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Abstract

This study investigates the degradation of textured High-Density Polyethene (HDPE) geomembranes (GMs) subjected to natural weathering for 8.5 to 10.5 years. The GMs, denoted as GM-W/B (white and black), GM-G (green) and GM-B (black), had a nominal thickness of 1.00 mm and were manufactured using a flat die process with texture on both surfaces. Standard Oxidation Induction Time (Std-OIT) tests and Thermogravimetric Analysis (TG/DTG) were performed to assess the antioxidant depletion and thermal decomposition. Additionally, degradation due to Ultraviolet (UV) radiation and environmental agents was assessed through retained physical and mechanical properties, including the Melt Flow Index (MFI) measured under various loading conditions. Antioxidant depletion and TG/DTG analyses indicated that environmental exposure compromised the thermal stability of these GMs. Among the tested GMs, GM-W/B exhibited the greatest reduction in both Std-OIT and MFI, followed by GM-G and GM-B, suggesting a direct correlation between these properties. While GM-B appeared to be still in the antioxidant depletion stage (Stage I), GM-W/B and GM-G showed signs of degradation beyond Stage I. This study provides insights into the degradation of textured HDPE GMs in the face of weathering exposure effects and the durability of colored HDPE GMs.

Keywords: geosynthetics; geomembranes; durability; textured HDPE geomembranes; colored HDPE geomembranes

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Introduction

To enhance the resistance of polyethene GMs to UV radiation, 2-3% of carbon black is added to their formulation (Scheirs 2009). This practice is applied to both High-Density Polyethene (HDPE) and Linear Low-Density Polyethene (LLDPE) GMs following the GRI-GM13 (GRI 2024a) and GRI-GM17 (GRI 2024b) specifications, respectively. Carbon black is widely recognized as the best UV radiation stabilizer due to its long history of effectiveness under solar exposure in various industries (Donnet 2018). The black coloration of HDPE GMs, resulting from the addition of carbon black, absorbs the majority of solar energy incidents on their exposed surface. This leads to an increase in surface temperature, which can accelerate thermo-oxidative degradation (Scheirs, 2009). This temperature rise can cause problems such as increased wrinkle formation, which can lead to Stress Cracking (SCR) and heightened desiccation of the subgrade beneath the GM (Basnett and Bruner 1993; Cadwallader *et al*. 1993; Scheirs 2009; Hornsey *et al.* 2010).

GMs can be manufactured in various colors depending on the specific needs. For example, green HDPE GMs may be used for landscape integration in landfill covers, blue GMs for ornamental tanks, sand-colored GMs for artificial beaches, and white GMs in photovoltaic parks, among other applications. Different stabilizers, other than carbon black, are required to protect the GM from UV radiation to achieve this. One alternative is Hindered Amine Stabilizers (HALS), which can also provide thermo-oxidative protection (Scheirs 2009). Manufacturers typically use a combination of two or more types of antioxidants and stabilizers that operate across different temperature ranges to protect the GM throughout various phases, from production to its service

life. However, the exact stabilizer package used in a given GM's formulation is proprietary

(Mueller and Jakob 2003; Scheirs 2009; Rowe *et al*. 2020).

In the literature, there are few records of projects using colored GMs. For example, Eichelberger

et al. (2013) describe the application of a white GM with a conductive layer in a reconstruction

project for cooling water reservoirs and evaporation ponds at a nuclear generation station.

Ramsey (2016) details using a green GM in landfill covers, where the material's performance

was monitored over the years. Amtsberg *et al.* (2024) mention using a white GM in caustic

bladder storage facilities at an alumina refinery. Among colored GMs, the white-faced HDPE

GM has been the most utilized in various applications, and its performance has been studied in

different research works (e.g., Cadwallader *et al.* 1993; Koerner *et al.* 1993; Pelte *et al.* 1994;

Dolez *et al.* 2017; Rentz *et al.* 2017; Rowe *et al.* 2020; Zafari *et al.* 2023a; Zafari *et al.* 2023b;

Amtsberg *et al.* 2024). The white layer is typically manufactured by dispersing titanium oxide

pigments into the polymer matrix, usually in a coextruded multilayer (three-layer) GM. The

white layer of the GM generally has a thickness of approximately 0.13 mm (Cadwallader *et al.*

1993; Koerner *et al.* 1993; Scheirs 2009).

Many studies have compared differences in surface temperature between white-coated and black

GMs' (e.g. Cadwallader *et al.* 1993; Koerner *et al*. 1993; Pelte *et al.* 1994; Koerner and Koerner

1995; Dolez *et al.* 2017; Rentz *et al.* 2017). Regarding durability, previous investigators have

examined the effects of UV radiation on HDPE GMs, primarily focusing on smooth black

HDPE. However, recent studies have explored the durability of colored and white smooth HDPE

GMs. Morsy et al. (2020) investigated the impact of chlorinated water on HALS, reporting a

retention of 1.24% for Std-OIT and 29.85% for HP-OIT in a 1.5 mm white smooth HDPE

geomembrane after 35 months of incubation in chlorinated water at 85°C. Ramsey and Maskal

(2023) evaluated GMs, including green and white smooth samples exhumed from various

applications, as well as samples of GMs described as 'stored in a warehouse, aged but without

UV/solar exposure,' which were subsequently subjected to oven aging. The results demonstrated

excellent retention of initial HP-OIT values across different oven aging durations. The only GM

for which an initial value comparison was possible was a 1.5 mm green GM, which retained

25.76% of the HP-OIT after 21 years of exposure in a landfill. Amtsberg *et al.* (2024) conducted

UV exposure tests in the laboratory on white smooth HDPE GMs, reporting HP-OIT retention

25% higher than the minimum required by GRI-GM13 specifications (GRI 2024a). This suggests

a high concentration of HALS and other additives in these GMs. Their findings also indicated

superior durability of white-surfaced GMs when exposed to UV radiation and aggressive liquids

compared to black GMs.

