 32 months at 85°C.

4.1.4 Discussion of the degradation behaviour in low pH environments

At 85°C and during the 3 years of immersion in all seven low pH solutions, there was no change in the physical and mechanical properties investigated except a consistent change in the SCR in all solutions not attributed to chemical degradation. This 3-year retention time of the GMB properties at 85°C was longer than its retention time in other incubation media reported in previous studies. For instance, Ewais et al. (2014b) investigated the degradation of the same GMB examined herein but in synthetic MSW leachate. This leachate had a pH of 7, 5 mg/l of surfactant (same concentration as in Solution L1-S), a low trace metal concentration, and reduced conditions (Eh = -120 mV). It was shown that at 85°C, Stage I based on Std-OIT was 2.4 months depleting to a residual value of 3 min (1.7 % of the initial Std-OIT and the same as in L1-S after 4.3 months) while HP-OIT depleted to a residual value of around 613 min (0.64 HP-OIT$_o$) after 5.5 months compared to 717 min (0.75 HP-OIT$_o$) after 4.3 months in L1-S. In MSW leachate, the GMB exhibited changes in MI, break strength, and SCR (below the SCR_m value) after 19, 25, and 7 months of incubation, respectively. Nominal failure was reached (i.e., 50 % of the initial values) after 27, 30, and 16 months, respectively, from the start of incubation. If the time to depletion to residual Std-OIT is the time to end of Stage I (i.e., 2.4 months), this means that the length of Stage II ranged between 4.6 and 16.6 months while Stage III was 4 to 9 months based on the three investigated properties. This shows that the GMB can experience chemical degradation at such high residual HP-OIT values. It also suggests that the antioxidants detected by HP-OIT as residual values were not the reason for the retention of the GMB properties in the low pH media.

The comparison between Solution L1-S with pH 0.5 examined herein and the neutral synthetic MSW leachate in Ewais et al. (2014b) implies that the combined effect of the acidic condition and the high salt concentration tested was beneficial to the GMB durability and prolonged its Stage II even in the absence of effective antioxidants (i.e., those detected by Std-OIT) in L1-S. This also implies that the residual antioxidants detected by Std-OIT in L1, L2, L3, L4, and L2-Cl may not be effective in protecting the GMB and hence the GMB started Stage II of degradation in all low pH solutions once the Std-OIT reached this residual Std-OIT values (i.e., after around 20 months). However, longer incubation is needed to investigate the value of the Std-OIT at the onset of degradation in case it was slowly depleting beyond the monitoring period of the current study. Nevertheless, the current interpretation of the data collected over the 3-year incubation duration represents conservative (i.e., shorter) estimates of the duration of Stage I in these low pH solutions. Overall, under the conditions examined, the GMB showed better durability in the low pH conditions simulating acidic heap leaching operations than MSW leachate and, decreasing the pH or increasing the salt concentration did not have any noticeable effect on its chemical durability.

4.2 Degradation in high pH environment

4.2.1 Effect of increasing the pH

The antioxidant depletion patterns of the GMB in high pH environments presented by Abdelaal and Rowe (2017) were more complex than those in the low pH solutions in terms of predicting the polymer degradation behaviour. For instance, when there was a fast depletion in Std-OIT (L8), there was also fast depletion of the HP-OIT but to a high residual value (90 % of the initial value) whereas for the slower Std-OIT depletion case (L6), HP-OIT was depleting over the 36 months to reach ~300 min (~30 % of the initial value) as previously discussed (Figs. 1c and d). Thus, investigating the changes in the physical/mechanical properties of the GMB should reveal the role of the different antioxidant packages detected by the two OIT tests in protecting the GMB in such high pH solutions.

In Solutions L6, L7, and L8, the GMB experienced a decrease in MI at 95 and 85^{o}C (Fig. 9) but not at lower temperatures. This decrease in MI with time indicates a degradation by crosslinking. At 85^{o}C, the MI was retained for 29.3, 26, and 20 months indicating a Stage II duration of 2.3, 3, and 8.4 months (after Std-OIT depletion; Table 5) in pH = 9.5, 11.5, and 13.5 (L6, L7, L8) respectively. MI then decreased to 88, 75, and 61 % of the initial MI value after 36 months (Fig. 9a) in Solutions L6, L7, and L8, respectively.

At 95^{o}C, MI was retained only for 22, 19, and 12 months with a Stage II of 1, 2, and 6.1 months in pH = 9.5, 11.5 and 13.5 6 (L6, L7, L8), respectively. After 36 months, MI decreased to 64 and 12 % of the initial value in Solutions L6 and L7, respectively, while in L8, MI reached 0 % (i.e., complete clogging of the specimen in the MI machine) after 32 months. This shows that while the durations of both Stage I (based on Std-OIT) and Stages I+II combined decreased with increasing the pH, the duration of Stage II increased with increasing the pH (i.e., longest Stage II was for Solution L8 followed by L7 then L6; Table 5).

The results for the break strength and strain in both machine direction and cross machine directions were fairly similar. For the break strength in machine direction presented in this paper and at 85^{o}C, the fastest degradation was in Solution L8 then L7 then L6 starting after 20, 25.5, and 29 months respectively, (Fig. 10a). Subtracting the time for Stage I based on Std-OIT (Table 4) from the previous durations gives a Stage II duration of 2, 2.5, and 8.4 months in Solutions L6, L7, and L8, respectively, indicating the longest Stage II was for the solution with the highest pH similar to MI. At the end of the incubation duration of 3 years, break strength decreased to 76, 72, and 65 % of the initial break strength value in Solutions L6, L7, and L8, respectively.

At 95^{o}C, break strength in machine direction was retained at the initial value for 22, 18.5, and 12 months in Solutions L6, L7, and L8, respectively, with Stage II duration of 1, 1.5, and 6.1 months, respectively (Table 4). Break strength then decreased to reach 75, 65, and 43 % of the initial value at the end of incubation in Solutions L6, L7, and L8, respectively (Fig. 10b).

Similar to low pH solutions, SCR decreased at the early time of incubation before chemical degradation as evidenced by MI and break strength properties. At 85^{o}C, SCR decreased to SCR_m of 58, 54, and 45 % of the initial SCR value after 7.5, 6, and 2.0 months of incubation in Solutions L6, L7, and L8, respectively. After being retained at these values, SCR further decreased after 24 months of incubation in the three high pH solutions reaching 21, 19, and 9 % of the initial SCR value in Solutions L6, L7, and L8, respectively, at 36 months (Fig. 11a). The lowest stabilized value of the SCR before chemical degradation and the lowest SCR value reached at the end of incubation in Solution L8 show that more degradation was exhibited by the GMB in Solution L8 followed by Solution L7 then Solution L6 similar to MI and break strength properties.

Estimation of Stages II and III based on SCR was defined based on the decrease in the SCR to 50 % of SCR_m (Rowe et al. 2019) since the decrease to 50 % of the initial value (400 h) took place at early incubation times due to physical ageing reducing the SCR before chemical degradation (Rowe et al. 2019; Ewais and Rowe 2014b). Based on this criterion, at 85^{o}C, Stage II was estimated to be 1 and 12.4 months in Solutions L7 and L8 respectively, whereas, in Solution L6, SCR started to decrease at 24 months at around 5 min of Std-OIT before the full depletion to a residual OIT value of 3 min reached at 27 months (Table 5). This also shows that based on SCR, Stage II was longer in L8 than L7 and diminished in L6. Stage III was estimated to be 11, 10, and 7 months in Solutions L6, L7, and L8, respectively, showing a decrease in Stage III duration with the increase of the pH (i.e., similar to Stage I but not Stage II).

The decrease of the SCR at 95^{o}C was masked by the effect of annealing (i.e., morphology change) at such a high temperature that led to the retention of SCR at higher values than at 85^{o}C and delayed the decrease of SCR due to chemical degradation (Abdelaal et al. 2015). In Solution L6, there was a decrease in the SCR to around 85 % of the initial value at 7 months (compared to 58 % SCR_o at 85^{o}C) then SCR started to increase to stabilize at the initial value for the remaining time of the incubation (Fig 11b). In Solutions L7 and L8, SCR decreased to 80 and 74 % of the initial value (compared to 54 and 45 % SCR_o at 85^{o}C) within the first 7 months and stabilized at these values until 32 and 28 months of incubation, respectively. SCR then decreased in both solutions reaching 55 % of the initial SCR in Solution L7 and 47 % of the initial SCR in Solution L8 after 36 months of incubation. These results show the effect of the incubation media on the stabilized SCR value since the lowest values of SCR were encountered in the most chemically aggressive solution (i.e., L8) examined herein. Furthermore, the higher effect of annealing at 95°C than that at 85°C delayed the decrease of SCR at 95°C to a longer period than at 85°C.

4.2.2 Discussion of the degradation behaviour in high pH environments

At temperatures of 75°C and below there was no degradation in any of the high pH solutions. At 85 and 95°C, degradation of the GMB was initiated in most of the three high pH solutions but nominal failure was reached only in a few cases. For the solutions in which nominal failure was not reached during the 36 months of incubation at 85 and 95°C, Table 5 shows the predictions for Stage III based on the current data and hence the time to nominal failure (t_{NF}). However, a more precise estimation of Stage III duration and hence the t_{NF} requires further incubation at these temperatures.

