

Assessment of Polyethylene Geomembrane Properties after Accelerated Thermal Ageing

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Application temperatures and exposure environments are among the causes of premature antioxidant loss in polymer geomembranes. Therefore, over the long term, polymer degradation takes place which is reflected in geomembrane properties. In this work, accelerated thermal ageing of polyethylene geomembrane was carried out in a climatic chamber at 70°C with 21% oxygen. The evolution of tensile properties, puncture resistance, and shore D hardness with exposure time was assessed. Changes in chemical and crystalline structure and melt flow index were made. According to the findings, geomembrane surface oxidation takes place in the polyethylene matrix after 9 months of exposure. This fact is confirmed by evaluating carbonyl, vinyl, and hydroxyl indexes. Uniaxial tensile properties, puncture resistance, and shore D hardness indicated slight changes after one year of exposure. While the crystallinity index, determined by XRD measurement, has shown an increase with exposure. Further, melt flow index measurements confirmed the absence of chain scission during the early exposure periods. However, for longer periods, chain scission reactions occurred and MI values increased moderately after five months of accelerated aging. All results indicated no significant bulk degradation while maintaining a certain mechanical resistance with applications under a temperature of 70°C. This temperature value is relevant in a waste storage center, but the studied geomembrane is not recommended for this case.

1. INTRODUCTION

Geomembranes are widely used in transportation, environmental and geotechnical applications such as ponds, barrier liners for landfills, dams, or canals, as well as in waste storage centers [1-3]. They are useful to prevent not only water but also hazardous substances contained in water, liquid chemicals or gases from migrating into the environment (e.g. subgrade, soil or groundwater) [4, 5]. To ensure this primary function, they should be waterproof and flexible with good weldability [6, 7].

Geomembrane materials are usually made from synthetic polymers, i.e. polyethylene, polypropylene or polyvinyl chloride [8]. Polyethylene geomembranes are formulated with 96-97.5% polyethylene, 2-3% carbon black, and 0.5-1% antioxidants and thermostibilizers mixture [9-11]. The damage to molecular chains of these materials may be due to one or more stresses applied to the material or chemicals in contact as well as climatic factors exposition such as ultraviolet radiation, heat, liquid medium, and also microorganism contact [12]. Polyethylene geomembrane is widely used in landfill sites, which are subjected to punching stresses linked to the drainage layer [4]. This factor could have a synergic effect with high temperatures also existing in waste storage facilities and other factors such as oxygen and liquid medium, which affect their service life [13, 14]. Examination of GM's actual field over the service life could be the ideal way of assessing geomembrane service life. However, this would take too much time to obtain results under field conditions. Laboratory accelerated ageing tests constitute one of the alternatives to service life assessment [15, 16].

Literature [16] has reported geomembranes submitting to higher temperatures at various levels of service life: prior, during, and after installation. This fact could cause GM stick, split, or tear, thereby making GM become unserviceable. Changes in GM properties, such as physical, chemical or mechanical ones, occur when UV and oxidative degradation are fastened by high temperatures up to 80-90°C. Higher temperatures like 105-125°C should be avoided due to the morphological changes causing thickening of crystals and an increase in melting temperature, as reported by different studies [8, 9, 17-19].

In a landfill liner, the temperature might reach 70 to 90°C and in some cases above 140°C. This affects antioxidant (AO) depletion time and rate dependently on the immersing environment, annealing, and chemical degradation [18-23]. Other studies also reported the considerable effect of high temperatures on the swelling of high-density polyethylene geomembrane (HDPE GM) subjected to hazardous organic liquids [17, 24]. They attest that a temperature of 85°C is sufficient to degrade HDPE geomembrane and causes a 60% reduction in stress cracking resistance. The latter depends on the polymer used [25]. Since the advent of geomembranes, there have been modifications in the resins and additive packages used in HDPE GMs [19]. With the existence of several GMs resin producers around the world using different additives and polymer technologies, in addition to that, due to the great growth of GMs manufacturers, there has been a need





to assess the performance of these different GMBs, requiring the use of elevated temperatures to keep up with the developments in the GMB industry [5, 26].

Thus, in this study, the thermal aging of a local polyethylene geomembrane was monitored by evaluating mechanical properties, structural changes, crystallinity, and MFI, which are often used as tracers of aging materials [14]. Puncture resistance and shore D hardness were also evaluated under the studied conditions to assess the durability of geomembrane under a temperature of 70°C to be used in waste storage centers.

Under previous conditions and for early exposure periods, HDPE GM has demonstrated surface oxidation without affecting tensile (module, stress/strain at break) and puncture (maximum load) properties in addition to hardness. However, crystallinity changed in tandem with tensile strain/stress at yield, particularly for longer exposure periods where the melt flow index increased, indicating the presence of chain scission reactions but no significant bulk degradation.

