Geosynthetics: Leading the Way to a Resilient Planet – Biondi et al (eds)

Effect of UV radiation exposure on HDPE geomembrane properties

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ABSTRACT: This study investigates the resulting changes in the properties of a high-density polyethylene geomembrane (HDPE GMB) subjected to an accelerated UV (ultraviolet) ageing test. A commercially available GMB having a nominal thickness of 1.5 mm was exposed to UV radiation for varying durations for three years using an Atlas make UV weatherometer. Properties including thickness, density, melt flow index, tensile behaviour, oxidative induction time (OIT), crystallinity and microstructural changes using Fourier transform infrared (FTIR) spectroscopy were studied. The results showed that the thickness of GMB was not affected by UV radiation. However, density and melt flow index of the GMB showed a significant variation. At the end of 26095 hours of exposure, OIT was reduced by more than half the value of the initial OIT. The degradation by cross-linking was verified from FTIR spectra which showed an increased crystalline content against the ageing time.

1 INTRODUCTION

The high-density polyethylene geomembranes (HDPE GMBs) have become an integral part of the modern composite liner of engineered landfills. It has been the material of choice for most landfill liners because of its good physical, mechanical, and endurance properties (Rowe *et al*. 2010). In general, the durability of GMB mainly depends on the ageing rate of the liner material. Among all, the ageing of GMB is primarily governed by the exposure conditions pervading its service life. In landfill applications, the GMB may be exposed to different exposure conditions such as ultraviolet (UV) radiation, thermal, oxidative, and chemical exposures (Lavoie *et al*. 2020).

When the GMB is used as a basal and cover liner of a landfill, it may be exposed to UV radiation for short-term and long-term durations, respectively. Improper liner installation methods, delay in protecting GMB liner, and the formation of a whale/hippos may result in the exposure of GMB to UV radiation even for years (Anjana *et al*. 2023). It can trigger photodegradation and imparts discoloration, brittleness, and stress cracking in the liner material (Arnepalli & Rejoice 2012). This leads to damage to GMB and causes a reduction in the engineering properties of the material. The prolonged exposure to UV radiation may lead to the progressive degradation of polymeric liner material and alter its properties. These changes impair the geosynthetic material and eventually affect the service life of the GMB (Hsuan & Koerner 1995).

Ageing due to UV exposure is known to affect the physical and mechanical properties of the GMB (Arnepalli & Rejoice 2013a, b). Therefore, it is paramount to understand the behaviour of GMB under UV exposure conditions to ascertain its long-term performance in adequately providing the containment function. Given this, the present study aims to evaluate the effect of UV ageing on the depletion of properties of HDPE GMB subjected to

 DOI: 10.1201/9781003386889-46

26095 hours (approximately three years) of exposure to UV radiation using a UV weatherometer in the laboratory. The present study focuses on the variation in the physical, mechanical, and endurance attributes of the GMB, including thickness, density, melt flow index, tensile behaviour, oxidative induction time (OIT), crystallinity, and microstructural changes examined using Fourier transform infrared (FTIR) spectroscopy.

2 MATERIALS AND METHODS

2.1 *Geomembranes*

A black smooth 1.5 mm-thick HDPE GMB was used in this study. Table 1 shows the featured properties of the selected GMB (Anjana *et al*. 2023).

Table 1. Properties of GMB used in this study.

Properties	Reference method	Values (Unit)
Thickness	ASTM D5199	1.51 ± 0.01 (mm)
Density	-	0.961 ± 0.001 (g / cm^3)
Melt flow rate	ASTM D1238	0.145 ± 0.001 (g / 10 min)
Oxidative induction time	ASTM D3895	132 (min)
Crystallinity	ASTM E794	49 (%)

2.2 *Accelerated UV ageing test*

The GMB specimens were exposed to UV radiation in the laboratory using an Atlas make UV Weatherometer. The samples were exposed to fluorescent UV light using UVA-340 lamps under controlled environmental conditions, according to ASTM G154. The exposure cycles of eight-hour UV radiation at 0.89 W / m^2 and four-hour condensation were followed. To study the effect of long-term UV exposure on GMB properties, the samples were subjected to 26095 hours (nearly three years) of accelerated ageing. The GMB samples were retrieved at various time intervals of UV ageing and tested for their desired properties.