Inspecting Table 5 shows that, at 85 and 95°C and based on the examined three properties, L8 had the shortest t_{NF} due to the shortest Stages I and III despite the longest Stage II while decreasing the pH to 9.5 resulted in longer t_{NF}, Stage I, and Stage III but shorter Stage II. The effect of increasing the pH (from 9.5 to 13.5) on the duration of Stage II seems to be inconsistent with the behaviour of GMB observed in Stages I and III since the majority of the GMB properties showed a faster decrease with increasing the pH within the examined range. The only GMB property that showed the same behaviour of Stage II duration with increasing the pH was the depletion of the HP-OIT in which increasing the pH increased the HP-OIT residual values (Fig. 12). This limited depletion of HP-OIT (specifically in L8 and L7) can be attributed to the basic nature of HALS (as part of the HP-OIT package) that is expected to show good resistance to strong caustic solutions (Scheirs 2009; Abdelaal and Rowe 2017). This implies that the antioxidants detected by HP-OIT at the residual values in L8 may have a role in delaying the initiation of the GMB degradation. However, it is not clear how the essentially inactive antioxidants detected by HP-OIT could potentially delay the GMB degradation in such high pH solutions.

Another possible explanation for this behaviour could be related to the different effects of the high pH on the GMB antioxidants (specifically those detected by Std-OIT) and the GMB resin. Excluding the antioxidant depletion time and considering the degradation of the unprotected GMB resin until nominal failure is reached (i.e., t_{NF} – Stage $I_{Std\text{-}OIT}$), the durations at 85°C were 8, 11, and 19.4 months based on SCR in L6, L7, and L8 respectively. This shows that the unprotected GMB resin had more resistance to degradation in pH 13.5 than in the pH 9.5 and pH 11.5 solutions. Likewise, the durations of Stage II +Stage III (i.e., t_{NF} – Stage $I_{Std\text{-}OIT}$) based on MI and break strength were shorter in L7 with pH 11.5 than in both L6 and L8 (Table 5). Thus, while pH 13.5 was clearly the most aggressive solution on the antioxidants detected by Std-OIT, it may become relatively less aggressive on the GMB to initiate the degradation in the physical and mechanical properties than the lower pH solutions (L6 and L7 based on SCR and L7 based on the other properties) once the antioxidants are no longer effective in protecting the GMB. This may have resulted in the longer retention of the GMB properties after the depletion of antioxidants (i.e., Stage II) at pH 13.5 than at pH 11.5 and pH 9.5. In this case, the inactive antioxidants detected at the high residual HP-OIT values may not have a significant role in delaying the GMB degradation.

The validity of these two explanations of the duration of Stage II warrants further investigation of different GMBs with and without high molecular weight antioxidants such as HALS to examine their degradation behaviour in high pH solutions. However, both hypotheses infer that the Std-OIT depletion times represent a conservative assessment of Stage I duration irrespective of the (doubtful) efficacy of the antioxidants detected by the high HP-OIT at the residual values in delaying the GMB degradation. Overall, the current results collected over 3 years show that increasing the pH within the examined range resulted in a shorter t_{NF} from the onset of incubation and hence the pH 13.5 solution is overall, the most aggressive media examined herein.

Despite the clear degradation in the GMB properties encountered during the 3 years at 85 and 95°C in the high pH solutions, the performance of the GMB was still better than in the neutral reduced MSW leachate with surfactant presented in Ewais et al. (2014b) for the same GMB. This was shown in the Std-OIT depletion stage duration with 11.6 months in pH 13.5 versus only 2.4 months in MSW leachate (i.e., a factor of 4). For the subsequent GMB degradation, the nominal failure that was reached after 27, 30, and 16 months based on MI, break strength, and SCR, respectively, in MSW leachate, was reached after 42, 43, and 31 months, respectively, in pH 13.5 and after longer times in the pHs 11.5 and 9.5. This shows that while the examined GMB showed superior performance in the examined acidic environments, its performance in basic environments was still better than in the neutral reduced MSW leachate.

4.3 Practical implications of the longevity of HDPE GMBs in heap leach pads

Since the degradation in the GMB properties was only obtained at 95 and 85°C in some solutions, predicting the long-term performance at heap leaching field temperatures can be only established for the antioxidant depletion stage using the data provided by Rowe and Abdelaal (2016) and Abdelaal and Rowe (2017). The data provided in the current study showed that the estimates for Stage I presented in the aforementioned studies based on Std-OIT were not overestimating the antioxidant depletion stage duration. This is because chemical degradation in all the mechanical and physical properties of the GMB was not observed during the times at which the Std-OIT reached residual values. Thus, it can be conservatively assumed that the antioxidants detected at the residual OIT (both Std-OIT and HP-OIT) were inactive and were not protecting the GMB and hence the GMB was in Stage II once the residuals had been reached (i.e., Scenario 2 in Section 2).

The predicted time to antioxidant depletion given in Rowe and Abdelaal (2016) and Abdelaal and Rowe (2017) using Arrhenius modelling is established based on double sided immersion tests that are substantially faster than the depletion times obtained for composite liner configuration (Rowe et al.

2010). Thus, the depletion times given in these two studies can be conservatively multiplied by a factor of 3.4 to obtain an estimate of the depletion time in a composite liner configuration at a given temperature (Rowe et. al 2020). Considering a typical heap leaching liner temperature of 50°C (Thiel and Smith 2004) and applying the composite liner factor to the predictions of the Std-OIT depletion time at this temperature, the depletion times given by Rowe and Abdelaal (2016) for L1-pH 0.5, L2-pH 1.25, and L3-pH 2.0 can be increased to 51, 44, and 44 years, respectively. These predictions for Stage I were conservatively based on the high residual values obtained at the end of incubation and Stage I for all low pH solutions can be much longer if the Std-OIT is slowly depleting to lower values. However, an important practical implication that can be drawn from these predictions is that increasing the acidic content to maximize the metal recovery in some operations should not have any negative effect on the length of Stage I and hence the longevity of the GMB as long as it does not involve exothermic reactions that can increase the liner temperature. For the high pH applications, the predictions given by Abdelaal and Rowe (2017) can be increased to 48, 41, and 31 years, for L6-pH 9.5, L7-pH 11.5, and L8-pH 13.5 respectively, at 50°C. Thus, while increasing the pH from 9.5 to 13.5 can negatively affect the GMB longevity, the antioxidant depletion stage of the GMB can still meet a design life of a few decades for high pH heap leach operations. This may be adequate for some operations considering that the typical leaching period of the ore is around 20 years (Lupo 2010).

The above predictions only involve Stage I and are based on the data currently available. To obtain the t_{NF} in the field, the length of Stages II and III need to be added to the antioxidant depletion times estimated for the liner system. However, the current data did not allow establishing the t_{NF} predictions using Arrhenius modelling since the degradation in Stages II and III was only obtained experimentally at one or two elevated temperatures. This experimental data obtained at elevated temperatures also show that the durations of Stages II and III of the GMB examined in the different solutions do not necessarily follow its Stage I duration in these solutions. For instance, the degradation to nominal failure in L6 was faster than all the low pH solutions at 85°C although Stage I predictions for L6 were Longer than in L2 and L3. Thus, the relative performance of the GMB examined in the different solutions when considering the t_{NF} may be different from the predictions above that only consider Stage I. However, for a properly constructed liner (with high construction quality assurance during installation and welding of the GMB panels) that is designed to limit short and long-term tensile strains, the t_{NF} of the GMB under field conditions in all solutions can be longer than the above predicted numbers.

5. CONCLUSIONS

The effect of incubation in ten solutions simulating both low and high pH mining applications on the physical and mechanical properties of a HDPE GMB was examined at different temperatures using oven immersion tests. Seven synthetic low pH solutions were examined: L1 (pH = 0.5), L2 (pH = 1.25), L3 (pH = 2.0), L4 (cycles of boosted acid content), L1-S (pH = 0.5 + 5 ml/L surfactant), L2-Cl (pH = 1.25 + high chloride content), and water (pH = 0.5). These solutions simulate the pH and metal content of the pregnant liquor from copper, nickel, and uranium heap leaching. For the high pH solutions, the GMB was immersed in L6 (pH=9.5), L7 (pH=11.5), and L8 (pH=13.5) simulating the range of pH of solutions from gold and silver heap leaching. The investigated HDPE GMB had an initial Std-OIT (Std-OIT$_o$) of 160 min, initial HP-OIT (HP-OIT$_o$) of 960 min, and initial stress crack resistance (SCR$_o$) of 800 hours and met the minimum requirements specified in GRI-GM13 (2021). For the specific geomembrane tested and the exposure conditions examined, the following conclusions were reached based on the three years of data reported herein:

1. There was a decrease in the SCR in all solutions that appears similar to the GMB tending to a more thermodynamically stable state reported by Rowe et al. (2019). However, in this case, the

rate and magnitude of the decrease were not just a function of temperature but also depended on the chemical solution.

2. Other than the changes in SCR noted above, there was no change in the physical and mechanical properties in all seven low pH solutions investigated, suggesting that the GMB was highly resistant to these very acidic environments at temperatures at and below 95°C.

3. Although the Std-OIT depleted to a low residual value (3 min) in 4.3 months in pH=0.5 solution with surfactant (L1-S), the GMB retained its physical and mechanical properties for a period exceeding 32 months at 85°C. This suggests that the antioxidants retained at the high residual Std-OIT measured in all the other low pH solutions were not the primary factor contributing to the GMB's resistance to degradation in the low pH media. Rather, the long retention of the physical properties after antioxidant depletion is hypothesized to have been due to the synergistic effect of the high metal concentrations associated with the low pH solutions prolonging Stage II.