The durability of textured white-coated HDPE GMs under UV exposure (e.g. Lodi 2003) and

immersed in aggressive liquids has also been addressed (e.g. Rowe *et al.* 2020; Abdelaal *et al.*

2023; Zafari *et al.* 2023a, 2023b, 2024). However, few studies have assessed the durability of

HDPE GMs exposed to weathering conditions without exhuming the samples during service (e.g.

Reis *et al.* 2017). In addition, most of the aforementioned research has focused on analyzing the

durability of HDPE GMs manufactured using the round-die or blown film process. Studies on

colored textured HDPE GMs produced by the flat-die process have been limited (e.g., Lodi

2003), representing a significant knowledge gap regarding this type of liner, since the different manufacturing processes require resins with distinct characteristics.

This study explores the degradation of colored textured HDPE GMs (white and black, both sides green and black), 1.00 mm thick, manufactured using the flat-die process and exposed to weathering for 8.5 to 10.5 years. The analysis focuses exclusively on the textured region, which covers almost the entire liner surface. This exposure occurred in a region of Brazil with the highest incidence of solar radiation. Degradation was assessed based on the retained physical and mechanical properties after exposure and by thermal tests, including Std-OIT and TG/DTG. The objectives of this study were: (1) to analyze the degradation of textured HDPE GMs due to weathering, (2) to determine the oxidation stage of each sample after exposure, and (3) to assess the durability of colored HDPE GMs in comparison to traditional black ones.

2. Materials and methods

2.1 GMs

Three GM samples were manufactured using the flat-die extrusion process and textured on both sides, with a nominal thickness of 1.00 mm and commercialized as HDPE GM. The GMs were designated as follows: GM-W/B (white and black), GM-G (green) and GM-B (black). Table 1 shows the initial properties of the GMs. Carbon black properties, both in terms of content and dispersion, do not apply to the GM-G sample, as it is green on both sides and does not contain carbon black in its composition.

2.2 Test procedures

The GM samples (3 pieces of 300 mm in length by 200 mm in width for each sample) were

exposed to environmental agents on a weathering panel in Brazil (29°52'39.8" S; 51°11'3.1" W).

The panel was constructed with a steel frame and a wooden top, inclined at 29º, corresponding to

the latitude of the exposure site, to maximize the severity of UV radiation exposure. Figure 1

illustrates the arrangement of the samples on the panel, including a detailed cross-sectional view

of each of the three samples. The GMs were exposed to UV radiation and other weathering

agents for varying periods. Each sample was placed on the weathering panel after manufacturing

and was removed in August 2022. The GM-B sample was manufactured in February 2014 and

was exposed for around 8.5 years. The GM-W/B sample was manufactured in August 2013, with

the white side exposed, resulting in an approximate exposure period of 9.0 years. The GM-G

sample, produced in February 2012, had an exposure period of approximately 10.5 years.

Periodic sampling throughout the exposure period was not feasible due to limited access to

testing facilities. Additionally, the primary focus of the study was to maximize the exposure

duration of the samples to observe long-term degradation effects. The samples were eventually

removed because the panel needed dismantling, and the space was repurposed for other uses.

Direct temperature measurements on the GMs were unavailable for this study. However, the

surface temperatures of the GMs would vary depending on their color surface. Black GMs, for

instance, are likely to exhibit higher temperatures due to their ability to absorb a broader

spectrum of UV radiation, converting it into heat more efficiently than lighter-colored surfaces,

such as those with white or green faces. This increased heat absorption in black GMs may lead to

notable differences in their thermal behavior and degradation rates compared to GMs with

lighter-colored surfaces.

2.3 Environmental conditions

The weathering tests were conducted in the state of Rio Grande do Sul, Brazil. This region

experiences the highest monthly irradiation, according to the latest edition of the Brazilian Solar

Energy Atlas published by INPE (Martins *et al.* 2017). Meteorological data were obtained from

the nearest meteorological station, located 19.7 km from the weathering panel, provided by the

Brazilian National Meteorological Institute - INMET (30°03'13" S; 51°10'28.9" W). UV

radiation was estimated to account for 7.8% of the total global radiation, based on the ISO 13434

standard (ISO 2020). The climatic characteristics for each exposure period are summarized in

Table 2.

2.4 GMs' antioxidant depletion

Oxidative degradation, the primary degradation mechanism in polyethylene GMs, is

conceptually divided into three stages. Stage I involves the loss or depletion of antioxidants,

which can be identified through Std-OIT and HP-OIT tests. Stage II marks the initiation of

polymer degradation, but without measurable changes in physical (e.g., MFI) or mechanical

properties (e.g., tensile strength, stress-crack resistance or SCR). Stage III is marked by a drastic

decrease in these properties, until nominal failure of the GM material is reached. Nominal failure

is typically defined as the time at which a mechanical property reaches 50% of the unaged value,

or the time at which the SCR affected by physical aging reaches 50% of the SCR equilibrium value (Rowe et al. 2019).

The depletion of antioxidants (Stage I) is often described by an exponential decay model (e.g., Hsuan and Koerner 1998; Sangam and Rowe 2002, Rowe *et al.* 2009, 2020; Rowe and Ewais 2014; Rowe and Abdelaal 2016; e Silva *et al.* 2024). According to Rowe *et al.* (2020), the end of Stage I in the oxidation process is considered to have occurred when OIT values decrease to a residual level that no longer changes (OIT_R). If the OIT value is small or negligible (e.g., < 2% of the initial Std-OIT), the depletion is modeled using the first-order model presented in Equation 1. Studies on samples exposed to climatological conditions (e.g., Rowe and Ewais 2014) have also employed this first-order equation to estimate the antioxidant depletion rate based on Std-OIT and HP-OIT measurements.

$$OIT_t = OIT_0 e^{-st} \qquad\qquad\qquad (1)$$

Where OIT_t (minutes) is the OIT at the time of interest t (minutes), OIT_0 (minutes) is the initial OIT (minutes), s is the antioxidants depletion rate (months^{-1}), and t is the exposition time (months).

