The strange effect of increasing temperature in accelerated ageing of HDPE geomembranes immersed in liquids

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ABSTRACT: The most commonly used temperatures for accelerated ageing of HDPE geomembranes (GM) is at or below 85°. This study examined geomembrane ageing in air, water and leachate at 95, 105 and 115°C. Ageing in air was accelerated as expected at higher temperatures. For liquid immersion tests, very different results were obtained from tests in sealed stainless steel tanks (with a pressure release valve) and glass jars open to atmospheric pressure. The antioxidant depletion rates for GMs immersed in leachate using stainless steel tanks were not consistent with what observed at low temperatures. However, for the glass jars the results fitted well with the low temperature results. This suggests that vapour pressure may affect GM ageing. However, even with glass jars open to atmospheric pressure, ageing of GMs in water gave unusual and unexplained results.

1 INTRODUCTION

High density polyethylene (HDPE) geomembranes (GM) have been used as a component of landfill liners and final cover systems due to their excellent resistance to a wide range of chemicals. It is expected, however, that HDPE geomembranes will undergo ageing during their service life due to chemical interaction with leachate, physical stresses, and elevated operating temperatures (Hsuan and Koerner 1998; Rowe 2005; Rowe et al. 2009). Laboratory accelerated ageing tests are generally conducted to evaluate the service life of geomembranes because of the long time required to obtain results from field conditions.

The most commonly used accelerating temperatures in the laboratory are 65, 75, and 85°C since it takes a very long time to obtain the antioxidant depletion rates at low temperatures (e.g. 22, 40 and 55°C) as illustrated by many investigators (Hsuan and Koerner 1998; Sangam and Rowe 2002; Müller and Jacob 2003; Gulec et al. 2004; Rowe and Rimal 2008). However, even at the temperature of 85°C, it would take up to a year to confidently obtain the depletion rate. Therefore, the objective of this study is to investigate the depletion of antioxidants from an HDPE geomembrane at three elevated temperatures higher than 85°C.

2 EXPERIMENTAL PROCEDURE

2.1 *Materials*

The 1.5mm thick GM used in the study was manufactured by Solmax International, Varennes, Quebec and had initial standard OIT (ASTM D3895) of 115 min.

2.2 *Exposure conditions*

In the first part of this study, GM samples were incubated in stainless steel containers (250 mm square and 200 mm high) filled with synthetic leachate or distilled water. The container was equipped with a pressure release valve to release pressure in excess of 35kPa that may be generated at higher temperatures. The containers were kept in different temperature controlled ovens at 95, 105, and 115°C.

In the second part of this study, the GM samples were immersed in four liter glass containers filled with synthetic leachate or distilled water. Due to high evaporation rates of the incubation fluid at temperatures greater than 100°C, smaller coupons were used to ensure that the samples were always immersed under the incubation fluid. To prevent samples from floating, all the GM coupons were tied to glass rods using aluminum wires to anchor them to the bottom of the glass jar. To ensure that there was leachate on both sides of coupons, 5mm diameter glass rods were placed as separators between coupons. The containers were placed in ovens at temperatures of 95, 105, and 115°C. The plastic lids of the glass jars were perforated to prevent the build-up of any excess pressure inside the jars.

The synthetic leachate used in this study was made by mixing trace metals, surfactant, and reducing agents in distilled water (Islam and Rowe 2007). The leachate used in this study was considered to be the most appropriate for evaluating the potential degradation of HDPE geomembranes based by a study that examined the effect of different synthetic leachate compositions on antioxidant depletion (Rowe et al. 2008). Air aged samples were placed directly inside the oven and were separated by 5 mm glass rods.