4. Neither the simulated ultra-low pH pre-curing in acidic heap leaching (L4) nor high chloride content (L2-Cl) notably affected the GMB degradation over the period examined.

5. During the same 3 years of incubation of the same GMB that performed well at 95 and 85°C in low pH solutions (as noted above), this GMB degraded in all the high pH (pH 9.5, 11.5, 13.5) solutions indicating lower chemical resistance to the high pH than the low pH environments.

6. As the pH of the immersion solution increased from 9.5 to 13.5:
    a. the residual HP-OIT increased, and
    b. the induction stage (i.e., Stage II) increased, but
    c. both Stages I and III were significantly reduced, thus
    d. the time to nominal failure decreased (i.e., t_{NF} (pH=9.5) > t_{NF} (pH=11.5) > t_{NF} (pH=13.5)).

This study shows substantially different performance and rates of degradation of a HDPE GMB in ten solutions with pH ranging from 0.5 to 13.5. Most importantly, it demonstrates that a GMB that performs extremely well in low pH solutions may not perform so well in high pH solutions but may still perform much better than in a simulated MSW leachate. Thus, it cannot be inferred that good (or bad) performance in one environment implies that one can expect equally good (or bad) performance in another environment. One needs to test the chemical compatibility of the GMB with a specific chemical and thermal exposure that is anticipated in the field. Ideally, this should be conducted at different elevated temperatures to allow extrapolation of the GMB longevity at typical field temperatures.

The results presented in this paper are directly relevant to the particular GMB and solutions examined over the 3 years of this study. Since the resin and additive package vary from one GMB to another, the reaction with different chemical compounds in the mining solutions could vary substantially from one GMB to another even though the GMB meets the same basic specification or requirements (e.g. such as GRI GM 13). Thus, the results should not be extrapolated to other types of immersion fluids or GMBs without independent verification. The tests reported herein do not directly represent field conditions since previous studies (Rowe and Rimal 2008; Rowe et al. 2010, 2013a, 2020) demonstrated substantially faster depletion of antioxidants in immersion tests than in experiments simulating the field exposure conditions.

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Competing Interests Statement

There are no competing interests.

Data Availability Statement

Some or all data that support the findings of this study are available from the corresponding author upon reasonable request.

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Figure Captions

Fig. 1. Variation with incubation time at 85_{o}C of: (a) Std-OIT; (b) HP-OIT for the three different low pH solutions (modified from Rowe and Abdelaal 2016) and (c) Std-OIT; (d) HP-OIT for the three different high pH solutions (modified from Abdelaal and Rowe 2017). Data points represent mean values and the error bars represent the ± 1 standard deviation.

Fig. 2. Variation of normalized MI with incubation time at 85_{o}C for the three different low pH solutions. Data points represent mean values and the error bars represent the ± 1 standard deviation.

Fig. 3. Variation of normalized break Strength with incubation time at 85_{o}C in (a) Machine direction (F_{break}); (b) Cross machine direction (F_{break}) for the three different low pH solutions. Data points represent mean values and the error bars represent the ± 1 standard deviation.

Fig. 4. Variation of normalized SCR with incubation time for the three different low pH solutions at: (a) 85_{o}C and (b) 65_{o}C. Data points represent mean values and the error bars represent the ± 1 standard deviation.

Fig. 5. Variation with incubation time at 85_{o}C of: (a) Std-OIT; (b) HP-OIT incubated in Solutions 2, 4 and 2-Cl (modified from Rowe and Abdelaal 2016). Data points represent mean values and the error bars represent the ± 1 standard deviation.

Fig. 6. Variation with incubation time at 85_{o}C of normalized: (a) MI; (b) break strength in machine direction (F_{break}); (c) SCR incubated in Solutions 2, 4 and 2-Cl. Data points represent mean values and the error bars represent the ± 1 standard deviation.

Fig. 7. Variation with incubation time at 85_{o}C of: (a) Std-OIT; (b) HP-OIT incubated in Solutions 1, 1-S and Water: pH=0.5 (modified from Rowe and Abdelaal 2016). Data points represent mean values and the error bars represent the ± 1 standard deviation.

Fig. 8. Variation with incubation time at 85_{o}C of normalized: (a) MI; (b) break strength in machine direction (F_{break}); (c) SCR incubated in Solutions 1, 1-S and Water: pH=0.5. Data points represent mean values and the error bars represent the ± 1 standard deviation.

Fig. 9. Variation of normalized MI with incubation time for the three different low pH solutions at (a) 85_{o}C; (b) 95_{o}C. Data points represent mean values and the error bars represent the ± 1 standard deviation.

Fig. 10. Variation of normalized break strength in machine direction (F_{break}) with incubation time for the three different low pH solutions at (a) 85_{o}C; (b) 95_{o}C. Data points represent mean values and the error bars represent the ± 1 standard deviation.

Fig. 11. Variation of normalized SCR with incubation time for the three different low pH solutions at (a) 85_{o}C; (b) 95_{o}C. Data points represent mean values and the error bars represent the ± 1 standard deviation.

Fig. 12. Variation of different index properties in at 85_{o}C in: (a) L6: pH 9.5, (b) L7: pH 11.5, & (c) L8: pH 13.5. OIT data are from Abdelaal and Rowe 2017. The start of Stage III is presented as a range of

times at which the different properties start to change. Data points represent mean values, and the error bars represent the ± 1 standard deviation.

Table 1. Geomembrane properties

Properties	Method	Unit	Mean ± SD
Nominal thickness	ASTM D5199	mm	1.5
GMB designator	---	---	xC
Manufacturing date	---	---	May 2008
GMB Density	ASTM D1505	g/cc	0.946
Standard oxidative induction time (Std-OIT; 200°C/35 kPa)	ASTM D8117	min	160 ± 1.5[a]
High-pressure oxidative induction Time (HP-OIT; 150°C/3500 kPa)	ASTM D5885	min	960 ± 17
Suspected HALS[b]	---	---	Yes
Crystallinity	ASTM D3418	%	50.5 ± 0.7
HLMI (21.6 kg/190°C)[c]	ASTM D1238	g/10min	12.9 ± 0.4
LLMI (2.16 kg/190°C)[d]			0.115 ± 0.001
Melt flow ratio (MFR) = (HLMI/LLMI)	---	---	111
Single point stress-crack resistance (NCTL-SCR)	ASTM D5397	hours	800 ± 90
Tensile properties *(machine direction)*			
Strength at yield	ASTM D6693	kN/m	27.8 ± 1.2
Strength at break	Type (IV)	kN/m	49.8 ± 2.7
Strain at yield		%	20.6 ± 0.7
Strain at break		%	818 ± 18
Tensile properties *(cross-machine direction)*			
Strength at yield	ASTM D6693	kN/m	29.1 ± 1.0
Strength at break	Type (IV)	kN/m	50.7 ± 2.7
Strain at yield		%	18.3 ± 0.7
Strain at break		%	857 ± 23

[a] GMB initial properties are subjected to small changes with time due to storage of the roll in 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. The initial values reported in the current study are at 2010 that may be different from initial properties reported previously for the same GMB when roll was received or for studies will be initiated in future.

[b] Trace nitrogen analysis was conducted and reported by Ewais et al. (2014) inferring the presence of HALS

[c] High load Melt Index.

[d] Low load Melt Index.

Table 2. Laboratory analyzed composition of different solutions used in the current study (mg/L unless noted).

Component[a]	Water pH=7.0[d]	Water pH=0.5[e]	L1	L2	L3	L4[f]	L1-S	L2-Cl[g]	L6	L7	L8
Nominal pH	7	0.5	0.5	1.25	2.0	<0	0.5	1.25	9.5	11.5	13.5
Average pH[b]	6.5 ± 0.2	0.51 ± 0.03	0.53 ± 0.07	1.31 ± 0.12	2.11 ± 0.25	<0	0.51 ± 0.12	1.28 ± 0.16	9.8 ± 0.3	11.4 ± 0.2	13.4 ± 0.2
Ag^{+}	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	0.3	0.3	0.3
Al^{3+}	<1.0	<1.0	5,000	5,000	5,000	5,000	5,000	5,000	<1.0	<1.0	<1.0
As^{3+}	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.9	0.9	0.9
Ba^{2+}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cd^{2+}	<0.025	<0.025	1.7	1.7	1.7	1.7	1.7	1.7	<0.025	<0.025	<0.025
Ca^{2+}	<0.05	<0.05	515	515	515	515	515	515	0.42	0.64	0.86
Co^{2+}	<0.02	<0.02	20	20	20	20	20	20	0.03	0.03	0.03
Cu^{2+}	<0.2	<0.2	87	87	87	87	87	87	9	9	9
Fe^{2+}	<0.05	<0.05	710	710	710	710	710	710	<0.05	<0.05	<0.05
Li^{+}	<0.05	<0.05	1,000	1,000	1,000	1,000	1,0000	1,000	<0.05	<0.05	<0.05
K^{+}	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	173	181	198
Mg^{2+}	<0.05	<0.05	3,300	3,300	3,300	3,300	3,300	3,300	4	2.8	0.13
Mo^{6+}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.68	0.56	0.74
Mn^{2+}	<1.0	<1.0	620	620	620	620	620	620	<0.05	<0.05	<0.05
Na^{+}	<1.0	<1.0	50	50	50	50	50	42,500	60	138	27,500
Ni^{2+}	<1.0	<1.0	7.6	7.6	7.6	7.6	7.6	7.6	<0.3	<0.3	<0.3
Pb^{2+}	<0.03	<0.03	1.4	1.4	1.4	1.4	1.4	1.4	<0.03	<0.03	<0.03
S^{6+}	<1.0	11970	2,250	1,580	1.,420	77,770	23,100	14,100	99.5	91.6	124
Zn^{2+}	<0.01	<0.01	62	62	62	62	62	62	0.02	0.02	0.02
Cl^{-}	<0.5	<0.5	5,100	5,100	5,100	5,100	5,100	74,500	<0.5	<0.5	<0.5
O^{2-*}	0	0	0	0	0	0	0	0	0.59	0.59	0.59
OH^{-*}	0	0	0	0	0	0	0	0	43	9,440	20,410
SO_4^{2-}	<0.1	36,000	68,000	48,000	43,000	220,000	56,000	43,000	300	300	300
Surfactant[c] (ml/l)	0	0	0	0	0	0	5	0	0	0	0

[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 3 years of incubation. 98% concentrated sulfuric acid or 15 mol NaOH solution were used for pH adjustment.

