Comparison between the environmental stress-crack resistance of unaged and aged HDPE and LLDPE geomembranes

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Comparison between the environmental stress-crack resistance of unaged and aged HDPE and LLDPE geomembranes

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ABSTRACT: High-density (HDPE) and linear low-density polyethylene (LLDPE) geomembranes are used in barrier systems in various containment applications. The former is known for its better chemical resistance, while the latter is known for its higher stress-crack resistance (SCR). The SCR of high-density polyethylene is well defined in the literature, but the SCR of LLDPE as well as its failure mechanism are rarely addressed. This paper thus investigates the SCR of LLDPE versus HDPE geomembranes based on the fractured plane of unaged and aged specimens examined using the single-point notched constant load tensile test method. The GMBs were aged using a synthetic heap leaching solution with pH 13.5 at 85°C. Failed specimens are analyzed using scanning electron microscopy, after which the differences in fracture surface for both LLDPE and HDPE resins are discussed. The relationship between SCR, tensile break elongation, and melt flow index is also presented for the geomembranes examined.

1 INTRODUCTION

Stress-crack resistance (SCR) and its failure mechanism are some of the primary factors controlling the service-life of geomembranes (GMB). Environmental stress-cracking, in particular, arises when polyethylene geomembranes are exposed to sustained tensile stresses in the presence of fluids (e.g., municipal solid waste leachate or heap leaching liquors), and is a serious problem for base liners in geoenvironmental applications (Choi *et al*. 2009; Rowe *et al*. 2019).

High-density (HDPE) and linear low-density (LLDPE) polyethylene GMBs are typically chosen as the primary liners in these applications, but they do not have similar SCR. While the increased resin density of HDPE GMBs implies better chemical resistance and hardness, it increases the potential for stress cracking. For LLDPEs, the high side chain branching of the polymer molecule gives them more flexibility and a relatively higher off-roll SCR compared to HDPE (Brown *et al*. 1991; Lustiger & Markham 1983; Scheirs 2009). There are several methods for assessing the SCR for a broad range of polymeric materials (Robeson 2013), among which the notched constant tensile load test (NCTL; ASTM D5397) is well accepted and commonly used both in industry and research.

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Examining crack growth and propagation can be very useful in identifying fracture mechanisms such as brittle, semi-brittle and ductile, and this becomes especially important in the case of GMBs with very different SCR values being exposed to high levels of stress in the field. Nevertheless, the morphology of slow crack propagation has not yet been clarified for LLDPE GMBs tested using the NCTL method and thus it is still not clear how the fracture mechanisms change as the polymer density varies for both unaged and aged conditions. To fill this gap, this paper investigates the fracture surface of HDPE and LLDPE GMBs based on a microscopical analysis of the cross-section of broken SCR specimens from unaged and aged samples.

2 EXPERIMENTAL INVESTIGATION

2.1 *Geomembranes examined*

Two commercially available 1.5 mm thick smooth black HDPE and LLDPE GMBs were investigated in this study and are denoted as MxC15 and LxD15, respectively (Table 1). The two GMBs were produced by the same manufacturer using the blown film method. The performance of these two GMBs in different geoenvironmental applications has been extensively investigated (Abdelaal *et al*. 2012; Abdelaal & Rowe 2014; Abdelaal *et al*. 2011; Morsy *et al*. 2021; Rowe *et al*. 2019).

Table 1. Initial properties of the GMBs examined.

Property	Unit		
Designator	–	MxC15	LxD15
Type	–	HDPE	LLDPE
Nominal thickness (ASTM D5199, 2012)	mm	1.5	1.5
Resin density[1] (ASTM D1505, 2018)	g/cm^3	0.936	0.924
SCR (ASTM D5397, 2019)	hours	800 ± 90[2]	18,700 (24,000-15,000)[3]
HLMI(ASTM D1238, 2020)	g/10min	15.2 + 0.8	13.4 ± 0.8
Type V Break Elongation[4] (ASTM D6693, 2020)	%	800 ± 16.5	980 ± 34

Notes
[1]Provided by GMB manufacturer based on their results.
[2]Standard deviation.
[3](Maximum-minimum) SCR readings.
[4]Measured in the cross-machine direction.