2. BACKGROUND

Different studies [19, 27] have examined the effect of high temperature on various properties of HDPE geomembranes.

Abdelaal et al. [19] have examined four commercial geomembranes (GM1, GM2, GM3 and GM4) incubated in air at temperatures between 85 and 115°C for 30 months. The investigation of crystalline morphology by differential scanning calorimetry has demonstrated the thickening of lamella crystals of polymer with increasing incubation temperature in air to 105 and 115°C. The melting temperature of the polymer has also increased with an increase in incubation period and temperature. In terms of stress crack resistance (SCR) of GMs, those incubated at 105 and 115°C for shorter periods (5 months) showed an increase. In parallel to that, melt index (MI) decreased. For longer incubation periods, Abdelaal et al. [19] have observed a sharp thickening of lamella cristals while a decrease was observed for SCR. At the same time, MI increases before falling again for GM1 and continuously decreases for the other geomembranes. They have also shown that incubation temperatures affected the critical decay threshold of MI and that the decrease in MI values occurred at shorter periods for high temperatures. According to authors, early stage of geomembrane incubation at high temperatures induces recrystallization of the molten material with a formation of more perfect crystals what has increased SCR. At the same time, there was a decrease in antioxidants, which causes polymer degradation. Consequently, MI did change with values being affected by whether cross-linking (for GM2, GM3 and GM4) or alternating cross-linking and chain scission degradation (GM1) were dominant. With extensive aging of geomembranes, authors have indicated that further thermooxidative degradation resulting in oxidized polymer chains occurred. Latter induces chemicrystallisation phenomena involving their crystallization in the amorphous region that gave rise to the increase in the peak melting temperature of the major crystals. They conclude that when using geomembranes at elevated temperatures with different resins and formulations, they respond quite differently. Moreover, the magnitude of influence of phenomenon such as annealing, crosslinking or chain scission reactions depended on the GM used.

In another study by Mills and Beaumier [27], investigated antioxidant depletion of different GMs, including resins recommended for high temperatures (PE-HT) by different manufacturers from France, Europe (EU), and United States (US). Incubation was done in an air convection oven for one year at 70, 90, and 110°C. They found that oxidative induction time (OIT) of all tested geomembranes decreases, especially, for that aged at 90 and 110°C. However, geomembrane made of PE-HT resin from the US has shown a lower rate of OIT decrease. By evaluating the kinetic parameters from OIT testing, geomembrane made of PE-HT resin from the US has shown the lowest activation energy, leading to a slower depletion rate of AOs. Authors determined the time to reach antioxidant depletion. At the end of this time, the mechanical properties of the geomembrane decrease until they reach 50% of their initial values. After that, a failure is expected. They have found that the time to deplete all of the antioxidants at lower temperatures is less important. As temperature rises, the AO depletion time of the PE-RT resins (from the US and EU) increases when compared to the common HDPE grade. For common HDPE used in GM, lifetime prediction was 2.4 years at 85°C; however, for PE-HT, lifetime calculation was 18.2 and 8.8 years, respectively, for geomembrane made of US and EU resin. Keeping exposure temperatures below 60°C results in a rise in PE-HT GMs lifetime. The authors suggested that it is not always practical to take test data from other industries and apply that data without verification. In addition, a carefully selected resin can be expected to perform as GM in higher temperature applications.

Gómez [28] has investigated the relationship between GM behavior, particularly, against stress cracking, and some characteristics of PE resins used in GMs like: density linked to crystallinity; MI related to molecular weight of the polymer; and the molecular weight distribution. According to the author, no direct relationship exists between molecular weight distribution or density and stress cracking resistance. Nevertheless, the use of low-density polyethylene with wide molecular weight distribution results in GM with good SCR, but it is necessary to check the required mechanical and chemical geomembrane properties. However, it is possible to improve SCR by using polyethylene with a higher density but a wider molecular weight distribution or, inversely, a narrow molecular weight distribution but lower density.

In another study, Abdelaal and Rowe [18] investigated the synergic effect of high temperatures and incubated medium (air, water, and synthetic leachate) on the AOs depletion from different commercial geomembranes (GM1-4). They found that for the different GMs, the AOs depletion rate was not affected by incubation at a high temperature in air, but later affected the depletion of standard oxidative induction time (OIT). For GMs incubated in leachate, the same mechanism governed the depletion of AOs for all geomembranes immersed in leachate at temperatures ranging from 25 to 115°C, and a similar reduction in time to depletion was obtained.

For GMs immersed in water at high temperatures, the authors noticed that the early and later stages of AOs depletion rate of geomembrane containing phosphite antioxidants (GM1) were affected compared to other tested GMs.