2.5 Evaluation of physical and mechanical Properties

The physical properties evaluated included thickness (ASTM D5994), density (ASTM D792) and carbon black content (ASTM D4218). Asperity height was not considered in the analysis, as its variation was not significant. Another important physical property used to evaluate the durability of HDPE GMs is the MFI, as outlined in GRI-GM13 (GRI 2024a). This test measures

the flow rate of the GM resin, following the ASTM D1238 standard (ASTM 2020), and reports results in g/10 min. For HDPE GMs, the test is typically conducted at 190ºC and can be performed under various loads. The most common are 21.6 kg, known as the High Load Melt Index (HLMI), and 2.16 kg, referred to as the Low Load Melt Index (LLMI). The ratio between these two indices is commonly referred to as the Melt Flow Ratio (MFR). In addition to the standard HLMI and LLMI tests, this study also measured the melt index under 5 kg and 10 kg loads at 190ºC, as specified in ASTM D1238 (ASTM 2020). These intermediate loads were included to provide a broader understanding of the material's flow characteristics. MFI is a key metric for assessing the molecular weight distribution of polymer chains in HDPE GMs (Struve 1994). The melt index test in this study was performed using a Göttefert MI-2 Plastometer.

The mechanical properties examined included tensile strength and strain at break and at yield (ASTM D6693; Type IV), measured in both the machine direction (MD) and the cross-machine direction (CMD), using an EMIC Universal Testing Machine, model DL 3000. The results are the average of five specimens. Tear resistance (ASTM D1004) was evaluated as the average between MD and CMD.

Statistical validation of the differences between the virgin and exposed GM properties was performed using the student's t-distribution, with a confidence level of 95%. Changes due to weathering exposure were expressed as retained properties (RP, in %), calculated for all the physical and mechanical parameters assessed. The calculation of RP (Equation 2) was adapted from Dias Filho et al. (2024), who applied this methodology to geotextiles, and Lavoie et al. (2021), who used it for HDPE geomembranes.

$$RP = \frac{P_{exposed}}{P_{virgin}} \; x \; 100 \qquad\qquad (2)$$

2.6 Thermoanalytical methods

To analyze thermal stability temperatures and antioxidant depletion, TG/DTG (ASTM D 6370) and Std-OIT (ASTM D 3895) tests were performed. The Std-OIT test, also conducted using thermal equipment, was carried out using a Differential Scanning Calorimetry (DSC) device. The Std-OIT measurements were performed with a DSC1 Stare, manufactured by Mettler Toledo in Columbus, United States, at a temperature of 200°C and a pressure of 35 kPa. The TG/DTG analysis was conducted using Mettler Toledo equipment, model TGA/SDTA 851. Samples weighing approximately 5 mg were placed in an aluminum crucible under nitrogen purge gas, with a heating rate of 10°C/min and a flow rate of 100 mL/min.

Although colored GMs were inferred to contain HALS in their composition, it was not possible to measure the HALS content in this study, as HALS are volatile at temperatures above 150°C. The only method to assess their presence in the GM is through the HP-OIT test, which is conducted at temperatures up to 150°C; however, this test was not available. Despite this limitation, the results obtained from the Std-OIT remain highly relevant and provide a significant evaluation of the oxidative resistance of HDPE GMs.

3. Results and discussion

3.1 Antioxidant depletion based on Std-OIT

The initial Std-OIT of GM-B was 77.66 minutes, which decreased to 8.71 minutes (RP of 11.2%) after exposure. For GM-W/B, the initial Std-OIT was 104.88 minutes, dropping to 0.85 minutes (RP of 0.8%) after exposure. The GM-G showed an initial Std-OIT of 12.75 minutes, reducing to 0.52 minutes (RP of 4.0%) post-exposure. This suggests that little to no antioxidants remain available in the GMs that were exposed, and that GM-W/B and GM-G have likely reached their residual Std-OIT values.

Based on the Std-OIT measured in the samples after each exposure period, and assuming that antioxidant depletion follows a first-order exponential decay model (Equation 1), the depletion rates of Std-OIT for the samples were 0.021 month^{-1} for GM-B, 0.045 month^{-1} for GM-W/B, and 0.026 month^{-1} for GM-G. It is observed that the depletion rates for the GM-B and GM-G GMs were similar. On the other hand, GM-W/B exhibited a depletion rate nearly twice as high as the other GMs and the lowest Std-OIT value after exposure. It is important to note that for GM-W/B and GM-G, the residual value may have been reached before the total exposure period analyzed in this study. Consequently, the depletion rates presented here might be conservative; if complete antioxidant depletion occurred over a shorter period, the depletion rates would have been faster.

Assuming the residual values for GM-W/B and GM-G were reached at the end of the exposure period, it can be concluded that the colored GMs have completed Stage I after exposure durations of 9 years for GM-W/B and 10.5 years for GM-G. In contrast, GM-B is expected to

require an additional 5.7 years of exposure to reach the 2-minute residual value, leading to an

estimated total duration of Stage I of approximately 14.2 years for GM-B.

3.2 Melt Index

Table 4 presents the MFI values obtained under different load conditions for virgin and exposed

samples. It is observed that the MFI under the different loads analyzed was consistently higher in

GM-G, indicating that this material is more fluid and is likely manufactured with a resin different

from that used in the other GMs containing carbon black in their composition (GM-W/B and

GM-B). In GM-G, the MFI retention ranged from 54.09% to 82.43%, and in GM-W/B, from

49.87% to 75.47%, increasing as the applied load increased. The MFI under different loads is

typically presented as a material characterization parameter in the form of LLMI and HLMI

without accounting for the variations in MFI caused by the applied loads. Most MFI analyses

primarily focus on HLMI values. The observed differences in MFI RP under varying loads can

be attributed to the intrinsic characteristics of the polymer matrix and its response to applied

stress. Additionally, the increase in MFI retention at higher loads observed across all samples

may reflect the effects of polymer degradation processes, such as chain scission, which reduce

molecular weight and enhance fluidity under higher shear forces (Hsuan & Koerner 1998).

 On the other hand, in GM-B, the MFI retention was greater than 90% under all load conditions,

with the lowest retention (90.23%) observed under the 5 kg/190°C condition, a load condition

that has been adopted in recent studies on GM durability (e.g., Lavoie *et al.* 2020, 2021, 2024). It

is worth noting that all the mean values presented in Table 4, along with their respective standard

deviations, were calculated from five specimens, except for HLMI, which, due to limitations of

the test itself (length of the standard die of the plastometer), only allowed for two specimens.