[c] IGEPAL® Ca-720: $(C_2H_4O)_n.C_{14}H_{22}O$, n~12.5.

[d] Reverse osmosis (RO) water was prepared by filtering tap water through a semi-permeable membrane under sufficient pressure allowing the passage of water but not ions such as Ca^{2+}, Na^{2+} and Cl^{-},etc and was used in the preparation of all solutions.

[e] Sulfuric acid was added to RO water to adjust pH to ~ 0.5.

[f] The incubation solution in the first 2 weeks of every precuring cycle (3 months) with an acid content of 100 g/l. The GMB is immersed in L2 during the remaining 10 weeks of the precuring cycle.

[g] L2 but with boosted chloride content by adding NaCl.

* Not measured directly.

Table 3. Predicted times to OIT depletion at the incubation temperatures based on Std-OIT and HP-OIT for the different incubation solutions

Temperature (°C)	Solution	Predictions			
		Std-OIT		HP-OIT	
		Std-OIT_r (min)	time to Std-OIT_r (years)	HP-OIT_r (min)	time to HP-OIT_r [b] (years)
40	L1: pH=0.5	60 [a]	28	690 [a]	45
	L2: pH=1.25	44 [a]	25	860 [a]	5
	L3: pH=2.0	47 [a]	25	810 [a]	9
	L6: pH: 9.5	3	24	80 [b]	26
	L7: pH: 11.5	3	21	840 [a]	11
	L8: pH: 13.5	3	17	912	2.4
65	L1: pH=0.5	42	6.4	525	9.4
	L2: pH=1.25	33	5.7	760	0.8
	L3: pH=2.0	35	5.7	710	0.9
	L6: pH: 9.5	3	6.1	80 [b]	13
	L7: pH: 11.5	3	5.2	750 [a]	6.6
	L8: pH: 13.5	3	3.6	885	1.5
75	L1: pH=0.5	38	3.8	439	5.3
	L2: pH=1.25	30	3.3	692	0.4
	L3: pH=2.0	31	3.3	693	0.5
	L6: pH: 9.5	3	2.8	80 [b]	10
	L7: pH: 11.5	3	2.3	650 [a]	5.5
	L8: pH: 13.5	3	1.5	864	1.2
85	L1: pH=0.5	30	2.3	357	3.1
	L2: pH=1.25	23	2	664	0.2
	L3: pH=2.0	26	2	590	0.2
	L6: pH: 9.5	3	2.3	80 [b]	8.1
	L7: pH: 11.5	3	1.9	595[a]	4.5
	L8: pH: 13.5	3	1	850	1.0
95	L1: pH=0.5	25	1.4	268	1.8
	L2: pH=1.25	19	1.3	624	0.1
	L3: pH=2.0	18	1.3	490	0.1
	L6: pH: 9.5	3	1.8	80 [b]	6.5
	L7: pH: 11.5	3	1.4	550	3.7
	L8: pH: 13.5	3	0.5	830	0.8

Data compiled from Rowe and Abdelaal (2016) and Abdelaal and Rowe (2017).
Predictions are in years unless otherwise noted.

[a] Estimated residual values from the available data during the 3 years incubation duration.

[b] Residual $HP\text{-}OIT_r$ values in pH=9.5 was assumed to be constant at all temperatures, HP-OIT_r = 80 min since the residual data was not reached at any temperature during the 3 years incubation duration.

Table 4. Test temperatures for the different incubation solutions

Solution	pH	Incubation temperatures (^oC)
L1	0.5	40-65-75-85-95
L2	1.25	40-65-75-85-95
L3	2.0	40-65-75-85-95
L4	<0	65-85
L1-S	0.5	65-75-85-95
L2-Cl	1.25	85
Water	0.5	85
L6	9.5	40-65-75-85-95
L7	11.5	40-65-75-85-95
L8	13.5	40-65-75-85-95

Table 5. Comparison of the performance of the tested GMB in high pH solutions

Property		units	85°C			95°C		
			L6	L7	L8	L6	L7	L8
Length of Stage I	Std-OIT*	month	27	23	11.6	21	17	5.9
	HP-OIT		97[**]	54.7[**]	12.3	78[**]	43.2[**]	9.6
	HP-OIT$_r$	min.	80[**]	595	850	80[**]	550	830
Length of Stage II	MI	month	2.3	3	8.4	1	2	6.1
	FB (MD)		2	2.5	8.4	1	1.5	6.1
	SCR		0[***]	1	12.4	NR	15	22.1
Length of Stage III	MI[a]	month	33[**]	24[**]	22[**]	24[**]	10	9
	FB (MD) [a]		31[**]	22.5[**]	23[**]	26[**]	22[**]	18
	SCR[b]		8	10	7	NR	22[**]	26[**]
Time to nominal failure	MI[a]	month	62[**]	50[**]	42[**]	46[**]	29	21
	FB (MD) [a]		60[**]	48[**]	43[**]	48[**]	40[**]	30
	SCR[b]		35	34	31	NR	40[**]	38[**]

[*] Std-OIT$_r$ = 3 min.

[**] Predicted based on current data collected up to 36 months of incubation.

[***] No Stage II since the degradation in SCR started at the Std-OIT depletion to the residual value of 3 min.

[a] Time to nominal failure when defined based on the property reducing to 50% of the initial value.

[b] Time to nominal failure when defined based on SCR being reduced to 50% of the stabilised SCR value (SCR$_m$).

NR= Not reached.

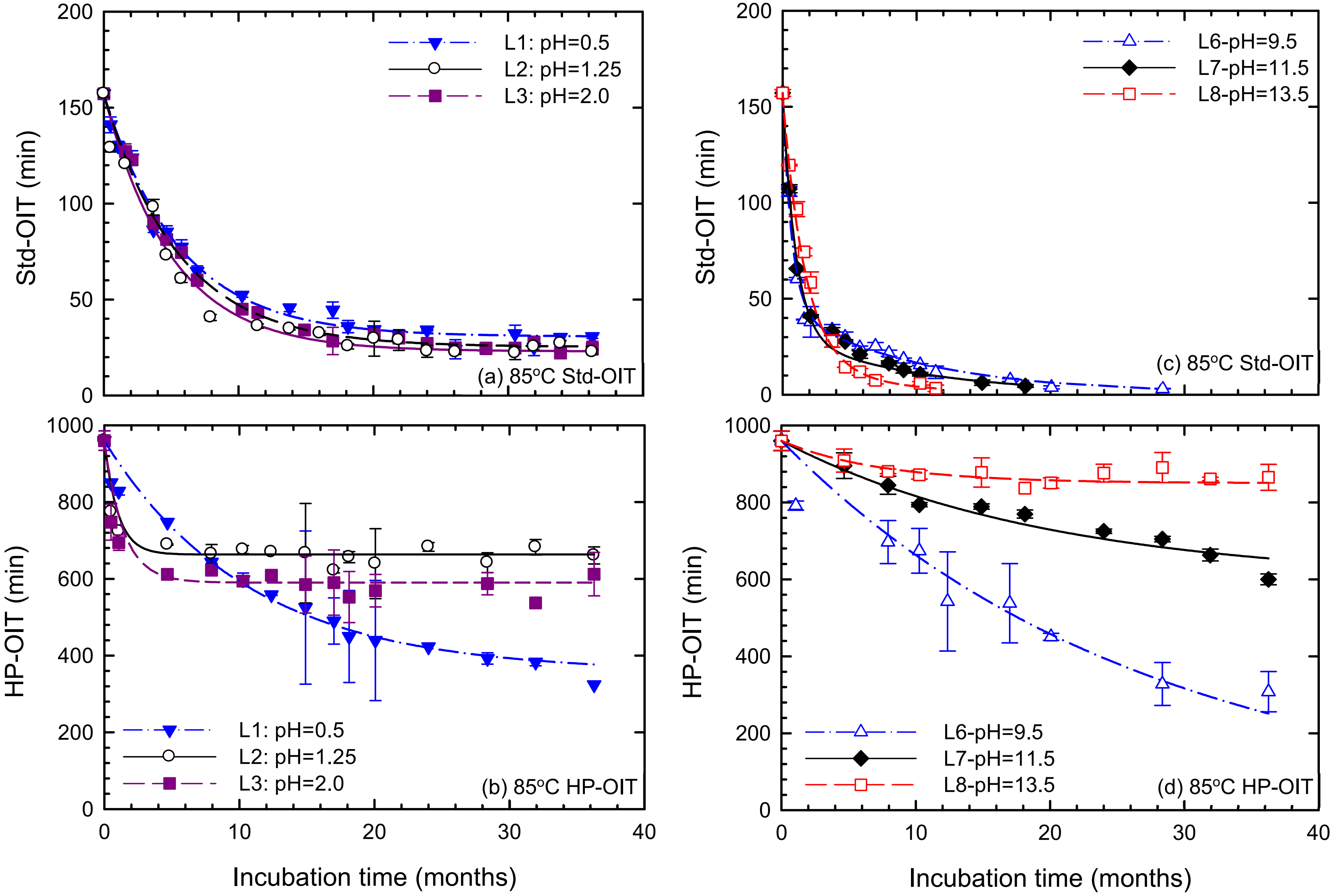

Fig. 1. Variation with incubation time at 85°C of: (a) Std-OIT; (b) HP-OIT for the three different low pH solutions (modified from Rowe and Abdelaal 2016) and (c) Std-OIT; (d) HP-OIT for the three different high pH solutions (modified from Abdelaal and Rowe 2017). Data points represent mean values and the error bars represent the ± 1 standard deviation.