They also observed that the early time depletion of phosphite AOs was faster in water than in air when the temperature was below 100°C, while, the later time depletion was slower in water than air because of the resistance of AOs at the later stage. With an increase in temperature above 100°C, the early time depletion of AOs decreased in water than in air thus reducing phosphites loss. In the case of geomembranes containing high molecular weight hindered amine light stabilizer (HALS), AOs depletion was delayed. While the low molecular weight hindered amine light stabilizer contained in GM4 was depleted n water and in air.

Authors have evaluated the tensile mechanical properties, SCR, and MI of studied GMs. They did not observe any changes in MI for GMs immersed in leachate or air for 30 months, while SCR and break strength decreased. This result confirmed the finding of another work [29]. They related that to counterbalancing chain scission and crosslinking degradation or due to GM swelling after disentanglement of tie molecules as a result of incubation in leachate.

For incubated GMs in water over the studied period (54 months), the authors observed a decrease in cross-direction break strength, SCR, and MI. All these decreases started before the depletion of antioxidants. This fact led authors to suggest that the traditional three-stage model used for lifetime prediction is not always applicable without looking at the overall performance of the GM.

The magnitude of reduction in properties observed on the studied geomembranes was affected by both applied temperatures as well as the immersion environment.

Ewais et al. [26] have conducted experiments on three different GMs containing three resins and antioxidant formulations, subjected to simulated leachate environment at 85°C. According to the authors, the AOs depletion time for HDPE GMs depends on the type of AOs rather than the initial OIT values due to the diffusion potential of AOs. Before immersion, they found that all geomembranes (noted A, B and C) met the requirements of the geomembrane industry in terms of high-pressure oxidative induction time (HP-OIT >>> 400 min). GM-C and GM-B have demonstrated a longer AO depletion time due to the presence of HALS than GM-A without HALS. Thus, depletion of HP-OIT was controlled by depletion of HALS. However, the depletion mechanism and rate depend on HALS type (GM-C and GM-B).

After three months of ageing, GM-C still met the requirement with an HP-OIT retained at 80%, although, degradation of the polymer occurred. As a result, GM-C reached 50% of the initial values for the melt index and tensile properties at break.

In contrast, GM-B still retained its tensile properties, MI, and SCR after 45 months.

The comparison of GMs failure time of divers properties led authors concluded that when GMs have lower SCR but better protection against oxidative degradation (as for GM-B), the time to nominal failure is longer than that of GMs having higher SCR and the lowest oxidative protection (as for GM-A).

Ewais et al. [26] also demonstrated that maintaining HP-OIT after ageing does not mean that a GM will be protected against polymer degradation and properties should be monitored to confirm the effectiveness of the AOs package detected by HP-OIT.

According to the presented studies, monitoring of the evolution of GM properties is often necessary to know their behavior against polymer degradation, especially when no information is present about antioxidants/stabilizers package.

3. EXPERIMENT

3.1 Geomembrane

The geomembrane (GM) used in this study is a commercial

one. It was produced using a local polyethylene polymer commercialized by CP2K of Skikda in Algeria. The carbone black used is a master batch. The formulation contains a fraction below 0.5% weight of antioxidant mixture in addition to linear low density polyethylene "LLDPE" used to insure more flexibility to the GM.

3.2 Accelerated tests

The test was achieved in a MEMMERT climatic chamber HPP-Model 260, to accelerate the aging process. First, specimens in the form of dumbbells (to be used for tensile tests) and discs (to be used for other tests) were catted. Then, specimens were hung vertically with a cotton thread on a rack inside the climatic room, respecting the distance between them as well as that of chamber edges. The climatic chamber works at 70°C with a normal oxygen atmosphere (air with 21% of oxygen) and without forced circulating air following EN-ISO 13438 standard. Samples were exposed for one year and an average of 10 specimens were taken out for tests periodically.

3.3 Chemical and structural characterization

Chemical and structural properties of studied geomembrane samples were measured by Fourier-transform infrared spectroscopy in an attenuated total reflectance mode (ATR-FTIR), on a Perkin Elmer Spectrum analyser. The spectral range was 4000 cm⁻¹ to 500 cm⁻¹ with a resolution of 4 cm⁻¹. The measurement depth was approximately 2 μ m using a diamond ATR crystal.

After baseline correction, all spectra of geomembrane samples, before and after aging, were normalised to the unchanged peak at 2912 cm⁻¹ [30, 31]. This peak is due to the bending vibration of the -CH₂- group in polyethylene. From the normalised spectra, vinyl, carbonyl and hydroxyl indexes were calculated as the ratio between the peak areas, of 1330-880 cm⁻¹, 1850-1650 cm⁻¹ and 3575-3125 cm⁻¹ and the peak area of the symmetric C-H stretching band of methylene groups [32-37].

