E3S Web of Conferences **569**, 11005 (2024) https://doi.org/10.1051/e3sconf/202456911005
GeoAmericas 2024

Effect of a PFAS solution on short-term behaviour of a LLDPE and an HPDE geomembrane

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Abstract. Per- and polyfluoroalkyl substances (PFAS) are synthetic chemicals formed by carbon chains where fluorine atoms replace one or more hydrogen atoms. These bonds are extremely stable and PFAS components are known to be persistent environmental contaminants. The impact of these contaminants on two geomembranes is studied. Specifically, the short-term behaviour of a linear-low density LLDPE and a high-density HDPE polyethylene geomembrane immersed in a PFAS solution at an evaluated temperature is examined after 6.5 months of ageing. Results are presented for a PFAS solution with each priority component at 20 ppm or 1 ppm, a control solution (deionized water with $CaCO_3$ 28 ppm), and an MSW leachate solution at two representative temperatures of landfills (65°C and 85°C). Results show significant depletion of oxidative induction time (OIT) due to the consumption of antioxidants present in these materials. The values obtained suggest the need to consider the potential impacts of PFAS on the performance of geomembranes used in barrier systems.

1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are synthetic and persistent chemicals that have been found in a variety of materials, like firefighting foams, textiles, food packaging, cookware, waterproofing products, electronics, etc. Numerous studies have been conducted and regulatory action has been taken to address the effects of PFAS because of their pervasive presence in the environment and the possible health and environmental dangers they pose. They can be found in soil, groundwater, and landfill leachate [1]–[4].

More than 12,000 PFAS compounds have been identified in recent years, among which PFOS and PFOA are the most widespread in the literature and regulations, as they have been manufacturing for a long time [1], [2].

Geomembranes, as part of landfill's barrier systems, play an important role in modern waste management and environmental protection practices. Hsuan and Koerner [5] proposed that the degradation process of polyethylene geomembranes occurs in a theoretical sequence consisting of three stages. The initial stage (Stage I) pertains to the depletion of antioxidants. (included in the formulation of geomembranes to delay the onset of thermos-oxidative

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degradation). Once antioxidants are depleted, the subsequent stage (Stage II) is initiated. In this phase, oxidative degradation begins although it is not measurable until the end of Stage II and the start of Stage III. Stage III is characterized by severe degradation significant enough to alter the properties of the geomembrane.

PFAS have surfactant properties. Recent literature dealing with PFAS's effect on geomembrane performance has shown the influence of this exposure on diffusion behaviour [2], [6], and some influence on the GMB service life. Based on 2.5 years of testing with HDPE geomembrane in PFAS solutions, Rowe and Somuah [3] showed that after 6 months of immersion, the depletion of antioxidants was accelerated by the addition of PFAS to either deionized water or simulated municipal solid waste landfill leachate. Also, PFAS geomembrane exposure can affect the mechanical behaviour of this material. Due to environmental stress cracking induced by the PFAS foams, its long-term storage in HDPE containers is not recommended [7]. However, to date, only one HDPE geomembrane has been examined with respect to its service life and that was in a high-concentration solution. More needs to be known about the effect of PFAS on different geomembranes in different leachates and for a range of concentrations and geomembranes [2], [3]. This paper will provide an initial approach to the short-term behaviour (6.5 months) of two geomembranes (HDPE and LLDPE) immersed in PFAS solutions, focusing on Stage I – antioxidant depletion.

2 Materials and methods

2.1 Antioxidant Depletion

Immersion tests (two-sided exposure tests) were conducted to evaluate the behaviour of selected geomembranes in PFAS solutions inside 4L glass jars (ASTM D5322, 2017). The geomembrane coupons' dimensions were 200 x 95 mm, and they were placed interleaving with glass rods to permit contact with the solution on all surfaces of the geomembrane. The jars were incubated in ovens at 65°C and 85°C, to accelerate the ageing process. These temperatures were selected to provide general information about the geomembrane behaviour for this initial research. Periodically, samples were collected for testing the standard oxidative induction time (Std-OIT [8]) to quantify the antioxidant depletion time for the aged GMB specimens in different experiments.

The two geomembranes examined (**Table 1**) were from the same manufacturer and are denoted herein as “MzB15” and “LzA15”. The MzB15 is a 1.5 mm-thick black HDPE geomembrane while the LzA15 is a 1.5 mm-thick black and white (layered) LLDPE geomembrane.