One could challenge the assessment of SCR from LLDPE since it may not display a clear yielding point, as is the case of HDPE (e.g., Krishnaswamy & Lamborn 2000). However, the resin density of LxD15 is at the upper bound of the LLDPE density range (0.919–0.925 g/cm^3; ASTM D883) and yields in a similar manner as medium density polyethylene.

2.2 *Oven ageing and immersion solutions*

Two-sided exposure tests (ASTM D5322, 2017) were used to investigate how the SCR value and morphology change with ageing. This immersion technique consists of placing 200 x 95 mm GMB coupons in 4 L vessels filled with synthetic chemical solutions that mimic the effluents found in field conditions. The vessels were incubated in a forced air oven at an elevated temperature of 85°C to accelerate the ageing of the GMBs. Coupons were separated with glass rods to ensure that the chemical solution is in full contact with the GMBs. Samples were then periodically extracted at different incubation durations to assess changes in the SCR over time.

The incubation fluid was an extremely basic solution (pH = 13.5) simulating the extreme alkalinity found in pregnant liquors for gold and silver heap leaching (Abdelaal & Rowe 2017). This solution was prepared by mixing de-ionized water with a trace metal solution and inorganic salts and was titrated with a 15 mol sodium hydroxide solution to achieve the target pH.

2.3 *Single-Point Notched Constant Tensile Load Test (SP-NCTL)*

Both SCR and morphology of slow crack growth were assessed using the single-point notched constant tensile load test (SP-NCTL, ASTM D5397). In this test method, an engineered defect (notch) is made on one surface of a dumbbell-shaped specimen such that the ligament thickness (i.e., the portion of GMB uncut under the notch) is 80% of the nominal thickness of the specimen. The notched specimen is subjected to a load equal to 30% of the initial GMB yield strength in a stainless-steel tank filled with a 10% (v/v) solution of Igepal CO-630 in water at 50 $\pm$ 1°C. The SCR value is then taken as the elapsed time to failure. After failure, the specimens were examined using scanning electron (SEM) microscopy.

3 RESULTS AND DISCUSSION

3.1 *Slow crack growth in unaged GMBs*

In all the SEM micrographs presented below the direction of crack propagation is from bottom to top. The fractured plane of an unaged HDPE specimen with a SCR of 750 h had generally a three-phase morphology (Figure 1a). Zone A is a relatively small region in the vicinity of the notched area (i.e., ahead of the crack tip) where crazing effectively began at lower stress levels. There was a non-uniform fiber pullout across that area, suggesting that the fibers of the craze being formed did not rupture immediately after loading. Once this rupture occurred, crack growth transitioned into a zone of relatively less pullout (Zone B) characteristic of brittle failure (Chen 2014; Francey & Rowe 2021; Lu *et al.* 1991). This surface fracture appearance was more dominant than that observed at the other two zones, indicating that the failure mechanism of the examined HDPE GMB was predominantly brittle. As the crack extended and the cross-sectional area of the specimen was increasingly reduced, the applied load exceeded the yield strength of the GMB, which in turn led to large fibre deformations and failure in a ductile manner, i.e., Zone C (Francey & Rowe 2021). The lengths of Zones A, B and C measured from the SEM micrograph were approximately 130 μ m, 410 μm and 290 μm, respectively.

The SCR morphology of an unaged LLDPE specimen that failed after 17,100 h in the NCTL test was quite different (Figure 1b). Near the razor blade cut and at the base of the craze (using the aforementioned designation, Zone A), there was a strong continuous film instead of the fibrous structure observed from the HDPE specimen. This suggests that the time required to engage a crack in the first craze was considerably greater (e.g., Lu *et al.* 1992). The region of brittle failure (Zone B) was characterized by several short, thin fibers uniformly distributed and of somewhat uniform length and orientation. Finally, Zone C still showed ductile, long-fibrous structures, but the fibres were less distinguishable than Zone B when compared with HDPE. Zones A, B and C in this case had approximate measured lengths of 230 μm, 275 μm and 400 μm, respectively.