3.4 Crystalline structure

The crystalline structure was characterized by the standard X-ray diffraction (XRD) technique with a PANalytical X'Pert Pro diffractometer, using a Cu K α source (λ =1.5406 °A, 40 kV, 40 mA). All phase analyses were performed using the HighScore plus software. Crystallinity (Xc) was determined following Eq. (1).

$$Xc~(\%) = 100. \frac{A_{cr}}{A_{cr} + A_{am}}$$
 (1)

where: A_{cr} and A_{am} are, respectively, the area of the crystalline and amorphous phase.

3.5 Mechanical characterization

Uniaxial stress-strain curves of geomembrane samples were obtained on an MTS Criterion 45 testing machine in accordance with the ISO 527-2 type 5A standard. The strain-stress curves of tested samples were used to calculate stress and strain at break, as well as yield and the elastic modulus based on 0.25% and 0.05% strain values. A 100 kN load cell and a cross-head speed of 50 mm.min⁻¹ were used. A minimum

of 6 samples were taken and the average value was calculated.

Puncture measurements were done using Zwick Roell Z2 testing machine, operating with 1 kN load cell, following the ASTM D 4833. During this test, a punch of 0.8 mm in diameter is brought into contact with the specimen (disc of 150 mm diameter) and pushed through it at a speed of 50 ± 5 mm min ⁻¹. The force-displacement curves were recorded starting with a preload of 20 N.

3.6 Melt Index (MI) test

The MI test is a qualitative method to assess molecular weight changes of polymers. It is used as an indicator of oxidation. The thermo-oxidative degradation of studied GM will induce either a crosslinking or a chain scission reaction in polymer matrix. In this study, MI of unaged and aged GM were measured following ASTM D 1238, using low to high loads (2.16, 5, 10 and 21.6 kg) for better results monitoring.

The flow rate ratio calculated by dividing high load melt index (HLMI) by low load melt index (LLMI) can be used as an indicator for the molecular weight distribution of polymer chains in the GM [10]. A higher flow rate ratio of a material indicates a broader molecular weight distribution.

4. RESULTS AND DISCUSSION

The infrared spectra of the aged geomembrane surface are reported in Figure 1. Spectra revealed the appearance of some bands in addition to the gradually increasing peak intensity upon longer exposure times. Bands were mostly found in the hydroxyl and carbonyl regions, between 3800 and 3100 cm⁻¹ and 1780-1680 cm⁻¹, respectively. Changes are observed also in the vinyl region between 1330-830 cm⁻¹.

The spectra region between 3800-3100 cm⁻¹ is assigned to the formation of oxidation products during exposure to high temperatures. The oxidation products fall into the broad groups of hydrogen-bonded "-OH" species and isolated ones. It is composed primarily of carboxylic acids (3210 cm⁻¹), hydroperoxides (3420 cm⁻¹), and alcohols (3430 cm⁻¹) for the former, and hydroperoxides (3550 cm⁻¹) and alcohols (3600 cm⁻¹) for the later [38, 39].

With extended aging, an increase in carbonyl peak intensity was observed. Products such as aldehydes (1735 cm⁻¹), ketones (1725-1718 cm⁻¹) and carboxylic acids (1760-1705 cm⁻¹) were formed during the exposure period to high temperature. Significant evolution in intensity peaks, was also observed with aging time, in the band ranged at 1330-830 cm⁻¹. The changes in this region were observed due to the accumulation of unsaturated vinylic products such as vinylidene (>C=CH₂ with maximum absorbance at around 875 cm⁻¹), vinyl (-CH=CH₂) and *trans*-vinylene groups (-CH=CH-) (with maximum absorbance at around 1026 cm⁻¹) [39].

The evaluation of carbonyl, hydroxyl, and vinyl indexes of the studied geomembrane was done. The results are shown in Figure 2. From the results, it is observed that different rates of oxidation products increased upon extended exposure time, to a thermal-oxidative environment. Vinyl index values rise was prominent before the 6th months, however, for hydroxyl index values, increasing was significant within this period. While carbonyl groups formation rate is slowing for, practically, all the studied period.

Abdelaal et al. [18] have shown a depletion of antioxidants after exposure of HDPE GM to high temperatures. They suggest that incubating HDPE geomembrane at high temperatures in air induces volatilization of antioxidants and slows down outward diffusion of antioxidants from the GMB surface. At the same time, inward diffusion of oxygen into the GMB to form free radicals and unstable hydroperoxides is expected to contribute to antioxidant depletion. The reaction rate of oxygen with the antioxidants is expected to increase with temperature, leading to a rise in the consumption of antioxidants at higher temperatures.