2.3 *Thickness*

The thickness of the GMB was determined using a thickness measurement device by following the guidelines presented in ASTM D5199. The thickness was measured after applying a pressure of 20 kPa for 5 seconds against the specimen by means of a presser foot. The value was recorded to the nearest 0.02 mm, and the average thickness of ten samples was reported.

2.4 *Density*

The helium gas pycnometer (Quantochrome, USA) was used to measure the density of the GMB. The pycnometer measures the solid volume of the sample by displacing it with helium gas. From the known weight and the solid volume of the sample, the density of the GMB was determined.

2.5 *Melt flow index*

A fully automated melt flow indexer was used to perform the test according to ASTM D1238. As per the codal provisions, procedure-A was used to determine the melt flow index of a thermoplastic material. The molten polymer of the GMB was extruded through an orifice under an applied load of 2.16 kg and 190 °C. The mass of molten polymer extruded in 10 minutes (in grams of material / 10 min) is expressed as the melt flow index.

2.6 *Oxidative Induction Time (OIT)*

The standard OIT test was carried out according to ASTM D3895 using a Netzsch DSC 200 differential scanning calorimeter (DSC). The known sample weight was initially heated to

200 °C from room temperature at 10 °C / min in an inert nitrogen atmosphere. The sample was then maintained at the isothermal condition for 5 minutes, following which oxygen was introduced at 35 kPa pressure. The test was terminated after an oxidative reaction peak was observed. The OIT was calculated as the time elapsed between introducing oxygen and the arrival of the oxidative reaction peak.

2.7 *Tensile strength test*

A tensile testing machine (ZwickRoell, Germany) equipped with pincer grips and a video extensometer was employed to assess the tensile properties of the GMB as per ASTM D6693. The dog bone specimens were cut from the GMB using a die cutter and tested at a strain rate of 50 mm / min. The variations in tensile properties such as yield strength, break strength, yield strain and break strain for various UV ageing durations were determined.

2.8 *Crystallinity of polymer*

The crystallinity of the polymer was determined as per ASTM E794 using a Netzsch DSC 200 differential scanning calorimeter (DSC). A known sample weight was heated to 200 °C at 10 °C / min in an inert nitrogen atmosphere to obtain the crystallization melt curve. The crystallinity of the polymer is defined as the ratio of heat of fusion of GMB specimen and the heat of fusion of 100% crystalline HDPE polymer. The heat of fusion of 100% crystalline HDPE polymer, i.e., 293 J / g (Brandrup *et al.* 1999), was used to calculate the percent crystallinity of the samples.

2.9 *Fourier transform infrared (FTIR) spectroscopy*

The FTIR analysis was performed using a Perkin Elmer Spectrum 100 in the spectral range from 4000 cm^{-1} to 400 cm^{-1}, 128 scans at 4 cm^{-1} resolution. The test was conducted on virgin and aged GMBs to study the surface-level molecular changes owing to UV radiation. Further, the spectrum was obtained on the UV irradiated side of the aged GMB, labelled as the exposed side, and the other side on which UV light was not exposed, labelled as the unexposed side.

3 RESULT AND DISCUSSIONS

3.1 *Thickness, density, melt flow index, oxidative induction time, and crystallinity*

The thickness of a GMB is one of the important properties since it significantly affects the service life of a GMB (Rowe *et al.* 2010). The thickness of the GMB was measured at various durations of UV exposure. The results indicated that the thickness of the aged GMB was invariable for the complete duration of UV testing. There was no considerable change in the GMB thickness with UV ageing time. This implies that exposure to UV radiation does not affect or have an insignificant effect on the GMB thickness.