The MFI values found for both virgin and exposed samples of GMs containing carbon black

were lower than those reported in the literature for HDPE GMs manufactured by the flat-die or

flat-sheet processes (e.g., Scheirs 2009; Muñoz Gómez 2016). The results indicate an increase in

the molecular weight of the polymer in the GMs after exposure, as MFI is inversely related to the

molecular weight of the polymer (Shenoy and Saini 1986). This increase may be caused by

polymer cross-linking due to the oxidation process (Hsuan and Koerner 1998).

3.3 Physical and Tensile Properties after degradation

Table 3 presents the physical and mechanical properties of GMs after exposition and their

retention (RP, in %). The analyzed GMs meet the physical and mechanical requirements of the

GRI-GM13 specification (GRI, 2024a), except for the GM-G sample, which exhibited a density

approximately 0.5% below the minimum reference value and a mean strength at a yield of 6.7%

to 1.2% lower than the reference minimum value of 15 kN/m, both before and after exposure. It

is important to note that the reference (virgin) samples were stored at room temperature for

extended periods, ranging from 8.5 to 10.5 years, with the data presented in Table 1 obtained

after the entire storage period. During this time, the samples likely underwent aging due to

thermo-oxidative degradation caused by prolonged exposure to oxygen and ambient temperature,

despite being stored in the manufacturer's archive.

The GM-G sample was exposed for the longest period, totaling 10.5 years. After analyzing the physical properties (thickness and density), no significant variation was observed after exposure. Regarding the mechanical properties, strain at break in both directions showed the most substantial reduction in the GM-G sample, with a retention of 41.05% in the MD and 23.05% in the CD. Additionally, a retention of 58.68% was observed for Strain at Yield in the MD. Although there was also a decrease in strength at break, the reduction was less pronounced, with a retention of 83.91% and 81.77% in the MD and CD directions, respectively.

Analyzing the tensile properties at break separately (Strain and Strength), it could be argued that if only Strain at Break were considered, the GM-G sample would have reached nominal failure (Stage III). However, this property exhibits high variability in textured GMs due to the thickness variation introduced by the texturing, which is reflected in the high standard deviation values, particularly for Strain at Break. This behavior has also been observed by Zafari et al. (2023b, 2023a), who suggest that thickness variation in textured GMs can significantly increase the variability of break properties.

In the GM-W/B sample (exposed for 9 years), the property that retained the least of its original value was strain at break in the MD, retaining 46.08% of its original value, like what was observed in GM-G. The second property with the greatest reduction after exposure was the carbon black content, which decreased by 26.88%. It is noteworthy that both the virgin and exposed GM-W/B samples do not meet the minimum carbon black content specification of 2% required by GRI-GM13 (GRI, 2024a), as one of its surfaces is white. This indicates the use of a UV radiation protector other than carbon black in this layer, likely titanium dioxide.

GM-W/B had an increase in thickness by 1.02%, density by 0.55%, and in several tensile properties, such as Strength at Yield in the MD and CMD, with increases of 3.23% and 5.25%, respectively, Strength at Break in the CMD by 2.26%, Strain at Yield in the CD by 6%, and Average Tear Resistance by 5.02%. For samples with a colored surface (GM-G and GM-W/B), an increase in strength at yield was observed after exposure in the MD for GM-G and in both manufacturing directions for GM-W/B, with variations ranging from 3% to 7%. Additionally, there was an increase in average tear resistance by 0.17% for GM-G and 5.02% for GM-W/B. The observed increases in mechanical properties are attributed to the formation of crosslinks between polymer chains after long-term exposure.

In the sample exposed for the shortest period, 8.5 years (GM-B), the most significant decrease was observed in average tear resistance, with the sample retaining 82.37% of the original property, followed by thickness, which retained 84.62%. There was an increase in both strain at break and strain at yield in both directions, with the largest increase occurring in Strain at Break in the CD, showing a 129.97% increase. Notably, strain at break in the CD also exhibited the highest coefficient of variation (CV) among all GMs, with values of 157.3% in GM-G, 88.6% in GM-W/B, and 84.3% in GM-B. Similarly, Zafari et al. (2023a) reported that the onset of thermo-oxidative degradation in textured GMs could not be reliably assessed based on break properties due to their high variability. The authors also observed more significant variability in tensile strength and strain values, specifically in the CD, which is consistent with the findings of this study.

3.4 Thermal decomposition based on TG

Figure 2a presents the TG/DTG curves for the virgin and exposed GM-B samples, both analyzed under a nitrogen purge. Both TG curves exhibit thermal decomposition occurring in a single stage. The primary difference between the curves lies in the thermal decomposition range, which is narrower for the exposed sample. This difference is also reflected in the DTG curve, where the exposed sample begins thermal decomposition at 390°C, whereas the virgin sample starts at 420°C. At the end of the thermal decomposition, another distinction is observed: the TG curve of the exposed GM-B sample concludes at 488°C, while that of the virgin sample finishes at 500°C. The observed changes in decomposition's onset and end temperatures indicate that the exposed material has lost thermal stability, making it more susceptible to failure in high-temperature environments.

Figure 2b shows the TG/DTG curves for the virgin and exposed GM-W/B samples. In this case, both samples exhibit nearly identical thermal stability, with only a slight difference in the residual mass at the end of the thermal decomposition.

Figure 2c presents the TG/DTG curves for the virgin and exposed GM-G samples. The onset of decomposition is similar for both samples, but as the process progresses, the TG curves diverge, which is also evident in the DTG curves. The final decomposition stage is similar between the two, though the residual material is slightly higher for the virgin GM-G sample. A second thermal decomposition stage is observed in both samples: between 476°C and 506°C for the exposed GM-G sample and between 491°C and 527°C for the virgin GM-G sample.