2.3 *Oxidative Induction Time (OIT)*

The oxidative induction time (OIT) is considered to be a good index for assessing the amount of antioxidant present in the geomembrane (Hsuan and Koerner 1998; Sangam and Rowe 2002; Gulec et al. 2004; Rowe and Rimal 2008). The OIT of the geomembranes was evaluated in accordance with ASTM D3895 (Std-OIT) test method. A TA Instruments Q-100 series differential scanning calorimeter (DSC) was used in this study. This geomembrane does not contain HALS in its antioxidant package and it has previously been shown (Islam 2009) that the depletion of HP-OIT is similar to that of Std-OIT, so only the latter is considered in this paper.

3 RESULTS AND DISCUSSIONS

3.1 *Antioxidant depletion in air*

The depletion of antioxidants is normally described by the first order decay relationship (Hsuan and Koerner 1998):

$$OIT_t = OIT_o \; e^{(-st)} \quad (1)$$

or, by taking the natural logarithm on both sides:

$$\ln(OIT_t) = -st + \ln(OIT_o) \quad (2)$$

where OIT_t is the OIT remaining at any time t (min), OIT_o is the initial OIT (min), s is the antioxidant depletion rate (month^{-1}), and t is the ageing time (month).

Figure 1 shows the variation in *ln(OIT)* with time at 95, 105, and 115°C in air. The slope of the linear regression lines represents the antioxidant depletion rate at each temperature. It can be seen that the depletion of antioxidants increased with the increase of temperature (Table 1) as was expected.

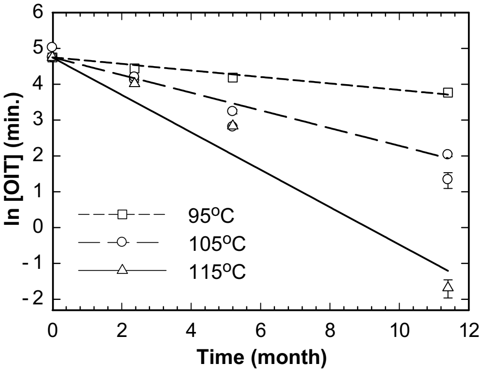

Figure 1. Variation in ln (OIT) with time at 95, 105 and 115°C in air.

3.2 *Antioxidant depletion in liquids using stainless steel tanks*

Figure 2 shows the variation in ln(OIT) with time at 95, 105, and 115°C in leachate. It is generally expected that the depletion of antioxidants should increase with the increase of temperature; however, surprisingly for the leachate immersed samples the depletion of antioxidants decreased with increasing temperature in this study. A similar antioxidant depletion pattern was observed when the geomembranes were incubated in distilled water (Figure 3).

It was not clear as to why the antioxidant depletion decreased with the increase of temperature for the liquid immersion tests. The antioxidant depletion rates for the leachate immersed GM were compared with the antioxidant depletion rates observed at 85°C (Table 1). The depletion rates at 95°C were found to be lower than the depletion rates at 85°C.

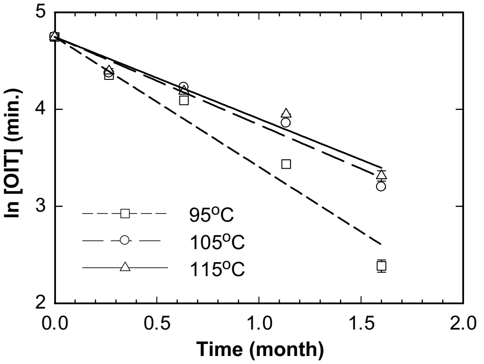

Figure 2. Variation in ln (OIT) with time at 95, 105 and 115°C in leachate using stainless steel tanks.

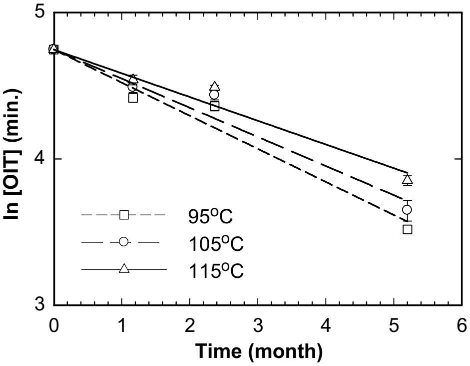

Figure 3. Variation in ln (OIT) with time at 95, 105 and 115°C in water using stainless steel tanks.