A notable change was observed in the density of GMB upon UV exposure (Table 2). When the ageing duration increased, the density of GMB decreased. For instance, the density of GMB reduced from 0.961 to 0.945 at the end of 11200 hours of exposure. This decrease in density reflects the localized change in the crystallinity or extraction of additives or absorption of solvents (Anjana *et al.* 2023).

The melt flow index measures the rate of extrusion of molten GMB resin. It is a useful measure for assessing the change in molecular weight of the polymer (Park *et al.* 2013). The degradation caused by cross-linking results in an increase in molecular weight, and chain scission causes a decrease in molecular weight (Hsuan & Koerner 1995). Table 2 shows the variation of the melt flow index with respect to ageing time. The melt flow index reduced for up to 11200 hours of ageing time and then increased. These characteristic changes denote the degradation of polymer caused by both cross-linking and chain scission reactions due to UV exposure. Thus, it can be inferred that UV exposure can deplete the GMB properties by one or more of the degradative reactions depending on the extent of exposure time (Guillet 1972; Anjana *et al.* 2023).

Table 2. Variation of GMB properties at various UV ageing durations*.

Ageing time hours	Density g / cm^3	Melt flow index g / 10 minutes	Oxidative induction time minutes	Crystallinity %
0	0.961	0.145	132	49
90	0.956	0.141	132	46
1000	0.95	0.139	111	52
3000	0.949	0.138	94.8	65
9000	0.95	0.132	80	54
11200	0.9447	0.130	–	51
13803	0.9577	0.137	65	51
26095	0.9533	0.138	55	56

*From (Anjana *et al.* 2023)

Oxidative induction time (OIT) indicates the amount of antioxidants in the GMB. From Table 2, OIT was found to reduce with the increase in UV ageing time. At the end of 26095 hours of UV exposure, the OIT was reduced by a factor of 0.42 from its initial value. The relationship between OIT and ageing time was linear, and the depletion of antioxidants followed a first-order exponential decay. Hence, the above trend of reducing OIT against ageing time confirms that antioxidant depletion is proportional to the level of deterioration caused due to UV exposure.

The role of crystallinity is essential in explaining the GMB behaviour upon UV exposure as it affects mechanical and chemical resistance. When the crystallinity of GMB is high, its stiffness and chemical resistance would be high (Scheirs 2009). The crystallinity determined using DSC denotes the overall crystallinity in the bulk of a material. It is clear from Table 2 that UV ageing has resulted in an overall increase in the crystallinity of the polymer. The crystallinity increase with the increasing ageing duration can be attributed to the post-crystallization of polymer molecules due to UV exposure (Anjana *et al.* 2023). This observation is similar to the melt flow index test results, where the cross-linking reactions led to an increased crystallinity of polymeric GMB.

3.2 *Tensile properties*

Table 3 shows the tensile properties of GMB in the machine direction as a function of UV exposure. The GMB did not exhibit a distinct trend in the increase or decrease of the tensile properties. However, the overall increase in the tensile properties can be attributed to the crystallinity changes in the polymer due to UV ageing. The increase in tensile strength and the decrease in yield strain indicates the occurrence of cross-linking and oxidative degradations (Anjana *et al.* 2023). Similar behaviour was noted for cross-machine direction as well.

Table 3. Variation of tensile properties with UV exposure*.