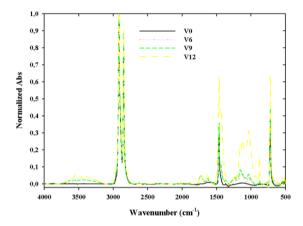


Figure 1. FTIR-ATR spectra of aged geomembrane

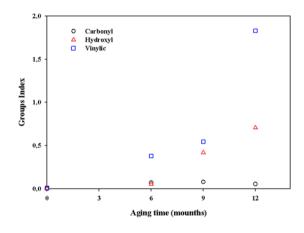


Figure 2. Carbonyl, Hydroxyl and Vinyl Index evolution

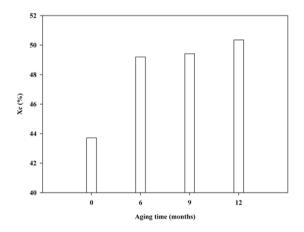


Figure 3. Polyethylene geomembrane crystallinity

With the consumption of antioxidants, chain scission reactions occur and become larger. This fact is supported by the rise in the formation of vinyl groups.

Figure 3 illustrates crystallinity index values before and

after geomembrane thermal aging. A prominent increase in crystallinity index was observed after six months of exposure. Beyond this period, crystallinity rise demonstrated lower extent until the end of exposure period. Changes in crystallinity index evidence that thermal degradation and recrystallization processes occur simultaneously with thermooxidation. Rowe et al. [23], found the same increase in crystallinity index determined by DSC measurement, upon polyethylene geomembrane ageing at 85°C in a leachate for 8.5 months. Dörner and Lang [40] clarify such an increase in crystallinity index values by the thickening of polyethylene crystals upon exposure to high temperatures. The extent of change obtained over 6 months of exposure was in agreement with that found in the work of Dörner and Lang [40] but could be considered lower due to the occurrence of the phenomenon at the surface of the HDPE geomembrane sample far from the bulk. For further exposition, chain recrystallization has reached a practically higher level at the GM surface and changes become less visible due to the estimation being limited to a shallow depth from the geomembrane surface when measured by XRD analysis. In addition to that, polymer degradation, probably, has not reached the core of the HDPE GM but extended to the surface as noticed by evaluating vinyl index.

Indeed, it is well known that loss in mechanical properties can be induced after bulk modification in the polymer structure induced by chain scission reactions, crosslinking, or the occurrence of both mechanisms. In the studied geomembrane, presence of less than 0.5% of stabilizing mixture of antioxidant prevented, in some extend, the occurrence of chain scission reactions in GM bulk but the surface was, seriously, affected as confirmed by the excess of vinyl groups' intensities in FTIR-ATR spectra.

The previous assumption is confirmed by examining tensile and PIN results obtained for the studied GM, summarized in Table 1. From these results, it is clear that almost after 12 months of thermal aging, a close variation of these properties was observed. To clearly reflect the change occurred after exposure to thermal aging, a ratio of a considered property, noted " R_p " is determined by Eq. (1):

$$R_p = \frac{P_t}{P_0} \tag{2}$$

where: P_t is the considered property value obtained after an exposure test for a period t; P_0 is the considered property value before the exposure test.

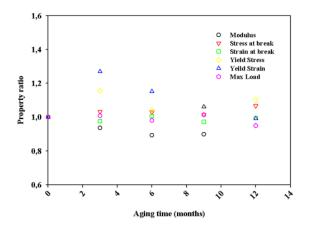


Figure 4. Evolution of tensile properties and maximum force load in puncture test

Variations in property ratios are shown in Figure 4. As shown, stress and strain at break after exposure showed similar trends to the initial value, but were completely different from those shown by the same properties at the yielding point. As seen, yielding properties are considerably affected by ageing due to the variation in additive content between bulk and surface geomembrane in addition to changes in crystalline structure. While the rigidity of aged geomembrane is affected differently, for shorter ageing periods of less than six months, a slight decrease in rigidity was observed before losing, progressively, the gain in elasticity. While for the maximum load, no clear trend was observed for the aged geomembrane and result fluctuation dominated the general trend until the end of the incubation period, where a decrease in puncture resistance was noticeable.

Table 2 summarizes results obtained from evaluating shore D hardness. As seen, for the studied period of geomembrane exposure, no effect on hardness was observed.

MI is a qualitative test but may be an indicative one for structural degradation. A test was conducted and the results are shown in Figure 5. As seen, some modification in values, more noticeable for 21.6 kg load, was observed after five months of exposure with the formation of a quasi-plateau [39], evidencing that degradation has already been done to some extent [41]. Changes in MI value are due to the occurrence of some chain scission reactions during ageing of geomembrane samples but focused more at the surface, as established by FTIR-ATR results and supported also by tensile properties at break.