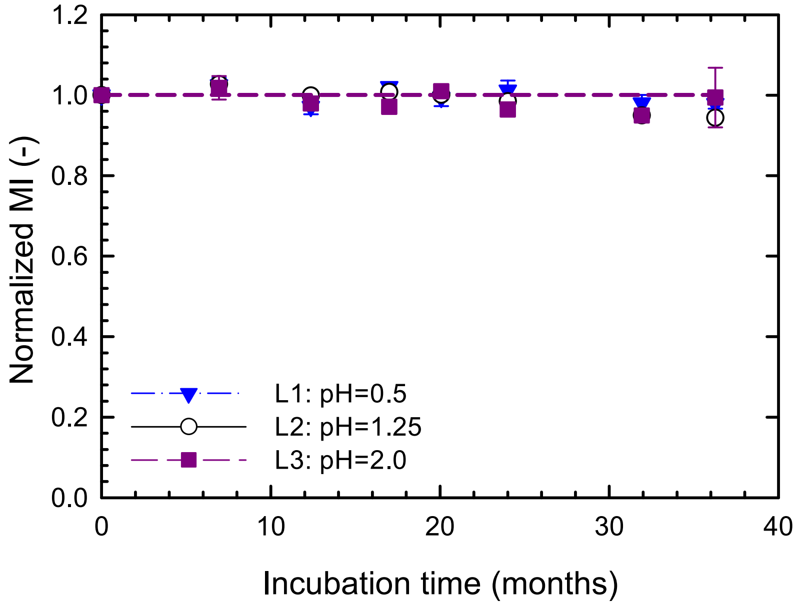

Fig. 2. Variation of normalized MI with incubation time at 85ºC for the three different low pH solutions. Data points represent mean values and the error bars represent the ± 1 standard deviation.

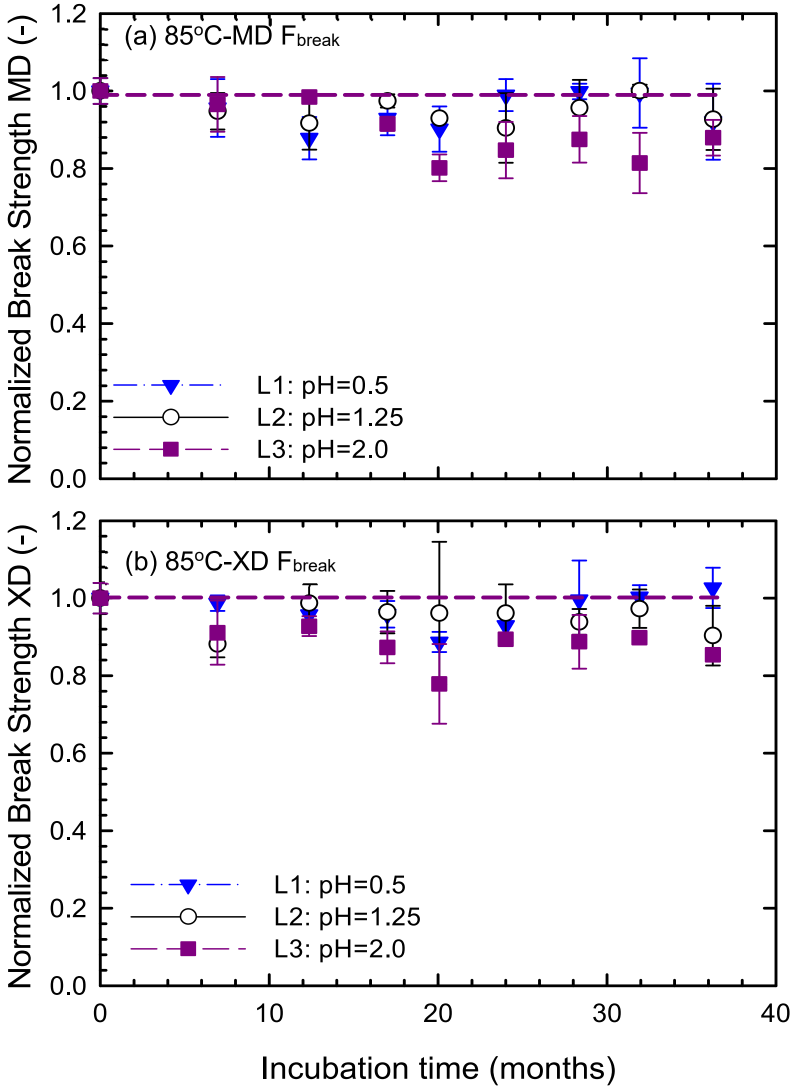

Fig. 3. Variation of normalized break Strength with incubation time at 85ºC in (a) Machine direction (F_{break}); (b) Cross machine direction (F_{break}) for the three different low pH solutions. Data points represent mean values and the error bars represent the ± 1 standard deviation.

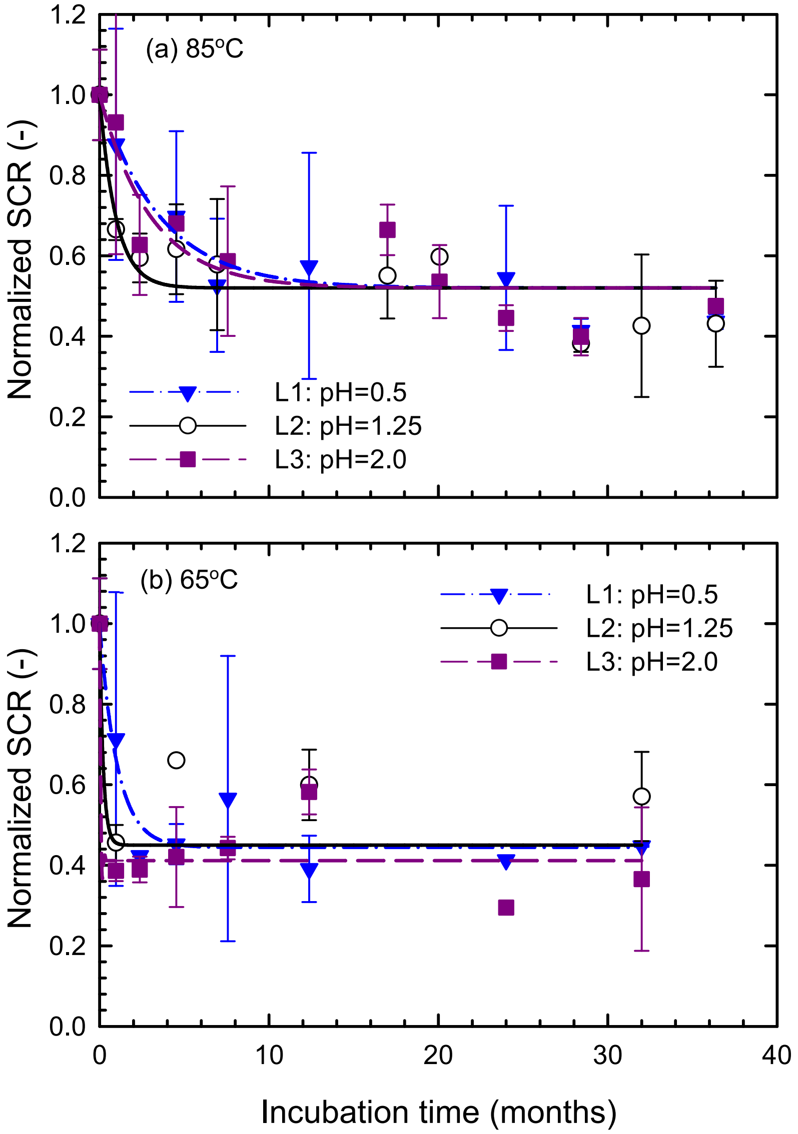

Fig. 4. Variation of normalized SCR with incubation time for the three different low pH solutions at: (a) 85ºC and (b) 65ºC. Data points represent mean values and the error bars represent the ± 1 standard deviation.