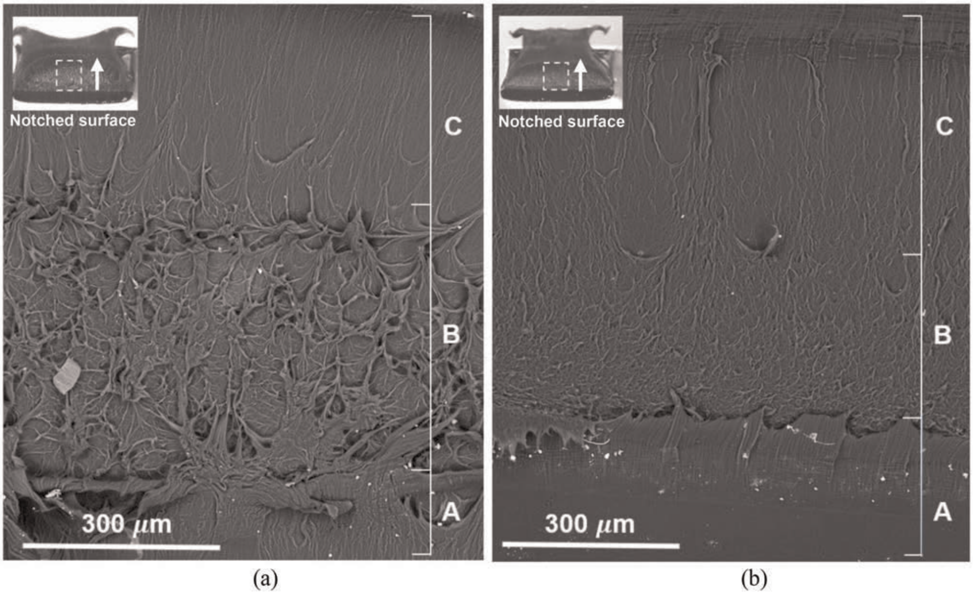

Figure 1. SEM micrographs of the fracture surface from: (a) an unaged HDPE specimen (SCR_o = 750 h); and (b) an unaged LLDPE specimen (SCR_o = 17,100 h).

3.2 *Effect of ageing on the morphology of crack growth*

Ageing can significantly reduce the environmental SCR of polyethylene GMBs due to the relaxation of residual stresses and changes in the semi-crystalline structure (i.e., physical ageing), and/or due to oxidative degradation (Ewais & Rowe 2014; Koerner *et al*. 2017; Morsy & Rowe 2020). Thus, the surface fracture morphology for aged specimens is also expected to change (Figures 2a and 2b).

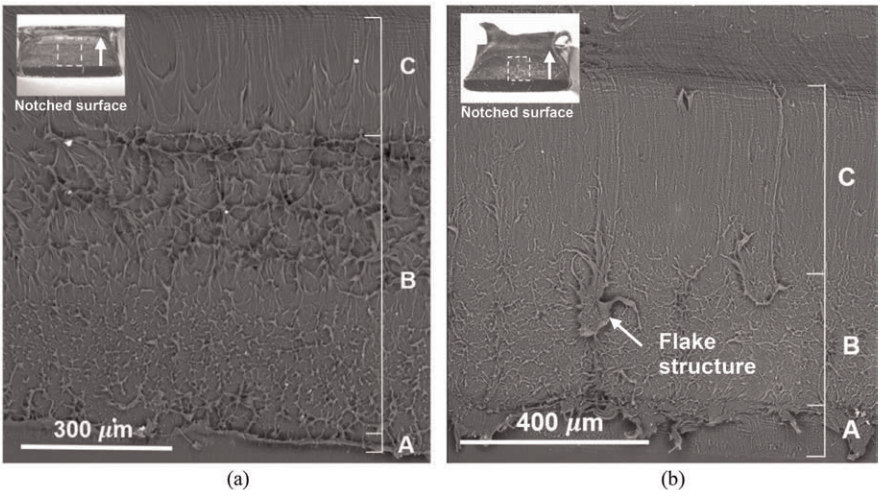

Figure 2. SEM micrographs of the fracture surface from: (a) a HDPE specimen aged for 6.8 years (SCR_{7years} = 5 h; $SCR_{7years}/SCR_0 < 0.01$); and (b) a LLDPE specimen aged for 4 years (SCR_{4years} = 617 h; $SCR_{4years}/SCR_0 = 0.03$).