GM-B's TG/DTG curves showed the most significant differences, potentially due to its carbon black composition. This technique can also be used to determine the carbon black content in HDPE GMs. However, its relevance may be limited when analyzing colored GMs. In contrast, Std-OIT and MFI are the properties that provide the most valuable insights into the degradation processes of colored textured HDPE GMs.

4. Conclusions

For the test conditions and GMs examined, the following conclusions can be drawn:

The Std-OIT results indicate substantial antioxidant depletion across all GMs, with findings suggesting that while GM-W/B and GM-G have reached their residual OIT values, GM-B's Std-OIT might be still depleting. In addition, GM-W/B and GM-G samples showed a reduction in MFI and tensile properties, implying degradation beyond Stage I.

Comparing strain properties at break and yield was difficult due to the high variability in the data, likely an effect of texturing of the GMs studied, as evidenced by high standard deviation values.

Analyzing MFI under varying loads, especially low loads, is crucial, as HLMI alone may not capture property variations after exposure. The reduction in MFI suggests increased stiffness in the GMs, while differences in MFI RP highlight the polymer matrix's characteristics and stress response. Higher retention was observed at greater loads.

GM-W/B exhibited the lowest retention of Std-OIT, as well as the lowest MFI retention across all loading conditions, followed by GM-G and GM-B. These findings indicate a strong correlation between Std-OIT and MFI properties, underscoring the interdependence of oxidative stability and melt flow characteristics in the degradation process.

The relevance of TG/DTG analysis may be limited when applied to colored HDPE GMs, as this technique appears to be more suitable for analyzing black HDPE GMs.

Despite its higher heat absorption characteristics, GM-B did not exhibit the fastest degradation. While it was exposed to UV radiation at the same location as the other GMs, it had a shorter exposure duration than the colored GMs—6 months less than GM-W/B and 2 years less than GM-G. This shows the critical role of exposure time in the degradation process.

Excluding strain at break and yield, tensile property retention exceeded 80% across all GMs, indicating maintained resistance despite prolonged exposure and supporting their continued functionality as effective barriers. Given the extended exposure of colored GMs it can be concluded that colored GMs may offer durability comparable to that of traditional black GMs.

Author contributions

The individual contributions of each author are highlighted as follows: MAA-A: methodology.

investigation. data analysis. validation. and writing (original draft); MK: methodology. data

analysis. validation. and writing (original draft); CAV: methodology. Investigation; CFP:

Investigation. project administration; LPS-P: supervision. methodology. writing (reviewing and

editing); JLS: conceptualization. project administration. resources. supervision. methodology.

funding acquisition and resources. writing (reviewing and editing).

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Availability of data and material

The data presented in this study are available on request from the corresponding author.

Code availability

Not applicable.

Declarations

Notations

Basic SI units are shown in parentheses.

Std-OIT   Standard Oxidation Induction Time (s)

OIT_R residual Oxidation Induction Time (s)

OIT_t Oxidation Induction Time at the time of interest (s)

OIT_0 initial Oxidation Induction Time (s)

t time of interest (s)

ΔT temperature variation (K)

MFR   Melt Flow Ratio (dimensionless)

Abbreviations

ASTM   American Society for Testing and Materials

CMD   Cross Machine Direction

DSC   Differential Scanning Calorimetry

DTG   Derivative Thermogravimetry

EESC   São Carlos School of Engineering

GM-B   GM with both sides black

GM-G   GM with both sides green

GMs   Geomembranes

GM-W/B   GM with one white and one black side

GRI   Geosynthetic Research Institute

HALS   Hindered Amine Stabilizers

HDPE   High-Density Polyethene

HLMI   High Load Melt Index

HP-OIT   High-Pressure Oxidation Induction Time

INMET   Brazilian National Meteorological Institute

ISO   International Organization for Standardization

LLDPE   Linear Low-Density Polyethene

LLMI   Low Load Melt Index

MD	Machine Direction
MFI	Melt Flow Index
MSW	Municipal Solid Waste
N.A	Not Apply
RP	retained property
SCR	Stress Cracking Resistance
TG	Thermogravimetry
USP	University of São Paulo
UV	ultraviolet radiation

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Tables

Table 1. Initial properties of the GMs examined

Property (Unit)	Method	Mean ± (Standard deviation)		
Geomembrane designator		GM-G	GM-W/B	GM-B
Thickness (mm)	ASTM D5994	0.96 (±0.07)	0.98 (±0.08)	1.04 (±0.14)
Asperity height (mm)	ASTM D7466	0.94 (±0.14)	0.56 (±0.18)	0.68 (±0.16)
Geomembrane density (g/cm³)	ASTM D792	0.935 (±0.0010)	0.948 (±0.0002)	0.946 (±0.0002)
Carbon Black Content (%)	ASTM D4218	N.A	0.93 (±0.11)	2.00 (±0.09)
Carbon Black Dispersion (Category)	ASTM D5596	N.A	Category I	Category I
Std-OIT (min)	ASTM D3895	12.75 (±0.64)	104.88 (±0.80)	77.66 (±0.72)
HLMI (g/10min)	ASTM D1238	16.780 (±0.026)	11.860 (±0.025)	12.354 (±0.040)
LLMI (g/10min)		0.413 (±0.013)	0.110 (±0.0002)	0.095 (±0.004)
MFR (-)		40.66	107.56	130.06
Strength at Break MD (kN/m)	ASTM D6693	18.83 (±1.51)	23.80 (±0.88)	26.23 (±5.28)
Strain at Break MD (%)		417.30 (±53.50)	467.20 (±50.46)	407.90 (±14.48)
Strength at Yield MD (kN/m)		13.99 (±1.14)	18.25 (±0.31)	19.72 (±3.04)
Strain at Yield MD (%)		30.25 (±0.06)	17.25 (±1.13)	22.75 (±2.16)
Strength at Break CMD (kN/m)		18.71 (±2.10)	19.49 (±1.41)	20.36 (±2.92)
Strain at Break CMD (%)		479.30 (±15.03)	330.70 (±283.15)	147.50 (±240.43)
Strength at Yield CMD (kN/m)		14.83 (±1.92)	18.49 (±0.45)	19.99 (±3.39)
Strain at Yield CMD (%)		18.25 (±1.12)	12.50 (±2.13)	13.00 (±3.05)
Average Tear Resistance (N)	ASTM D1004	172.00 (±20.18)	173.40 (±9.46)	200.20 (±31.01)

MD= Machine Direction. CMD= Cross Machine Direction. N.A = Not Apply.