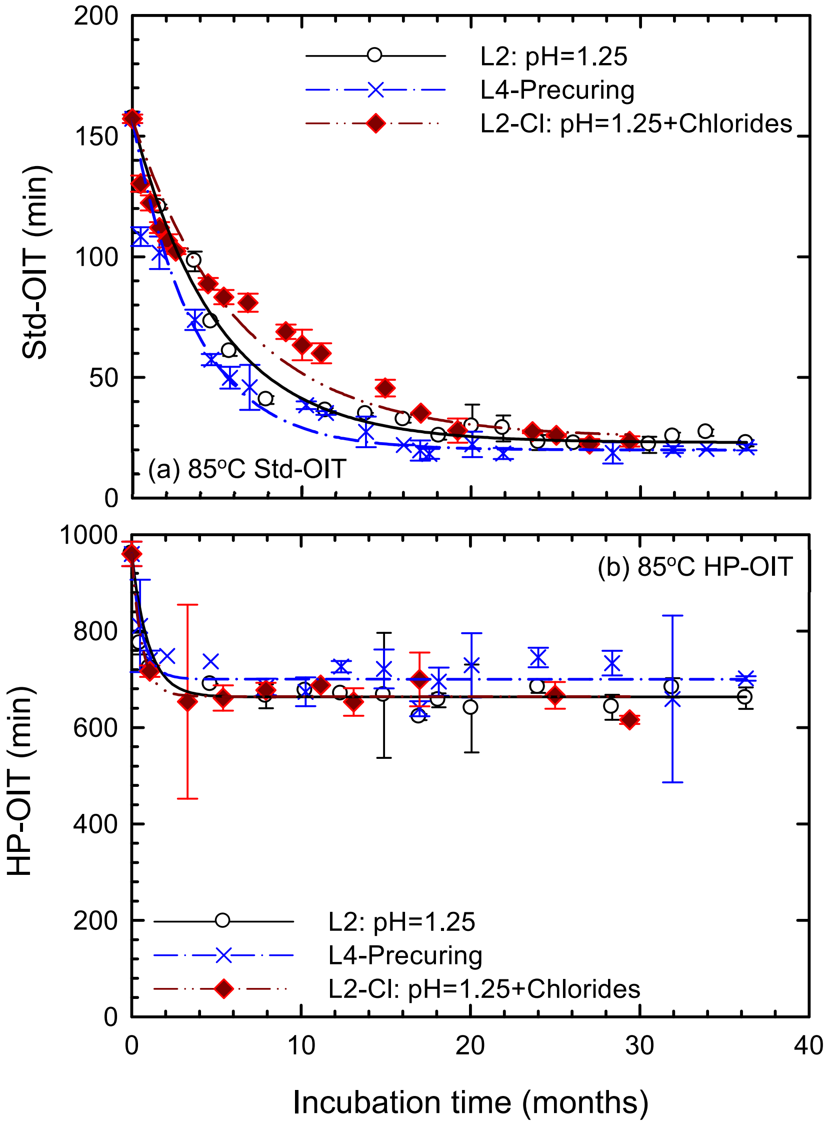

Fig. 5. Variation with incubation time at 85°C of: (a) Std-OIT; (b) HP-OIT incubated in Solutions 2, 4 and 2-Cl (modified from Rowe and Abdelaal 2016). Data points represent mean values and the error bars represent the ± 1 standard deviation.

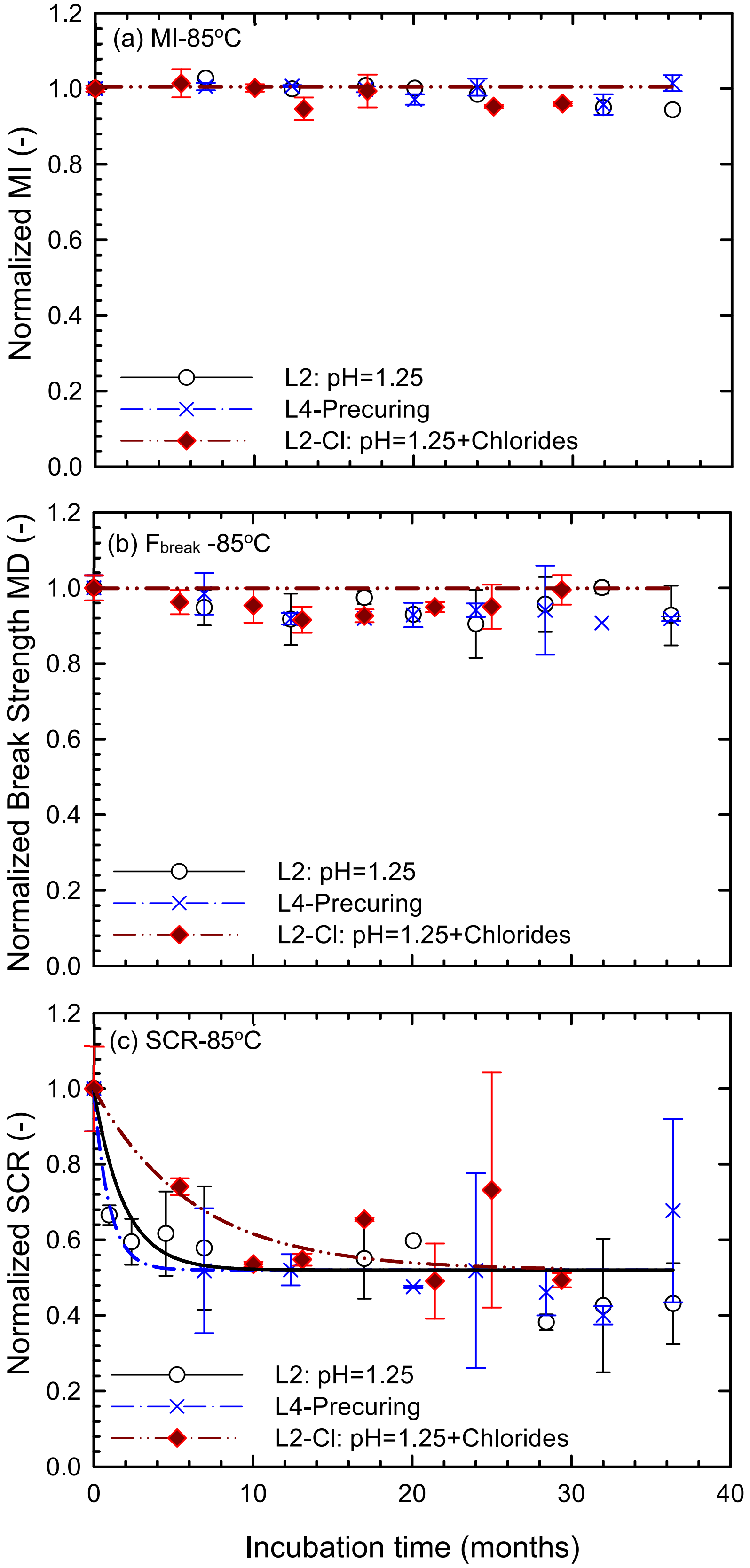

Fig. 6. Variation with incubation time at 85°C of normalized: (a) MI; (b) break strength in machine direction (F_{break}); (c) SCR incubated in Solutions 2, 4 and 2-Cl. Data points represent mean values and the error bars represent the ± 1 standard deviation.

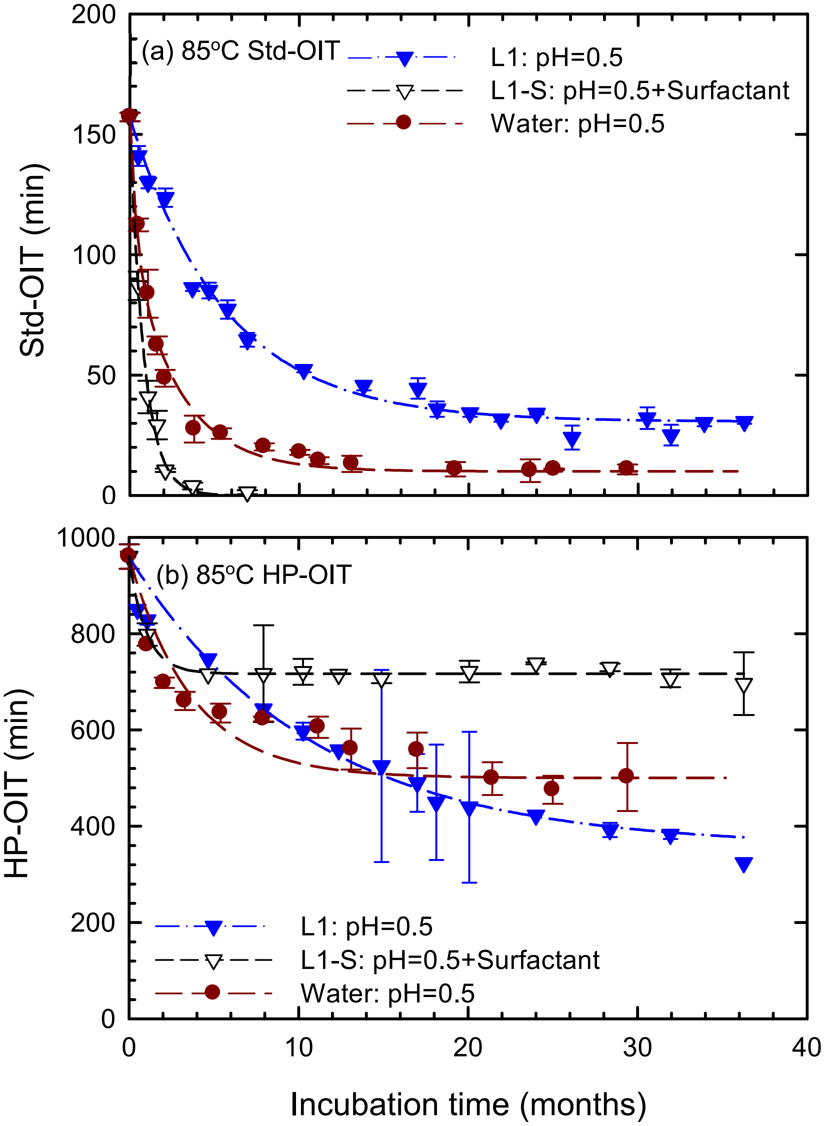

Fig. 7. Variation with incubation time at 85ºC of: (a) Std-OIT; (b) HP-OIT incubated in Solutions 1, 1-S and Water: pH=0.5 (modified from Rowe and Abdelaal 2016). Data points represent mean values and the error bars represent the ± 1 standard deviation.