In this study, four different immersion solutions were analyzed (**Table 2**). The control solution was a modified deionized water (MDIW) with 28 mg/L of calcium carbonate added to deionized water to mitigate the aggressiveness of the deionized water [3]. A typical inorganic landfill leachate (MSW) [3], [11]–[13], that contains salts, acid, surfactant, and trace metals was the second solution. Two PFAS solutions containing perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in MDIW were tested, one solution with the concentration of PFAS at 1 mg/L and the other with them at 20 mg/L. Although these concentrations are higher than usual reported in the literature, they can provide a general overview of the behaviour for this initial approach.

https://doi.org/10.1051/e3sconf/202456911005

Table 1. Initial properties of the tested GMBs (preliminary – additional testing is in progress)

Property	Method	Unit	Values for the tested roll (Mean ± Standard deviation)	
GMB designator			MzB15	LzA15
Texturing			No	No
Nominal Thickness*	ASTM D5199 [9]	mm	1.5	1.5
Type			Modern HDPE	LLDPE
Color			Black	Black/White
Std-OIT$_o$	ASTM D3895 [8]	min.	167 ± 16	174 ± 9
HP-OIT$_o$	ASTM D5885 [10]	min.	1095 ± 11	2654 ± 1994

Table 2. General composition of the tested solution

Chemical	Formula	MDIW	PFAS1	PFAS20	MSW
Perfluorooctanoic acid (PFOA)	$C_8HF_{15}O_2$	---	1 mg/L	20 mg/L	---
Perfluorooctanesulfonic acid (PFOS)	$C_8HF_{17}O_3S$	---	1 mg/L	20 mg/L	---
Calcium Carbonate	$CaCO_3$	28 mg/L	28 mg/L	28 mg/L	---
Others	---	---	---	---	See [3]
Solvent	---	Deionized water	Deionized water	Deionized water	

3 Results and Discussion

The depletion of the antioxidants follows a trend that the depletion rate increases as the temperature gets higher. This behaviour is shown in **Fig. 1** for all tested solutions and geomembranes for 65°C and 85°C. Results for Std-OIT were obtained for every sampling and normalized by the respective initial Std-OIT$_o$ (unaged) value.

For MzB (HDPE) tested geomembrane, the depletion rate for 85°C was fast in the initial 3 months and was slowed over the next 3 months as it appeared to approach a residual or quasi-residual value. In contrast, 65°C the depletion was still decreasing after 6.5 months and had not (yet) stabilized. Similar behaviour was observed for LzA (LLDPE) antioxidant depletion rate. After 6.5 months of incubation, the results for retained Std-OIT are lower than 40% for 65°C (**Fig. 1a**) and 30% for 85°C (**Fig. 1b**). For the LzA (LLDPE) tested at 65°C (**Fig. 1c**) the normalized Std-OIT was lower than 55%, while at 85°C was lower than 40% (**Fig. 1d**).

The depletion of immersed samples immersed in MSW leachate was faster than all other test solutions due to the presence of surfactants that accelerate the antioxidant consumption. At the end of the tested period, the retained Std-OIT was lower than 10% for all geomembranes except MzB at 65°C, which was a little lower than 20%. The effect of PFAS solution is not yet clear and longer testing is required since the depletion rate was very similar for MzB at all tested temperatures in MDIW, PFAS1, and PFAS20 solutions. Considering the variability in the samples and results, a similar initial conclusion can be inferred for LzA geomembrane, due to the proximity of the data. So far, the effect of temperature is far greater than the effect of PFAS (**Fig. 1**). Rowe and Somuah [3] showed similar behaviour with a different HDPE GMB from those examined in this study, in which the effect of PFAS20 did not become clear until after 6 months immersion.