Ageing time hours	Yield strength kN / m	Break strength kN / m	Yield strain %	Break strain %
0	28.18	26.33	18	542
90	27.7	32.15	18	669
1000	27.1	30.1	17	649
3000	28	36	19	753
9000	29.98	44.35	16	913
11200	31.55	48.14	17	800
13803	32.09	37.59	14	869
26095	32.98	40.25	15	889

*From (Anjana *et al.* 2023)

3.3 *Fourier transform infrared (FTIR) spectroscopy*

FTIR analysis was performed on virgin and aged GMB in view of studying the molecular changes due to UV ageing. The methylene functional group peaks are the prominent features of HDPE GMB and are found at wave numbers 2915, 2848, 1472, 1462, 729 and 719 cm^{-1}. The peaks at 1462 and 1472 cm^{-1} correspond to the methylene deformation vibrations in the amorphous and crystalline regions, respectively (Anjana *et al.* 2023). Figure 1 shows the spectra of virgin and aged GMBs of exposed sides.

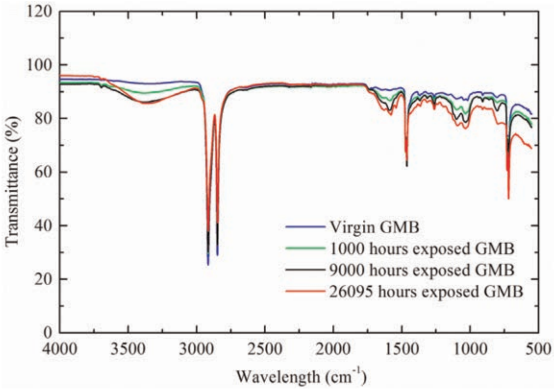

Figure 1. FTIR spectra of virgin and aged GMBs at varying UV ageing durations.

With the increasing duration of UV ageing, the peak corresponding to crystalline content was increased and the amorphous content was decreased. The variation of peak intensity in this region reflects the crystallinity increase in the polymer due to cross-linking reactions. This finding supports the results obtained in other tests of GMB properties. Thus, quantifying crystalline content in polymer becomes essential to validate those observations. Hence, the method described by Zerbi *et al.* (1989) was used to determine the crystalline content as per Equation 1 below:

$$Crystalline\ content = \left\{100 - \frac{[1-(I_a/I_b)]/1.233}{1+(I_a/I_b)}\right\} \times 100 \quad (1)$$

where I_a and I_b denote the peak intensities of bands at 1472 and 1462 cm^{-1}, respectively. The crystalline content determined using Equation 1 represents the surface-level modification. The spectra were collected on both exposed and unexposed sides of aged GMB and their corresponding crystalline content was calculated (Table 4). The values were found to be higher for the aged GMB relative to the virgin GMB. Further, the crystalline content on the exposed side was greater than that of the unexposed side in the aged GMB. There was a significant difference in the crystalline content of exposed and unexposed sides beyond 1000 hours of ageing. These results imply that with the increasing duration of UV ageing, there is an increase in the crystalline content. This shows the evidence for cross-linking reactions, as the same was also witnessed in the other tests (Anjana *et al.* 2023).

Table 4. Variation of crystalline content with UV exposure*.

Crystalline content (%)	Ageing time (hours)									
	0	48	90	400	1000	3000	9000	11200	13803	26095
Virgin GMB	88	88	88	88	88	88	88	88	88	88
Exposed side	90.05	91.03	91.91	91.66	91.98	93.41	94.4	95.48	95.55	95.8
Unexposed side	88.62	90.4	91.74	91.28	91.89	91.45	91.97	91.71	90.95	92.4

*From (Anjana *et al.* 2023)

4 CONCLUSIONS

The study investigated the effect of accelerated UV ageing on the properties of HDPE GMB exposed to UV radiation for three years. The variation of GMB properties such as thickness, density, melt flow index, tensile behaviour, OIT, crystallinity and FTIR spectra with varying exposure durations have been studied in detail. The results showed an inappreciable variation in the thickness of GMB with UV ageing time. However, the effect of UV degradation was considerable, as evidenced by the changes in density, melt index and tensile behaviour of GMB. The reduced density, increased tensile properties and reduced melt index values dictate the occurrence of cross-linking reactions. The standard OIT decreased significantly as the ageing duration increased. This can be attributed to antioxidant depletion owing to oxidative degradation. The FTIR spectra showed that the crystalline content measured at the exposed GMB surface increased with the increasing UV ageing duration. This suggests that due to UV ageing, the GMB is more prone to surface-level damage and the evidence for cross-linking reactions depicts superficial degradation. The reported findings are confined only to the tested exposure conditions, and based on the above findings, it can be concluded that the depletion of GMB properties depends on the severity and extent of UV ageing.