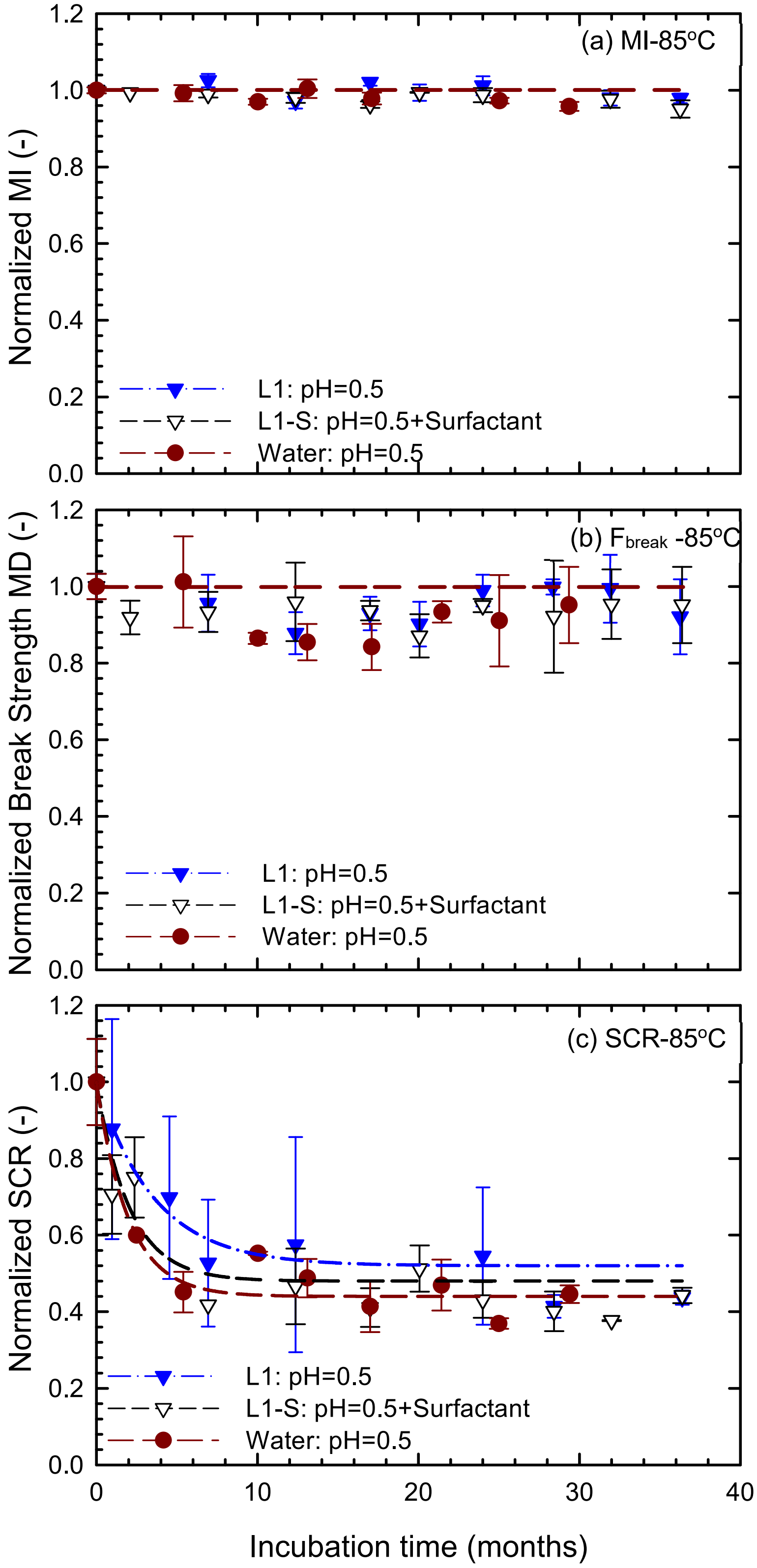

Fig. 8. Variation with incubation time at 85°C of normalized: (a) MI; (b) break strength in machine direction (F_{break}); (c) SCR incubated in Solutions 1, 1-S and Water: pH=0.5. Data points represent mean values and the error bars represent the ± 1 standard deviation.

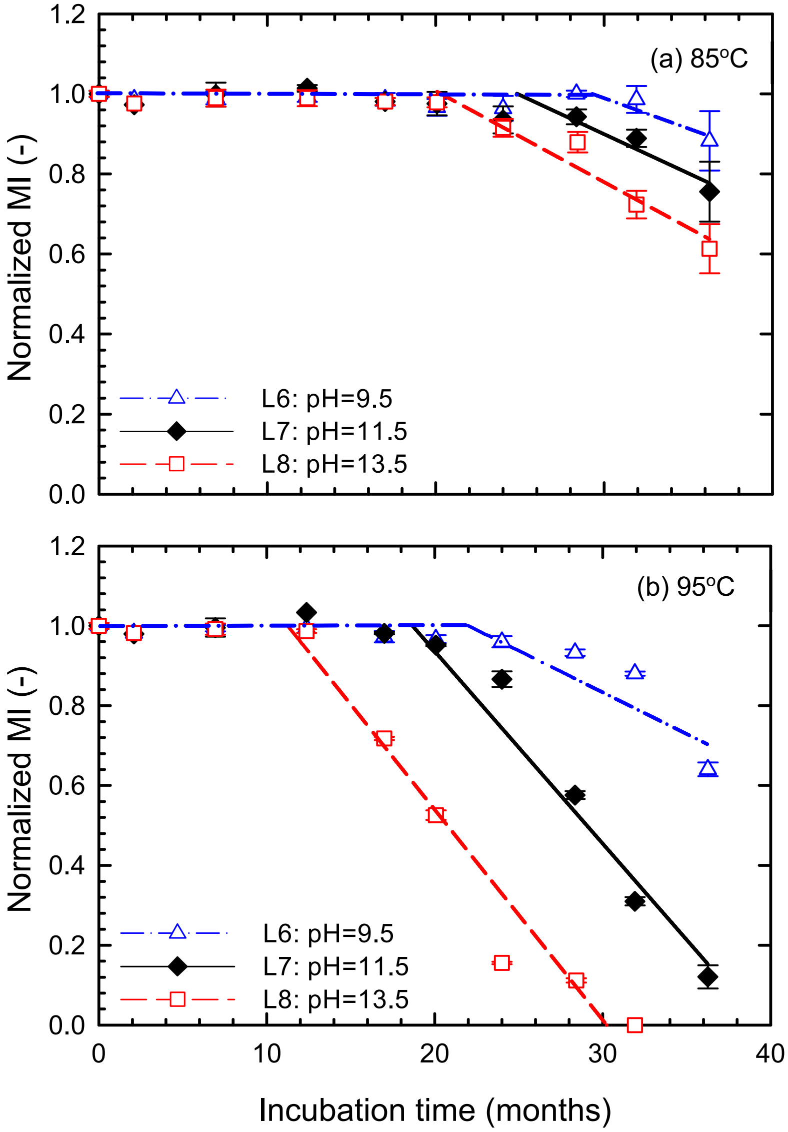

Fig. 9. Variation of normalized MI with incubation time for the three different low pH solutions at (a) 85ºC; (b) 95ºC. Data points represent mean values and the error bars represent the ± 1 standard deviation.