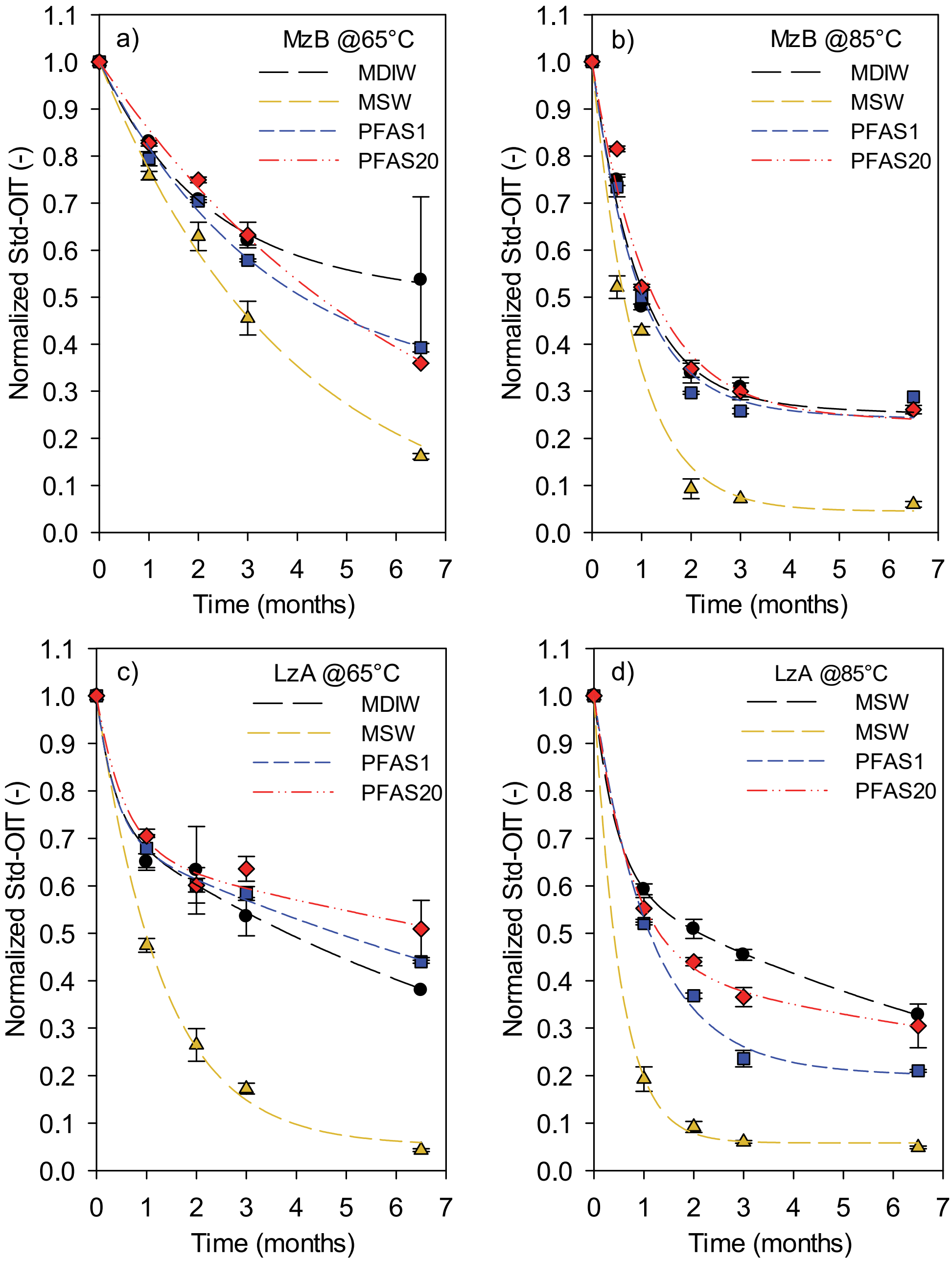

Fig. 1. Normalized Std-OIT during the tested period: (a) MzB at 65°C; (b) MzB at 85°C; (c) LzA at 65°C; (d) LzA at 85°C.

Generally, antioxidant depletion can be described as an exponential decay behaviour as a function of the time of exposure to the tested fluid as shown in **Eq. 1** for normalized data:

$$\frac{OIT_t}{OIT_0} = yo + a \times e^{-st} \tag{1}$$

where,
OIT_t is the Std-OIT obtained in a time t
OIT_0 is the Std-OIT of an unaged material
$a + yo$ is the initial ($t = 0$) normalized OIT ($a + yo = 1$)
y_o= residual value
s is the decay constant that determines the rate at which the quantity decreases
e is the base of the natural logarithm.