REFERENCES

Anjana, R.K., Keerthana, S. & Arnepalli, D.N. 2023. Coupled Effect of UV Ageing and Temperature on the Diffusive Transport of Aqueous, Vapour and Gaseous Organic Contaminants Through HDPE Geomembrane. *Geotextiles and Geomembranes* 51(2): 316–329.

Arnepalli, D.N. & Rejoice, A.A. 2012. Durability and Long-Term Performance of High Density Polyethylene Geomembrane. *Proceedings of ASCE Conference on Geosynthetic Lining Solution and Related Issues, 25 February*. Bangalore.

Arnepalli, D.N. & Rejoice, A.A. 2013a. Evaluation of Geosynthetic Liner Long-Term Performance Under Landfill Conditions. *Proceedings of Geopractices*, Hyderabad, India.

Arnepalli, D.N. & Rejoice, A.A. 2013b. Service Life and Long-Term Performance of Geosynthetic Liners Under Simulated Landfill Conditions. *Proceedings of Geosynthetics India - 2013*, New Delhi, India.

ASTM D1238 2004. Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer. ASTM International, West Conshohocken, Philadelphia, USA.

ASTM D3895 2014. Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry. ASTM International, West Conshohocken, Philadelphia, USA.

ASTM D5199 2006. Standard Test Method for Measuring the Nominal Thickness of Geosynthetics. ASTM International, West Conshohocken, Philadelphia, USA.

ASTM D6693 2001. Standard Test Method for Determining Tensile Properties of Non-reinforced Polyethylene and Non-reinforced Flexible Polypropylene Geomembrane. ASTM International, West Conshohocken, Philadelphia, USA.

ASTM E794 2012. Standard Test Method for Melting and Crystallization Temperatures by Thermal Analysis. ASTM International, West Conshohocken, Philadelphia, USA.

ASTM G154 2016. Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Non-Metallic Materials. ASTM International, West Conshohocken, Philadelphia, USA.

Brandrup, J., Immergut, E.H. & Grulke, E.A. 1999. *Polymer Handbook*. John Wiley & Sons.

Guillet, J.E. 1972. Fundamental Processes in the UV Degradation and Stabilization of Polymers. *Pure Applied Chemistry* 1(30): 135–144.

Hsuan, Y.G. & Koerner, R.M. 1995. Long Term Durability of HDPE Geomembrane: part i - Depletion of Antioxidant. *GRI Report* 16: 35.

Lavoie, F.L., Kobelnik, M., Valentin, C.A. & Silva, J.L.D. 2020. Durability of HDPE Geomembranes: an Overview. *Química Nova* 43(5): 656–667.

Park, Y.M., Khan, B.A. & Jeon, H.Y. 2013. Analysis of Degradation Behaviors of Geomembrane by Accelerated Test under UV Exposure Conditions. *Polymer Korea* 37(1): 5–14.

Rowe, R.K., Islam, M.Z. & Hsuan, Y.G. 2010. Effects of Thickness on the Aging of HDPE Geomembranes. *Journal of Geotechnical and Geoenvironmental Engineering* 136(2): 299–309.

Scheirs, J. 2009. *A Guide to Polymeric Geomembrane: A Practical Approach*. John Wiley & Sons.

Zerbi, G., Gallino, G., Del, F.N. & Baini, L. 1989. Structural Depth Profiling in Polyethylene by Multiple Internal Reflection Infra-red Spectroscopy. *Polymer* 30(12): 2324–2327.