Table 1. Antioxidant depletion rates in the leachate, water, and air at 95, and 105, and 115°C (using stainless steel tanks for liquid immersion).

Temperature (°C)	Antioxidant depletion rate ($month^{-1}$)		
	Air	Water	Leachate
85[a]	---	0.266	1.508
95	0.091	0.226	1.34
105	0.247	0.199	0.906
115	0.522	0.162	0.843

[a] The antioxidant depletion rates reported at 85°C are from ageing tests conducted by immersing the same geomembranes in 4 liter glass containers. The rate reported at 85°C is based only on 1.5 month incubation.

At first inspection these results might be interpreted to suggest that one can not do accelerated ageing test by immersing the HDPE geomembrane at temperature above 85°C. However, since this was the first time these stainless steel tanks had been used for GM accelerated ageing and all previous accelerated ageing tests had been conducted using glass jars, it was decided to repeat the experiments at temperature above 85°C using glass jars instead of stainless steel as described in the next section.

3.3 *Antioxidant depletion in liquids using glass jars*

In this part of the study the same geomembrane was immersed in distilled water and leachate using glass jars. Figure 4 shows the variation in *ln(OIT)* with time at 85, 95, 105, and 115°C in leachate. It can be seen that as the temperature increases the antioxidant depletion rate increases which is the opposite of what was observed using the stainless steal tanks but consistent with what would normally be expected based on an Arrhenius relationship.

To allow an assessment of whether the antioxidant depletion rates at these three high temperatures are consistent with those observed at lower temperatures, results from the present tests at 95, 105, and 115°C were compared with those obtained by Islam and Rowe (2007) for the same geomembrane at 85°C using the same synthetic leachate as this study. (Figure 4). The results follow a consistent trend which follows the Arrhenius relationship.

When considering depletion in distilled water at 95, 105, and 115°C the situation was more complex as shown in Figure 5. It appears that at 105 and 115°C there were two stages of Antioxidant depletion. At early time, the antioxidants deplete at a very fast rate for the first four weeks at 105°C and for the first two weeks at 115°C. During this period the higher temperature gave the expected higher rate of depletion at higher temperature. However at 115°C and 105°C, after the initial rapid depletions, there is a complete change in response and further antioxidant depletion is at a very slow rate that almost remains constant until the end of the incubation period examined. It is not clear why this happened in distilled water and not in leachate.

Figure 6 shows the antioxidant depletion at all temperatures (from 22 to 115°C). The depletion rates at 95°C and below were consistent with an Arrhenius relationship whereas this was only valid for the initial portion of of the depletion curve at 105 and 115°C in distilled water. Thus, in the following section only the early stage depletion rates at 105 and 115°C will be used for further comparison between the antioxidants depletion rates.

Table 2. Antioxidant depletion rates in the leachate and water using glass jars.

Temperature (°C)	Antioxidant depletion rate ($month^{-1}$)	
	Water	Leachate
22	0.027	-----
55	0.091	-----
70	0.153	-----
85	0.266	1.111
95	0.395	2.082
105	0.704	3.384
115	0.9836	5.386

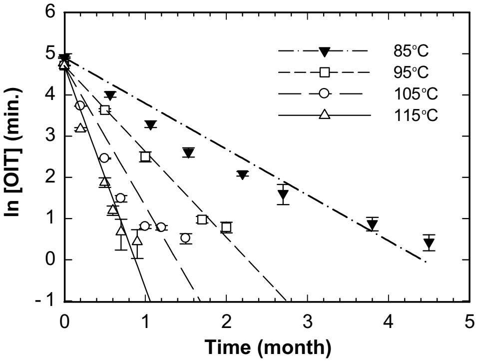

Figure 4. Variation in ln(OIT) with time at 85, 95, 105 and 115°C in leachate using glass jars.