Eq. 1 is known as the 3-parameter decay model and degenerates into the 2-parameter model when b=0. **Eq. 1** has been used to fit different antioxidant depletion in the literature [3], [5], [13]–[18]. But as the geomembrane chemical formulations and the exposure conditions (temperature, fluids) change, different behaviours can occur than that indicated by **Eq. 1**. [3], [14], [16], [17] and Abdelaal et al. [14] highlight that the general behaviour of antioxidant depletion can be described for **Eq. 2**:

$$\frac{OIT_t}{OIT_0} = a \times e^{-s_1 t} + b \times e^{-s_2 t} + y_0 \tag{2}$$

where,
OIT_t is the Std-OIT obtained in a time t
OIT_0 is the Std-OIT of an unaged material
y_0 is the normalized residual OIT parameter
a, b are the fitting parameters ($a + b + y_0 = 1$)
s_1, s_2 are the rate that determines the quantity decreases (early and later, respectively)
e is the base of the natural logarithm.

In **Eq. 2** when b tends to zero, we have the 3-parameter model. Likewise, when y_0 tends to zero, it reduces to the 4-parameter model. When both parameters tend to zero, it reduces to the 2-parameter model (**Eq. 1**). **Table 3** and **Table 4** describe the fitting parameters obtained with the available data until the testing period and that were used to build the fitting curves in **Fig. 1**. Based on the initial data fitting, only the MSW leachate solutions exhibited a consistent pattern that could be 3, 4 or 5 parameters but at 6.5 months it is too early to tell. At present, for the MzB geomembrane, the 3-parameter decay model appears to be a more representative fit, with the expectation of reaching residual values. In contrast, LzA was best fitted by a 4-parameter decay model, involving two rates for exponential decay, although it is still too early to be certain. The parameters are likely to change as new results are collected.

4 Conclusions

This initial study investigated the antioxidant depletion measured by Std-OIT tests with an LLDPE and HDPE geomembrane incubated in four different solutions (MDIW, PFAS1, PFAS20, MSW leachate) for 6.5 months. The incubation is still running, and more data will be collected, but some initial observations could be highlighted:

Table 3. Std-OIT fitting parameters for MzB15 (preliminary – additional testing is in progress)

MzB	65°C				85°C			
Parameter	MDIW	PFAS1	PFAS20	MSW	MDIW	PFAS1	PFAS20	MSW
a	0.494	0.709	1.000	1.000	0.742	0.752	0.759	0.955
s_1	0.453	0.297	0.156	0.260	1.041	1.070	0.863	1.157
b	---	---	---	---	---	---	---	---
s_2	---	---	---	---	---	---	---	---
y_0	0.506	0.291	---	---	0.258	0.248	0.241	0.045

Table 4. Std-OIT fitting parameters for LzA15 (preliminary – additional testing is in progress)

LzA	65°C				85°C			
Parameter	MDIW	PFAS1	PFAS20	MSW	MDIW	PFAS1	PFAS20	MSW
a	0.265	0.294	0.331	0.948	0.392	0.785	0.568	0.942
s_1	2.908	2.677	1.807	0.762	2.277	0.901	1.344	1.916
b	0.735	0.706	0.669	---	0.608	0.215	0.432	---
s_2	0.100	0.071	0.040	---	0.095	0.010	0.055	---
y_0	---	---	---	0.052	---	---	---	0.058

- After 3 months all tested geomembrane and solutions showed antioxidant retention lower than 50% for 85°C and lower than 65% for 65°C. These numbers decreased to 40% and 55% respectively, with 6.5 months of incubation.
- So far, the presence of PFAS chemicals (surfactant) is not observably accelerating the antioxidant depletion. Probably, the time being analyzed is too short to verify this influence, and the effect of temperature (especially at 85°C) is dominating the rate of depletion largely masking the effect of PFAS.
- During the tested period and with limited data, the Std-OIT depletion data could be fitted by different types of exponential decay expressions (3 or 4-parameter model) alternatively than the usual 2-parameter model, depending on the test configuration.

These preliminary findings will be re-examined as more data becomes available. More information is still required until the entire depletion of antioxidants to residual values is attained in order to compare the performance of various test configurations and determine how long Stage I will last.

The research was being funded by the Natural Sciences and Engineering Research Council of Canada grant RGPIN-2022-03928.

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