For the HDPE specimen aged for almost 7 years in the synthetic heap leaching solution at 85°C (SCR_{7years} = 5 h), fibre length was significantly reduced in Zones A and B (Figure 2a), although the number of residual fibres was greater. While these shorter, isolated fibres increased relative to the unaged specimen, their resistance to crack propagation became considerably lower. The least affected region appears to be Zone C. This implies that, even in a highly aged HDPE specimen there was a portion of the material experiencing ductile failure (Scheirs 2009). The lengths of Zones A, B and C after ageing were approximately 35 μ m, 590 μm and 235 μm, respectively.

In the LLDPE specimen aged for 4 years (SCR_{4years} = 617 h; Figure 2b), initiation of crack growth was marked by a non-uniform long-fibrous detachment between Zones A and B very similar to that of the unaged HDPE specimen. Zone B displayed an increased number of long, thick fibres and flake structures that were not observed in the unaged specimen. The morphology of Zone C, once again, did not seem to be significantly affected. Zones A, B and C were 110 μm, 275 μm and 395 μm in length, respectively.

3.3 *Ageing of other physical and mechanical properties*

The SCR of the aged HDPE and LLDPE specimens are compared with the high-load melt index (HLMI) and tensile break elongation values at the same incubation duration (Table 2). The HDPE GMB retained 40% of its initial tensile break elongation after 7 years of ageing. The extremely low melt index value indicates the domination of cross-linking oxidative reactions. The generation of a more "tightly packed" structure due to excessive cross-linking makes the polymer more susceptible to brittle failure (Lustiger 1985), which might explain the short fibre structure depicted in Figure 2a.

Table 2. Physical/mechanical properties of HDPE and LLDPE GMBs after ageing.

Property	Percent retained (%)	
	MxC15 (aged for 7 years)	LxD15 (aged for 4 years)
SCR[1] (ASTM D5397, 2019)	0.6	3.3
HLMI[2] (ASTM D1238, 2020)	10.5	131.2
Type V Break Elongation[2] (ASTM D6693, 2020)	39.6	14.8

Notes
[1]Value from one single specimen
[2]Mean value

Even with less ageing time than the HDPE GMB, the LLDPE GMB lost 85% of its break elongation and 97% of its SCR. This was accompanied by a significant increase in HLMI, which implies chain scission reactions typically dominant in LLDPE GMBs (Morsy *et al.* 2021). Despite the extremely large reduction in SCR and break elongation, the GMB was still able to retain some flexibility, as depicted by the short to long-fibrous fracture surface (Figure 2b) and by the pullout of material in the macroscopic view of the specimen (Figure 2b, top left corner).

4 CONCLUSIONS

The environmental SCR performance of HDPE and LLDPE GMBs has been investigated. Unaged specimens as well as those aged in synthetic mining leachate at 85°C were tested using the single-point notched constant tensile load (NCTL) testing method. Broken specimens were recovered from the SCR test and were further analyzed by scanning microscopy to investigate the differences in failure mechanisms. The SCR results from aged specimens were then compared to the melt index and tensile break elongation values at the same incubation duration. For the GMBs and test conditions (e.g., ageing temperature, incubation fluid) investigated in this paper, the following conclusions can be reached:

- LLDPE had an initial very high SCR but after 4-years ageing it had reduced to 3% of its initial value.
- The fractured plane of SCR specimens tested in the NCTL test generally displays a three-phase morphology, namely: (1) a small zone of relatively longer pullout in the vicinity of the notch, or Zone A, (2) an intermediate zone wherein brittle failure dominates (Zone B), and (3) a zone of ductile failure (Zone C). The main difference in brittle failure between unaged HDPE and LLDPE was the length, orientation, and distribution of fibres.
- The length of the aforementioned zones is markedly different between HDPE and LLDPE. In the unaged HDPE, Zone B was 40% longer than Zone C in the direction of crack propagation, while the unaged LLDPE had Zone B only about two-thirds the length of Zone C. For the aged HDPE specimen, Zone B was 150% longer than Zone C. In the aged LLDPE, the length of Zones B and C remained the same as the unaged condition. In other words, the large decrease in SCR of the LLDPE GMB mainly reflects the change in morphology of Zone A.
- The morphology of Zone A from a 4-year aged LLDPE specimen is relatively similar to its HDPE counterpart in an unaged condition.

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