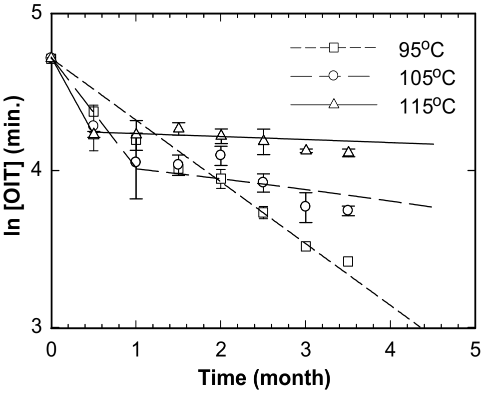

Figure 5. Variation in ln(OIT) with time at 95, 105 and 115°C in water using glass jars.

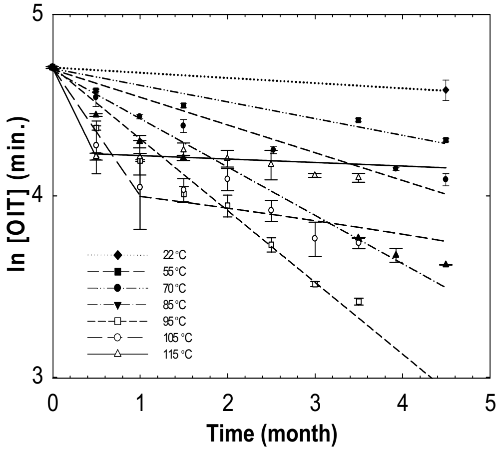

Figure 6. Variation in ln(OIT) with time at 22, 55, 70, 85, 95, 105 and 115°C in water using glass jars.

3.4 *Comparison between glass jars and stainless steel tanks used to age geomembrane in liquids at high temperatures*

Figure 7 and Figure 8 show a comparison of the antioxidant depletion rates in leachate and water, respectively at three high temperatures using glass jars and stainless steel tanks. The depletion behavior was very different at different temperatures and in different immersion liquids. These results beg the question of why the antioxidant depletion rate increases with temperature when using glass jars, while the contrary occurs when using the stainless steel tanks for leachate. Also the behavior when immersed in water both with stainless steel and glass jars is remarkable. A number of possible explanations are discussed below.

The first possibility is an effect of the difference in the container materials (stainless steel versus glass) due to a difference in thermal conductivity or interaction between the fluid, metal and geomembrane. To investigate this, one of the stainless steel tanks used in this study was used to age the same GM in water at 85°C. Figure 9 compares the antioxidants depletion rate obtained from this test and the previous results observed when using the glass jars. The similar antioxidant depletion rates obtained in jars and stainless steel tanks implies that difference in container material alone had no effect on the antioxidant depletion rates.

The second possibility is the vapor pressure that may be built up inside the stainless steel tanks at these high temperatures with a the pressure release valve that would allow 35kPa pressure build up in the containers before release. It has been observed during this study that there is a lot of evaporation of the immersion liquid (especially at 105 and 115°C) when the glass jars were used. This implies that there was no significant vapor pressure inside the vented jars. On the other hand, no significant evaporation was observed when using the stainless steel tanks. It can also be inferred from Figure 7 that the difference between the antioxidant depletion rates when using the glass jars and the stainless steel tanks varies with the temperature. To investigate this, the ratio of the antioxidant depletion rates in glass jars (s_j) to the antioxidant depletion rates in the stainless steel tanks (s_t) was plotted versus the temperature in Figure 10 for different immersion fluids. It can be observed from Figure 10 that with the increase of temperature the antioxidant depletion ratio (s_j/s_t) increases for both leachate and distilled water. It can also be seen that the rate of increase of the antioxidant depletion ratio (s_j/s_t) for both leachate and distilled water is almost the same with the temperature (which can be concluded from the slope of the linear regression lines).