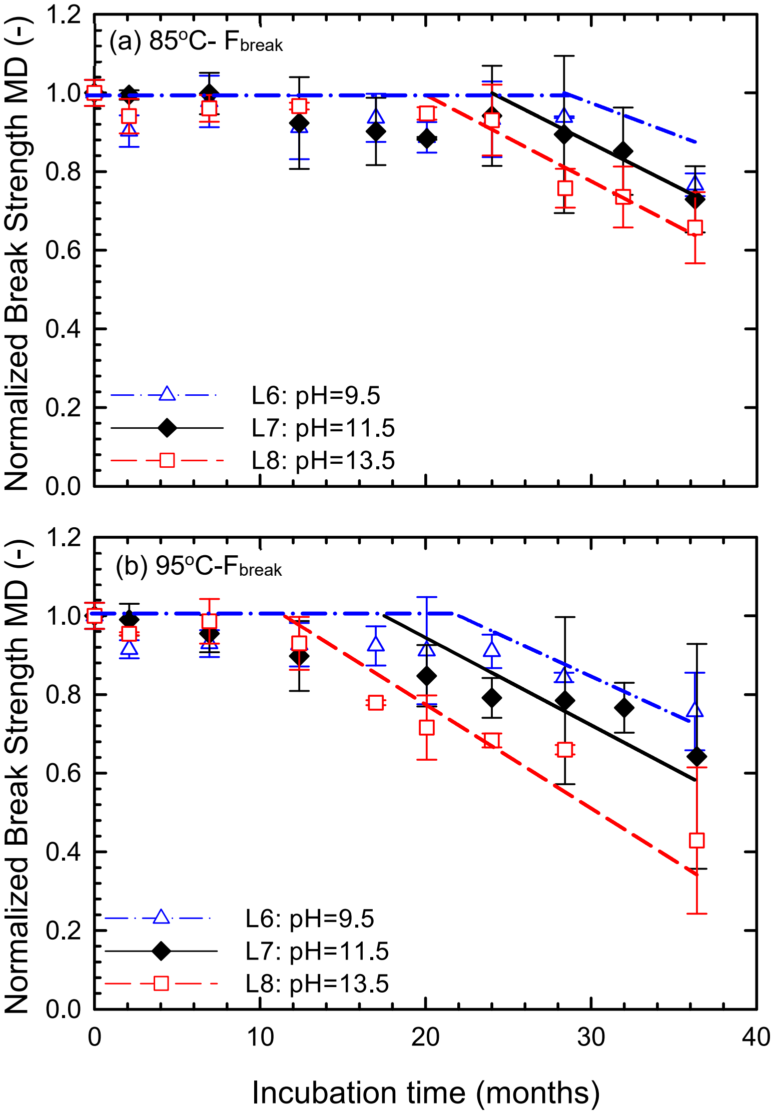

Fig. 10. Variation of normalized break strength in machine direction (F_{break}) with incubation time for the three different low pH solutions at (a) 85°C; (b) 95°C. Data points represent mean values and the error bars represent the ± 1 standard deviation.

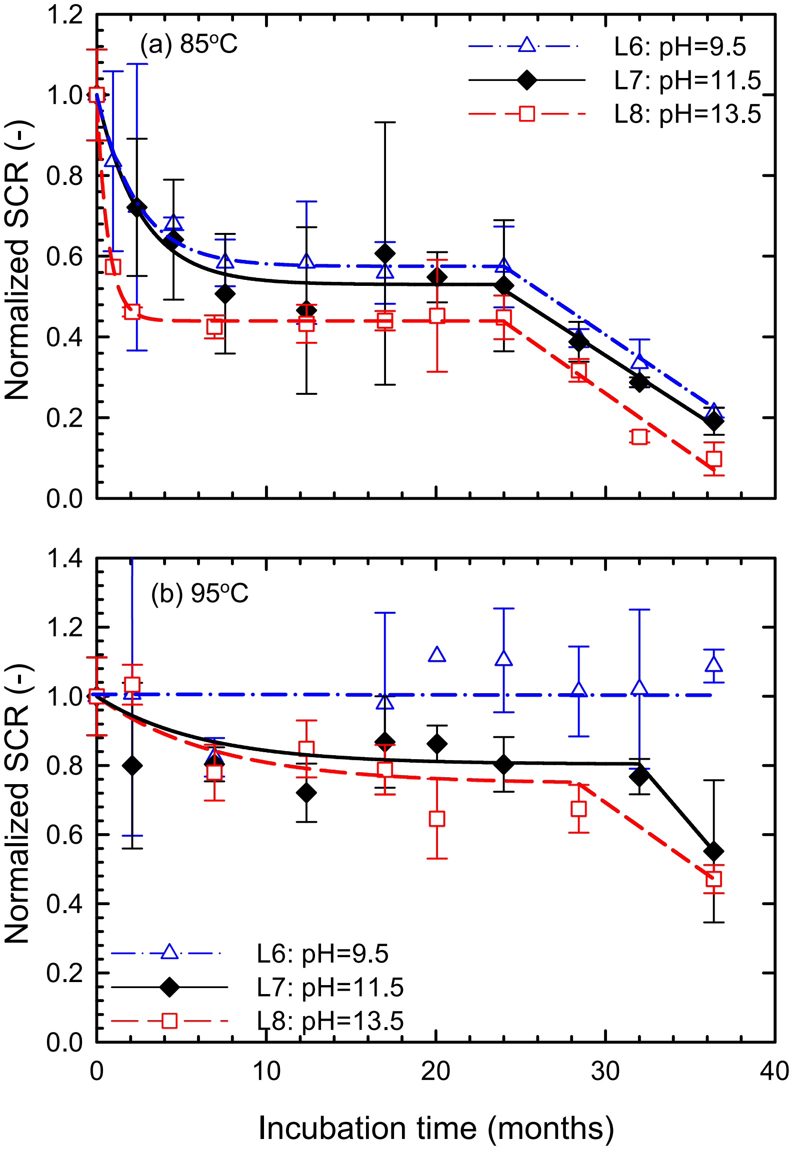

Fig. 11. Variation of normalized SCR with incubation time for the three different low pH solutions at (a) 85ºC; (b) 95ºC. Data points represent mean values and the error bars represent the ± 1 standard deviation.

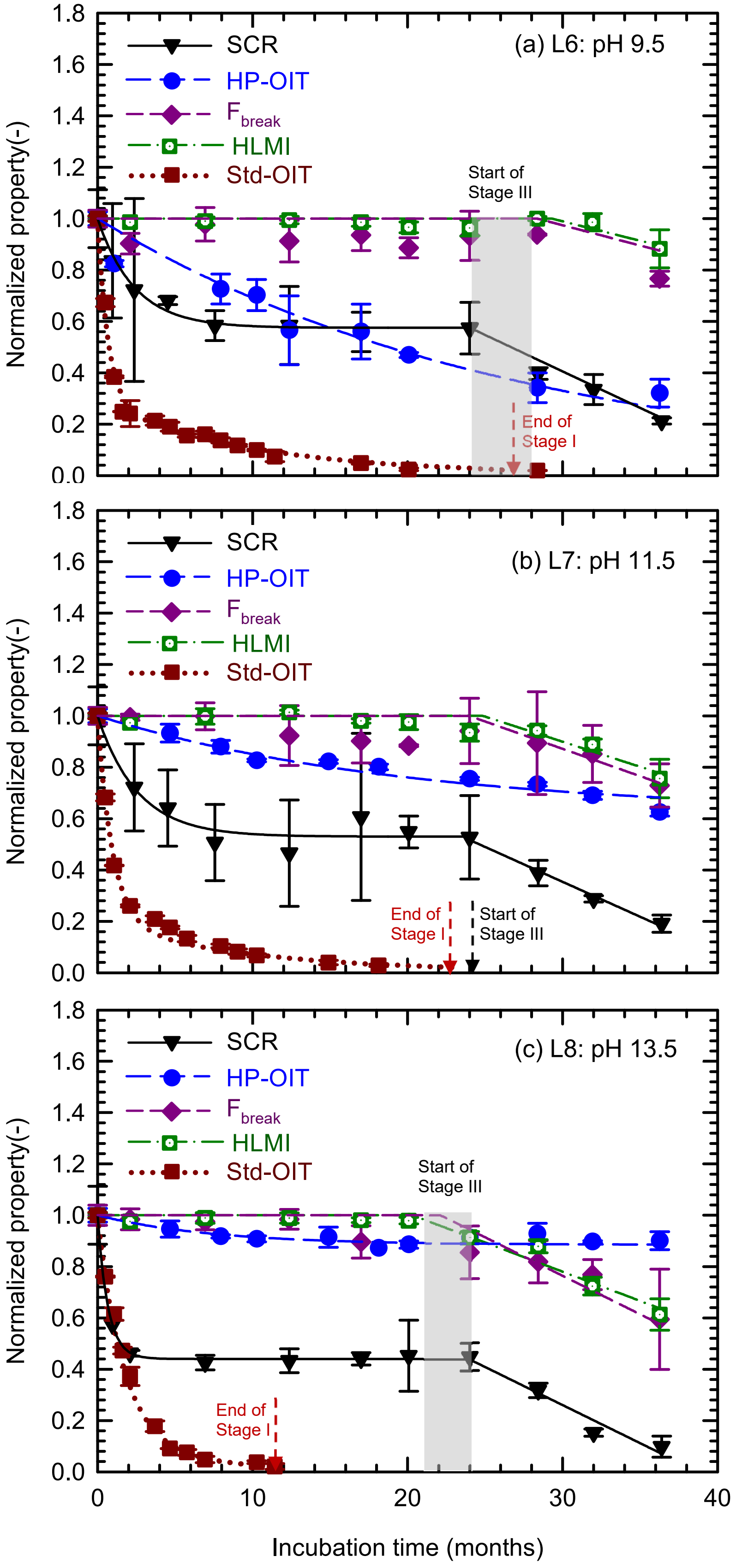

Fig. 12. Variation of different index properties in at 85°C in: (a) L6: pH 9.5, (b) L7: pH 11.5, & (c) L8: pH 13.5. OIT data are from Abdelaal and Rowe 2017. The start of Stage III is presented as a range of times at which the different properties start to change. Data points represent mean values, and the error bars represent the ± 1 standard deviation.