Table 1. Tensile and PIN properties of aged GM

		E (MPa)	G Break (MPa)	EBreak (%)	Gy (MPa)	EY (%)	Load max (N)
	0	369 ± 27	30.6 ± 2	1525 ± 13	18 ± 2	15 ± 0.5	502 ± 11
	3	346 ± 47	31.5 ± 3	1487 ± 73	21 ± 1	20 ± 1	506 ± 18
Exposure time (months)	6	330 ± 29	31.4 ± 1	1535 ± 0.2	19 ± 1	18 ± 1	492 ± 1.4
	9	332 ± 30	31 ± 2	1482 ± 129	19 ± 2	16 ± 1	509 ± 10
	12	351 ± 56	32.6 ± 2	1516 ± 31	20 ± 1	15 ± 0.7	477 ± 5

Table 2. Shore D hardness of aged GM

Aging time (months)							
Shave D havdrage	0	3	6	9	11	12	
Shore D hardness	52 ± 1.3	53.8 ± 0.7	53.7 ± 2	53.6 ± 1.6	54.5 ± 1.2	53.4 ± 1.7	
Retention on property	1	1.03	1.03	1.03	1.04	1.02	

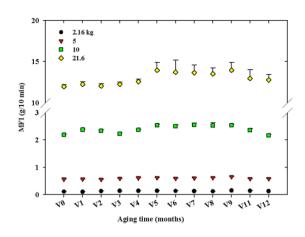


Figure 5. Evolution of melt flow index

By calculating the flow rate ratio (HLMI/LLMI), a decrease was observed from the initial value (HLMI/LLMI=106) to approximately 98 after 12 months of exposure. This is an indication of some changes in molecular weight distribution after GM exposure.

The whole result shows that when exposed to air at a temperature of 70°C, the studied HDPE geomembrane experienced a loss in the antioxidant at the surface. This, triggered a surfacic thermooxidative degaradation. At the initial stage of exposition, the degradation phenomenon does not reach the geomembrane core. Until now, no changes will be observed in mechanical properties and the geomemebrane will maintain its performance. With further exposure, the geomembrane subjected to this temperature will undergo, gradually, a diffusion of AOs from the core of GM to the surface. As discussed previously in the background, the rate of diffusion will depend on the type of AO and on the nature of environment. In practice, this geomembrane is being considered for use in waste storage facilities (whose life service should exceed 20 years) containing leachate and liquids. Hence, loss of AOs will be accelerated from the bulk and polymer degradation will take place at an early stage, which gives rise to severe changes in matrix molecular weight and crystallinity. With time, polymer brittleness takes place, and the resistance of this geomembrane against perforation (puncture) and propagation of cracks will be reduced considerably. Consequently, liquid infiltration through geomembrane will be possible. Thereby, geomembrane will lose its primary functionality, which is waterproofing.

5. CONCLUSION

The accelerated aging of PE geomembrane was provided in a climatic chamber for a period of 12 months. Changes in chemical structure, mechanical and physicochemical properties were monitored and results attest:

-The formation of an aged layer on samples with a high degree of oxidation was confirmed by an increase in carbonyl, vinyl, and hydroxyl groups after exposure to 70°C and oxygen.

-The occurrence of polyethylene matrix degradation affects GM crystallinity, which increases.

-Yielding tensile properties (stress and strain), rigidity, PIN and MI of aged geomembrane samples were affected to a lesser extent.

-Retention in tensile properties at break as well as shore D hardness values were observed over the 12 months of

accelerated aging tests at 70°C, which confirms geomembrane surface degradation more than bulk.

The result indicates that high temperature (70°C) is not recommended to the studied geomembrane, and the assessment of the accelerated aging process of PE geomembranes is important for a judicious choice of geomembrane service life conditions.