Based on this investigation, the answer of the previously stated question on why there is a huge difference in antioxidant depletion rates when using glass jars and the stainless steel tank may be due to the vapor pressure that developed in these steel tanks. It appears that for these high temperatures, if vapor pressure is not properly released then lower antioxidant depletion rates can be obtained than if it is released. However, it is unclear why the vapour pressure affects the antioxidant depletion rates.

4 CONCLUSIONS

HDPE geomembrane samples were incubated in synthetic leachate, water, and air at 95, 105, and 115°C. Immersion in liquids was examined using sealed stainless steel tanks and then repeated using glass jars open to atmospheric pressure. Based on the results the following conclusions can be reached:

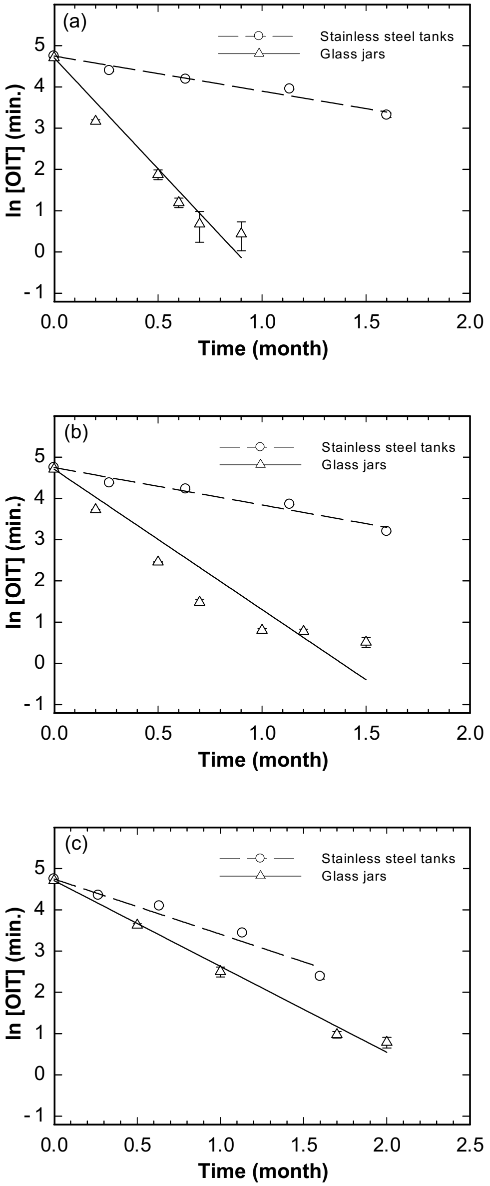

Figure 7. Variation in ln(OIT) with time in leachate when using glass jars and stainless steel tanks: (a) 115°C, (b) 105°C and (c) 95°C.