Table 2. Summary of the climatic characteristics

Sample	Exposure time (months)	Average temperature (ºC)	Accumulated rainfall (mm)	Accumulated UV radiation (MJ/m²)
GM-B	102	22.0	13549.4	376887.9
GM-W/B	108	22.0	14405.8	404055.5
GM-G	126	21.9	16244.0	468841.5

Table 3. Properties of GMs after exposition and RP

Property (Unit)	Method	Mean ± (Standard deviation)			RP (%)		
Geomembrane designator		GM-G	GM-W/B	GM-B	GM-G	GM-W/B	GM-B
Exposure time (Years)		10.5	9.0	7.5			
Thickness (mm)	ASTM D5994	0.95 (±0.05)	0.99 (±0.07)	0.88 (±0.04)	98.96	101.02	84.62
Geomembrane density (g/cm³)	ASTM D792	0.934 (±0.0002)	0.953 (±0.0007)	0.946 (±0.0003)	99.89	100.55	99.97
Carbon Black Content (%)	ASTM D4 218	N.A	0.68 (±0.04)	1.98 (±0.06)	-	73.12	99.00
Std-OIT (min)	ASTM D3895	0.51 (±0.03)	0.85 (±0.09)	8.71 (±0.12)	4.00	0.81	11.22
Strength at Break MD (kN/m)	ASTM D6693	15.80 (±0.85)	20.35 (±0.36)	22.60 (±1.45)	83.91	85.50	86.16
Strain at Break MD (%)		171.30 (±144.32)	215.30 (±179.65)	422.80 (±17.56)	41.05	46.08	103.65
Strength at Yield MD (kN/m)		14.96 (±1.11)	18.84 (±2.20)	16.91 (±0.48)	106.93	103.23	85.75
Strain at Yield MD (%)		17.75 (±1.18)	14.50 (±3.18)	25.00 (±4.32)	58.68	84.06	109.89
Strength at Break CMD (kN/m)		15.30 (±0.59)	19.93 (±0.40)	18.50 (±1.20)	81.77	102.26	90.86

Strain at Break CMD (%)		110.50 (±173.82)	271.40 (±240.49)	339.20 (±285.91)	23.05	82.07	229.97
Strength at Yield CMD (kN/m)		14.82 (±1.21)	19.46 (±0.40)	17.40 (±0.35)	99.93	105.25	87.04
Strain at Yield CMD (%)		16.50 (±2.18)	13.25 (±1.25)	13.25 (±2.47)	90.41	106.00	101.92
Average Tear Resistance (N)	ASTM D1004	172.30 (±13.57)	182.10 (±9.77)	164.90 (±10.06)	100.17	105.02	82.37

MD= Machine Direction. CMD= Cross Machine Direction. N.A = Not Apply.

Table 4. MFI (g/10min) at 190ºC under different loads and RP.

Load (kg)	GM-G			GM-W/B			GM-B		
	Virgin	Exposed	RP (%)	Virgin	Exposed	RP (%)	Virgin	Exposed	RP (%)
2.16*	0.413 (±0.013)	0.223 (±0.007)	54.09	0.110 (±0.0002)	0.055 (±0.001)	49.87	0.095 (±0.004)	0.089 (±0.001)	93.46
5	1.365 (±0.024)	0.824 (±0.006)	60.41	0.524 (±0.006)	0.300 (±0.002)	57.26	0.494 (±0.014)	0.446 (±0.004)	90.23
10	4.060 (±0.003)	2.851 (±0.001)	70.23	2.035 (±0.002)	1.374 (±0.001)	67.54	2.059 (±0.004)	1.992 (±0.002)	96.77
21.6**	16.780 (±0.026)	13.831 (±0.011)	82.43	11.860 (±0.025)	8.951 (±0.026)	75.47	12.354 (±0.040)	11.741 (±0.033)	95.04

Mean results in g/10min and standard deviations in brackets. *LLMI. **HLMI

Figure captions

Figure 1. Weathering panel scheme and samples details (without scale)