REFERENCES

- Rowe, R.K., Shoaib, M. (2018). Durability of HDPE geomembrane seams immersed in brine for three years. Journal of Geotechnical and Geoenvironmental Engineering, 144(2): 04017114-12. https://doi.org/10.1061/(ASCE)GT.1943-5606.0001817
- [2] Cen, W.J., Wang, H., Li, D.J., Wen, L.S. (2018). Largestrain tensile behaviour of geomembranes with defects using 3D digital image correlation. Geosynthetics International, 25(6): 644-655. https://doi.org/10.1680/jgein.18.00031
- [3] Vertimatti, J.C. (2015). Manual Brasileiro de Geossintéticos. In: Blucher CTG ABINT (eds), 2 ed. Sao Paulo.
- [4] Touze-Foltz, N., Xie, H., Stoltz, G. (2020). Performance issues of barrier systems for landfills: A review. Geotextiles and Geomembranes, 49(2): 475-488. https://doi.org/10.1016/j.geotexmem.2020.10.016
- [5] Lavoie, F.L, Kobelni, M., Clever Aparecido, V., Lins da Silva, J. (2020). Durability of HDPE geomembranes: An overview. Quim Nova, 43(5): 656-67. http://dx.doi.org/10.21577/0100-4042.20170540
- [6] Scheirs, J. (2009). A Guide to Polymeric Geomembranes: A Practical Approach. John Wiley & Sons.
- [7] Müller, W.W. (2007). HDPE Geomembranes in Geotechnics. Springer-Verlag, Berlin Heidelberg.
- [8] Islam, M.Z., Gross, B.A., Row, K. (2011). Degradation of Exposed LLDPE and HDPE Geomembranes: A Review. Geo-Frontiers, 1: 2065-2072. https://doi.org/10.1061/41165(397)211
- [9] Lodi, P.C., Bueno, B.D.S. (2012). Thermo-gravimetric analysis (TGA) after different exposures of High-Density Polyethylene (HDPE) and Poly Vinyl Chloride (PVC) geomembranes. Electronic Journal of Geotechnical Engineering, 17: 3339-3349.
- [10] Ewais, A.M.R., Kerry Rowe, R., Scheirs, J. (2014). Degradation behaviour of HDPE geomembranes with high and low initial high-pressure oxidative induction time. Geotextiles and Geomembranes, 42: 111-126. http://dx.doi.org/10.1016/j.geotexmem.2014.01.004
- [11] Kerry Rowe, R., Ewais, A.M.R. (2014). Antioxidant depletion from five geomembranes of same resin but of different thicknesses immersed in leachate. Geotextiles and Geomembranes, 42(5): 540-554. http://dx.doi.org/10.1016/j.geotexmem.2014.08.001
- [12] Carneiro, J.R., Almeida, P.J., Lopes, M.L. (2019). Evaluation of the resistance of a polypropylene geotextile against ultraviolet radiation. Microscopy and Microanalysis, 25: 196-202. http://dx.doi.org/10.1017/S1431927618000430
- [13] Lodi, P.C., Bueno, B.S., Vilar, O.M. (2008). Evaluation of geomembrane UV degradation using melt flow index and oxidative induction time tests. In Geosynthetics in Civil and Environmental Engineering, pp. 40-43.

http://dx.doi.org/10.1007/978-3-540-69313-0 9

[14] Lodi, P.C., Bueno, B.S., Zornberg, J.G. (2008) Considerations about weathering exposure and UV degradation of polymeric geomembranes. Minerva, 4(2): 201-205. https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.

1.1.611.9515&rep=rep1&type=pdf.
[15] Koerner, R.M., Hsuan, Y.G., Koerner, G.R. (2017). Lifetime predictions of exposed geotextiles and geomembranes. Geosynthetics International, 24: 198-212. http://dx.doi.org/10.1680/jgein.16.00026

- [16] Rollin, A. (1999). Comportement à long terme des géotextiles et des géomembranes. In: EAT I. Géosynthétiques - Matériaux et Applications, pp. 77-87. http://www.set-revue.fr/sites/default/files/articleseat/pdf/1999-PUB00007911.pdf.
- [17] Lavoie, F.L., Bueno, B.D.S., Lodi, P.C. (2012). Influence of the degradation on the stress cracking values of High-Density Polyethylene (HDPE) geomembranes after different exposures. Electronic Journal of Geotechnical Engineering, 17: 3097-104.
- [18] Abdelaal, F., Rowe, R. (2014). Effect of high temperatures on antioxidant depletion from different HDPE geomembranes. Geotextiles and Geomembranes, 42: 1-18. http://dx.doi.org/10.1016/j.geotexmem.2014.05.002
- [19] Abdelaal, F., Rowe, R., Hsuan, Y., Awad, R. (2015).
 Effect of high temperatures on the physical and mechanical properties of HDPE geomembranes in air. Geosynthetics International, 22(3): 207-224. http://dx.doi.org/10.1680/gein.15.00006
- [20] Rowe, R., Abdelaal, F. (2016). Antioxidant depletion in HDPE geomembrane with HALS in low pH heap leach environment. Canadian Geotechnical Journal, 53(10): 1-58. http://dx.doi.org/ 10.1139/cgj-2016-0026
- [21] Pons, C. (2012). Durability of HDPE geomembranes used in basal liner systems of municipal solid waste landfills. Ph.D. dissertation. Ecole Doctorale: Sciences, Ingenierie et Environnement, Université Paris-Est, Paris, France.
- [22] Pons, C., Farcas, F., Kallel, D., Richaud, E., Fayolle, B. (213). Influence du vieillissement sur la perte des antioxydants de films et de géomembranes en PE dans les ISDND. 9èmes Rencontres Géosynthétiques, Dijon, pp. 421-429.
- [23] Rowe, R.K., ASCE, F., Islam, M.Z., ASCE, M., Brachman, R.W.I., Arnepalli, D.N., Ragab Ewais, A. (2010). Antioxidant depletion from a high-density polyethylene geomembrane under simulated landfill conditions. Journal of Geotechnical and Geoenvironmental Engineering, 136(7): 930-939. http://dx.doi.org/10.1061/ASCEGT.1943-5606.0000302
- [24] Aminabhavi, T.M., Naik, H.G. (1999) Sorption /desorption, diffusion, permeation and swelling of highdensity polyethylene geomembrane in the presence of hazardous organic liquids. Journal of Hazardous Materials B, 64(3): 251-62. https://doi.org/10.1016/S0304-3894(98)00183-6
- [25] Gómez, J. (2020). Geomembrane stress cracking resistance depending on the polymer used. Proceeding of the 3rd GeoMEast International Congress and Exhibition, Cairo, Egypt, pp. 62-67. https://doi.org/10.1007/978-3-030-34242-5_6
- [26] Ewais, A.M.R., Rowe, R.K., Scheirs, J. (2014)