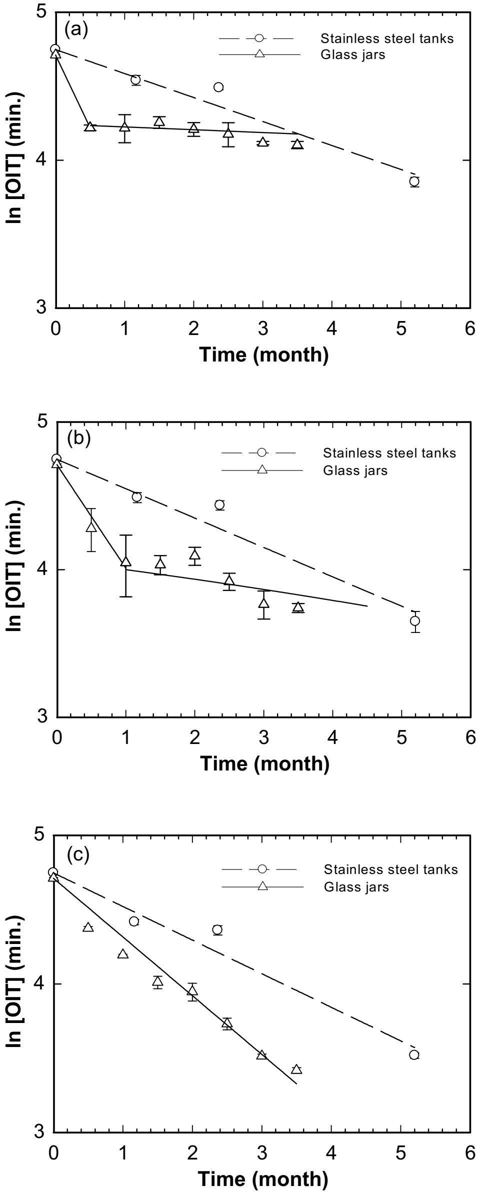

Figure 8. Variation in ln(OIT) with time in water when using glass jars and stainless steel tanks: (a) 115°C, (b) 105°C and (c) 95°C.

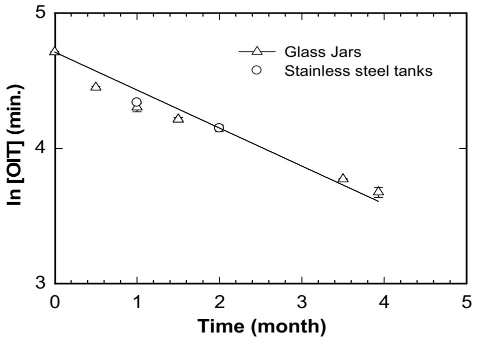

Figure 9. Variation in ln(OIT) with time at 85°C when using glass jars and stainless steel tanks.

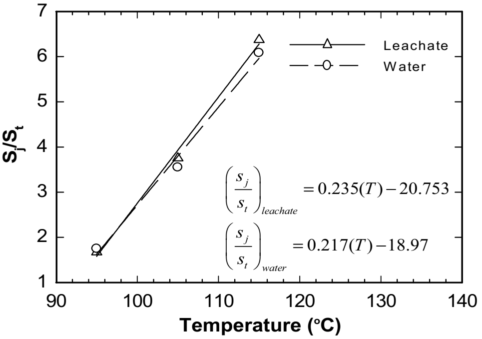

Figure10. Variation of the ratio of the antioxidant depletion rate in jars to the depletion rate ratio in stainless steel tanks with temperatures.

- For sealed stainless steel tanks, the results showed that the antioxidant depletion rate decreased with increasing temperature for leachate and water immersed geomembranes. The results also showed that the depletion of antioxidants was lower at 95°C than at 85°C for the leachate and water immersed geomembranes. However, for the air aged geomembranes, the antioxidant depletion rate increased with increasing temperature.
- For glass jars open to the atmospheric pressure, the antioxidant depletion rates increase with the increase of temperature for leachate immersion.
- For geomembranes immersed in water in glass jars, the results at 95°C were consistent with the low temperatures rates. However at 115°C and 105°C, after the initial rapid depletion, there is a complete change in response and further antioxidant depletion is at a very slow rate until the end of the incubation period examined.
- A comparison of results obtained in glass jars and stainless steel tanks, suggests that the valve, which allowed pressure build up to 35kPa above atmospheric in the steel tanks before release, may have affected the ageing of samples at temperature above 85°C and certainly above 95°C.

Based on the data the following questions are unresolved:

- Why is there a rapid depletion in the early stage followed by a very slow rate for geomembrane immersed in water at 105°C and 115°C?
- Why is the behaviour immersed in water so different to that immersed in leachate at the high (105°C and 115°C) temperatures?
- Why should an increase of vapour pressure (caused by the increase of temperature) cause the decease of the antioxidant depletion?

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