Figure 2. TG/DTG curves (a) GM-B Virgin and Exposed; (b) GM-W/B Virgin and Exposed; (c)
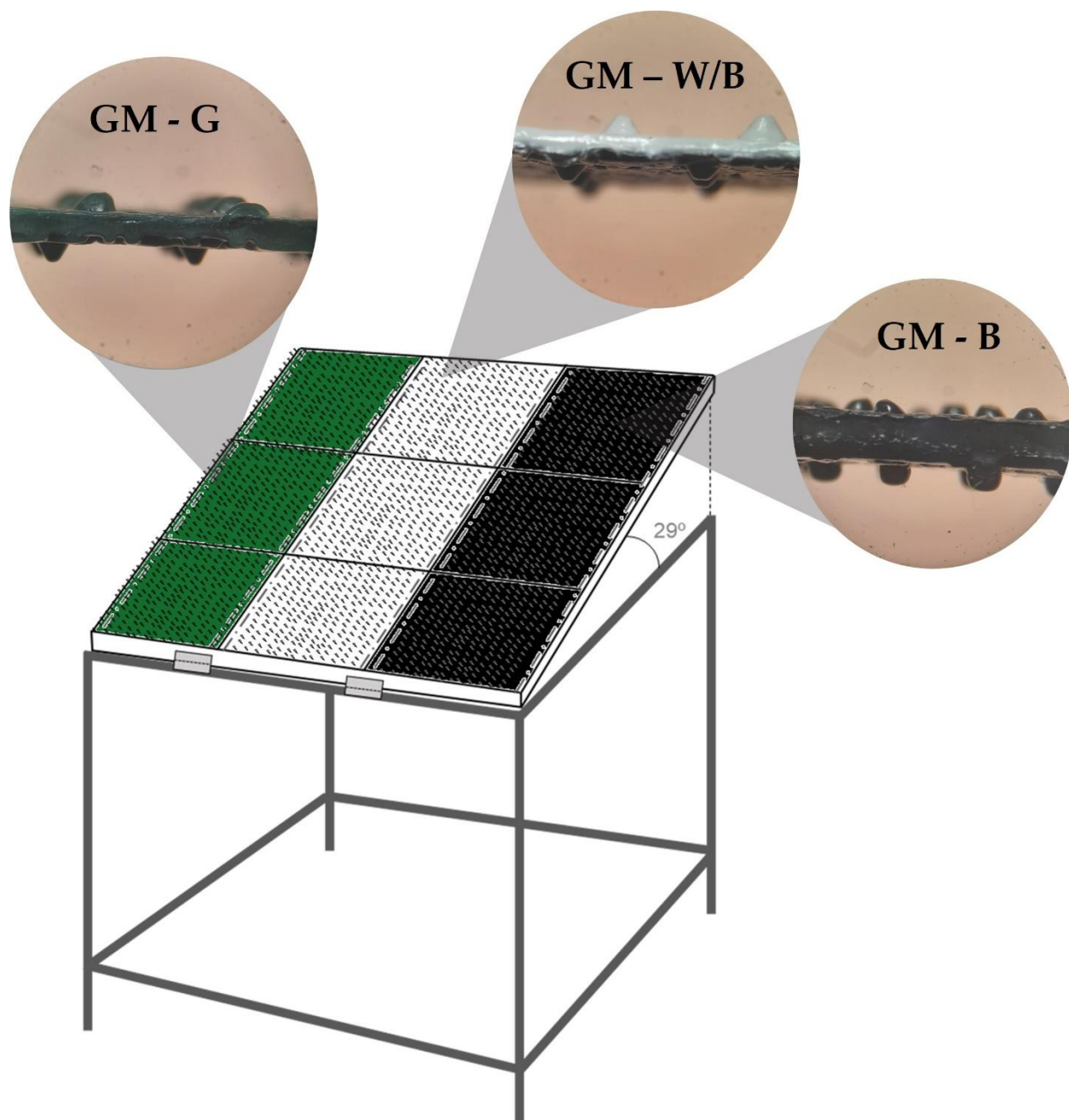