Degradation behaviour of HDPE geomembranes with high and low initial high-pressure oxidative induction time. Geotextiles and Geomembranes, 42: 111-26. http://dx.doi.org/10.1016/j.geotexmem.2014.01.004

- [27] Mills, A., Beaumier, D. (2017). Long-term performance of HDPE geomembranes exposed to high service temperature. Geotechnical Frontiers 2017 Conference, Orlando, Florida, pp. 22-31.
- [28] Gómez, J. (2019). Geomembrane stress cracking resistance depending on the polymer Used. 3rd GeoM East International Congress and Exhibition, Cairo, Egypt, pp. 62-67.
- [29] Abdelaal, F.M.B.M. (2013). Durability of HDPE geomembranes for municipal solid waste landfill applications. Ph.D dissertation, Department of Civil Engineering, Queen's University, Kingston, Ontario, Canada.
- [30] Vasile, C., Pascu, M. (2005). Practical Guide to Polyethylene. iSmithers Rapra Publishing, UK.
- [31] Zerbi, G., Siesler, H.W., Noda, I., Tasumi, M., Krimm, S. (2008). Modern Polymer Spectroscopy. WILEY-VCH Verlag GmbH.
- [32] Jabarin, S.A., Lofgren, E.A. (1994). Photooxidative effects on properties and structure of high-density polyethylene. Journal of Applied Polymer Science, 53(4): 411-423. https://doi.org/10.1002/app.1994.070530404
- [33] Tidjani, A. (2000). Comparison of formation of oxidation products during photo-oxidation of linear low-density polyethylene under different natural and accelerated weathering conditions. Polymer Degradation and Stability, 68(3): 465-469. https://doi.org/10.1016/S0141-3910(00)00039-2
- [34] Gardette, M., Perthue, A., Gardette, J-L., Janecska, T., Földes, E., Pukánszky, B., Therias, S. (2013). Photo- and thermal-oxidation of polyethylene: Comparison of mechanisms and influence of unsaturation content. Polymer Degradation and Stability, 98(11): 2383-90. https://doi.org/10.1016/j.polymdegradstab.2013.07.017
- [35] Carvalho, M.E.S., Cruz-Pinto, J.J.C. (1992). The kinetics of photo-oxidation of low-density polyethylene films. Polymer Engineering and Science, 32(8): 567-72. https://doi.org/10.1002/pen.760320808
- [36] Cruz-Pinto, J.J.C., Carvalho, M.E.S., Ferreira, J.F.A. (1994). The kinetics and mechanism of polyethylene photo-oxidation. Die Angewandte Makromolekulare Chemie, 216(1): 113-133. https://doi.org/10.1002/apmc.1994.052160108
- [37] Salvalaggio, M., Bagatin, R., Fornaroli, M., Fanutti, S., Palmery, S., Battistel, E. (2006). Multi-component analysis of low-density polyethylene oxidative degradation. Polymer Degradation and Stability, 91(11): 2775-85.

https://doi.org/10.1016/j.polymdegradstab.2006.03.024

- [38] Lacoste, D.J.C., Falicki, S., Wiles, D.M. (1991).
 Polyethylene hydroperoxide decomposition products.
 Polymer Degradation and Stability, 34(1-3): 309-323.
 https://doi.org/10.1016/0141-3910(91)90125-B
- [39] Lacoste, J., Carlsson, D.J. (1992). Gamma, photo, and thermally initiated oxidation of linear low-density polyethylene: A quantitative comparison of oxidation products. Journal of Polymer Science/ Part A Polymer Chemistry, 30(3): 493-500. https://doi.org/10.1002/pola.1992.080300316
- [40] Dörner, G., Lang, R.W. (1998). Influence of various

stabilizer systems on the ageing behavior of PE–MD—II. Ageing of pipe specimens in air and water at elevated temperatures. Polymer Degradation and Stability, 62(3): 431-440. https://doi.org/10.1016/S0141-3910(98)00049-4

[41] Lodi, P., Bueno, B., Hamada, J., Oliveira, E., Da Silva,

G. (2013). Evaluation of mechanical and thermal properties after chemical degradation of PVC and HDPE geomembranes. Electronic Journal of Geotechnical Engineering, 18: 1227-1236. https://citeseerx.ist.psu.edu/viewdoc/download?doi=10. 1.1.1084.7405&rep=rep1&type=pdf.