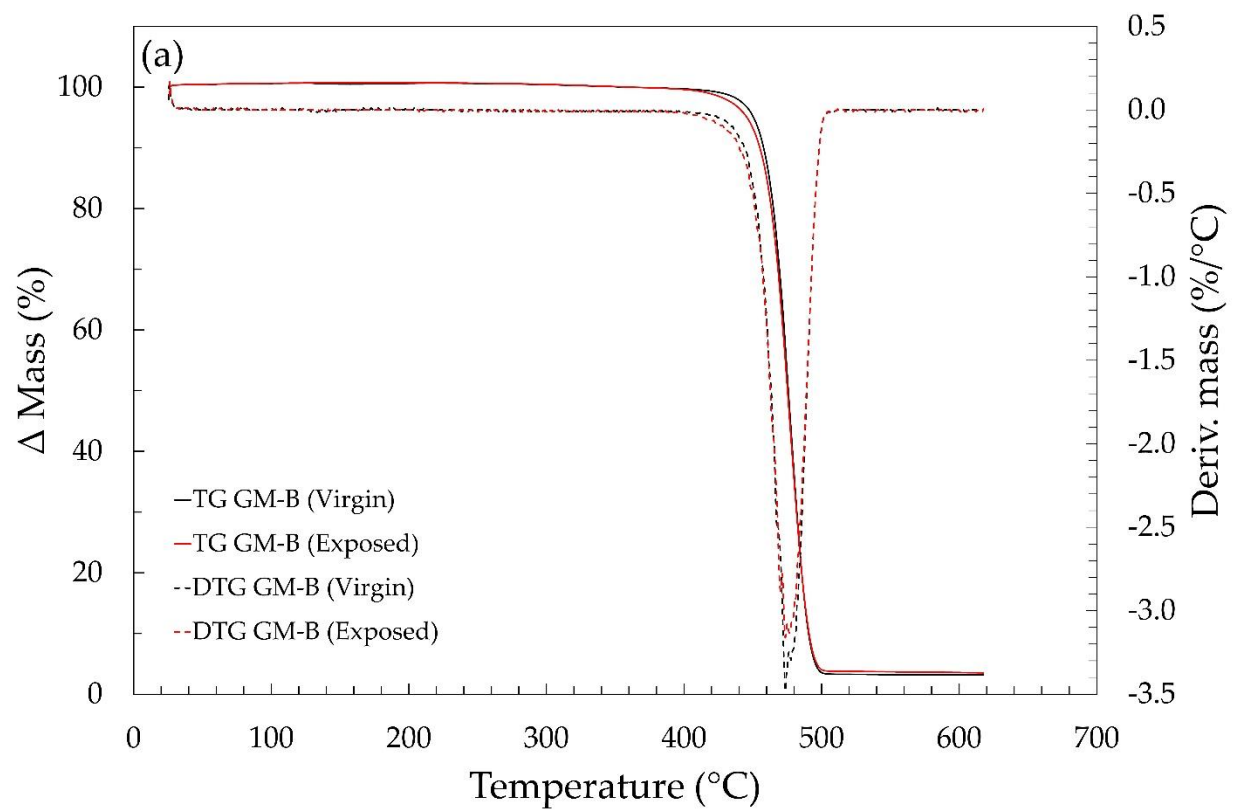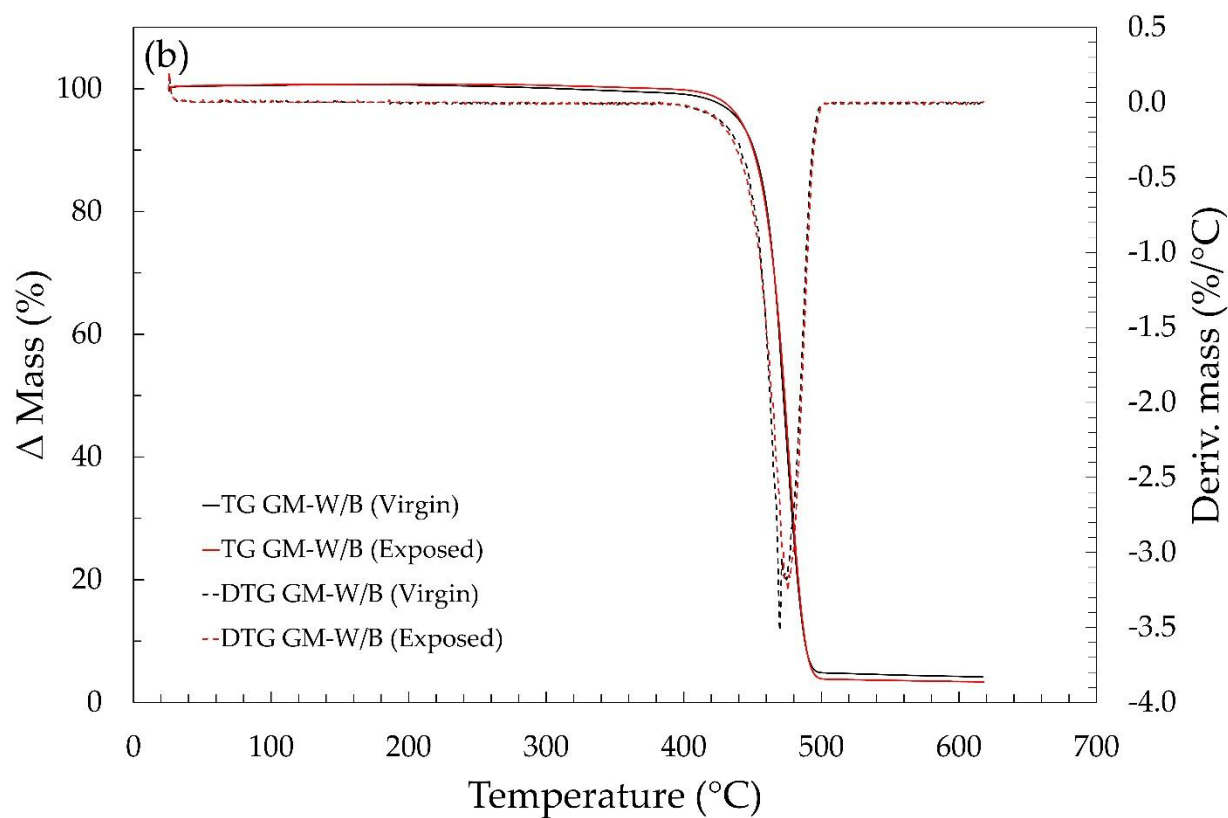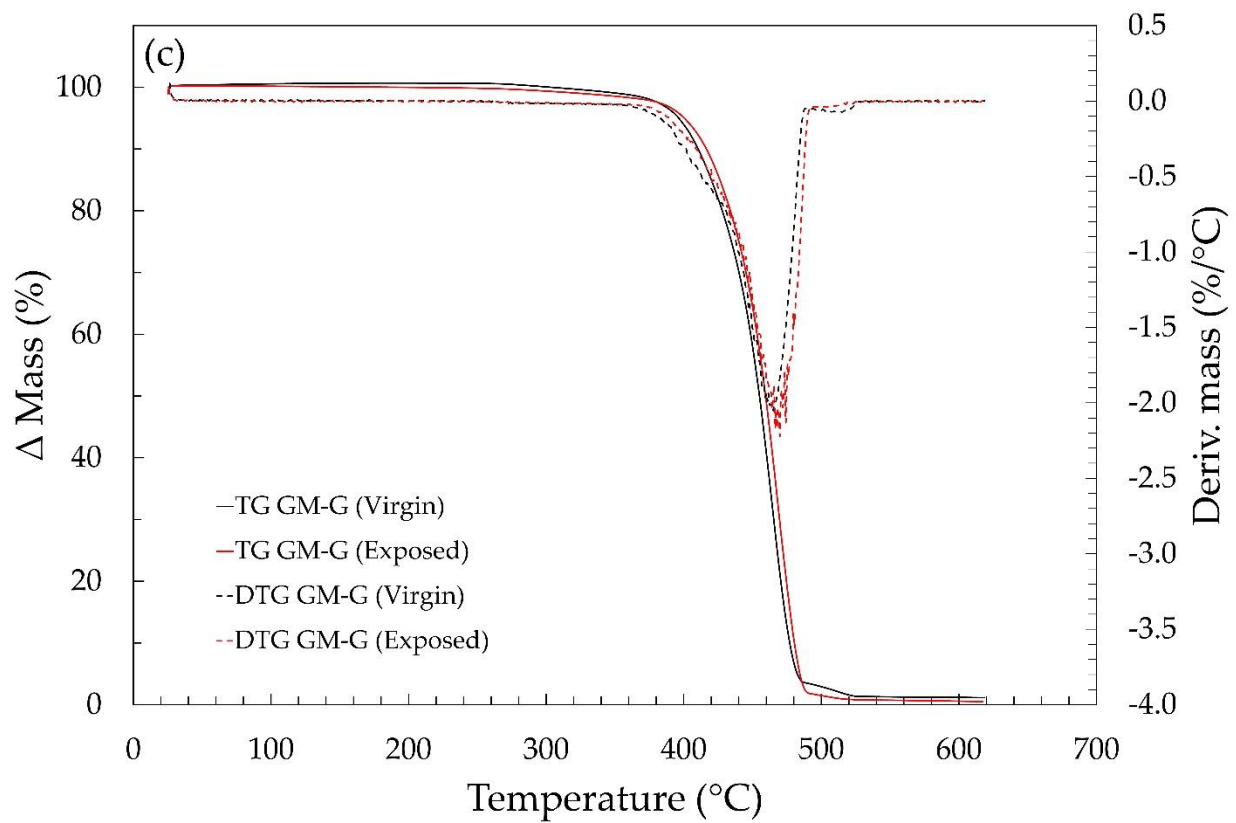
GM-G Virgin and Exposed

Fig. 1

Fig. 2