Thermo-Oxidative Degradation of HDPE Geomembranes: Effect of Phenolic Antioxidant and Hindered Amine Light Stabilizer Concentrations

Yasin Kocak
University of South Florida

Follow this and additional works at: https://scholarcommons.usf.edu/etd

Part of the Civil Engineering Commons, Materials Science and Engineering Commons, and the Polymer Chemistry Commons

Scholar Commons Citation

This Thesis is brought to you for free and open access by the Graduate School at Scholar Commons. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact scholarcommons@usf.edu.
Thermo-Oxidative Degradation of HDPE Geomembranes: Effect of Phenolic Antioxidant and Hindered Amine Light Stabilizer Concentrations

by

Yasin Kocak

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering
Department of Chemical and Biomedical Engineering
College of Engineering
University of South Florida

Major Professor: Venkat Bhethanabotla, Ph.D.
Manoj K. Ram, Ph.D.
John Kuhn, Ph.D.

Date of Approval:
October 25, 2019

Keywords: Geosynthetics, Accelerated Aging, Hydraulic Structure

Copyright © 2019, Yasin Kocak
Dedication

To My Family
Acknowledgments

I would like to express my sincere gratitude to my advisor Dr. Venkat Bhethanabotla for his continuous guidance, encouragement, and patience during my masters at USF. Special thanks to Dr. Manoj K. Ram for his advice and continues support, Dr. John Kuhn for his advice and participation as a member of thesis supervisory committee.

I would like to thanks to the State Hydraulic Works (DSI) on behalf of the Turkish Government for allowing me to pursue my master’s degree. Without their support, I would not have successfully conducted this study.

Finally, I would like to express my gratitude to BASF Corporation, Total S.A. and Modern Dispersions South Inc. for sending samples and their support.
## Table of Contents

List of Tables ........................................................................................................ iii

List of Figures ......................................................................................................... iv

Abstract .................................................................................................................. v

Chapter 1 Introduction and Background ................................................................. 1
  1.1 Introduction .................................................................................................. 1
  1.2 Literature Review ...................................................................................... 5
  1.3 Oxidation and Service Life ....................................................................... 9
  1.4 Polyethylene .............................................................................................. 11
  1.5 Morphology of HDPE Geomembranes ....................................................... 11
  1.6 Function of Additives ............................................................................. 13
    1.6.1 Carbon Black .................................................................................... 13
    1.6.2 Antioxidants/ Stabilizers ................................................................. 15
  1.7 Research Objective .................................................................................... 18

Chapter 2 Materials and Experiments ................................................................... 19
  2.1 Materials .................................................................................................... 19
  2.2 Experiments ............................................................................................... 21
    2.2.1 Accelerated Aging Tests .................................................................. 21
    2.2.2 Crystallinity Test with Differential Scanning Calorimetry (DSC) .... 22
    2.2.3 Tensile Test ...................................................................................... 23
    2.2.4 Melt Index Test (MI) ....................................................................... 23
    2.2.5 Fourier Transform Infrared (FTIR) ................................................... 23
    2.2.6 Scanning Electron Microscopy/ Energy Dispersive X-ray Spectroscopy (SEM/EDS) ................................................................. 25
    2.2.7 X-ray Photoelectron Spectroscopy (XPS) ....................................... 25
    2.2.8 Thermogravimetric Analysis (TGA) .................................................. 25

Chapter 3 Results and Discussion .......................................................................... 27
  3.1 Experiments ............................................................................................... 27
    3.1.1 Accelerated Aging Tests .................................................................. 27
    3.1.2 Crystallinity Test with Differential Scanning Calorimetry ............... 27
    3.1.3 Tensile Test ...................................................................................... 30
    3.1.4 Melt Index Test .............................................................................. 34
    3.1.5 Fourier Transform Infrared (FTIR) ................................................... 35
    3.1.6 Scanning Electron Microscopy/ Energy Dispersive X-ray Spectroscopy (SEM/EDS) ................................................................. 43
3.1.7 X-ray Photoelectron Spectroscopy (XPS) ......................................................... 44
3.1.8 Thermogravimetric Analysis (TGA) ..................................................................... 46

Chapter 4 Conclusion ........................................................................................................ 49

References .......................................................................................................................... 53
List of Tables

Table 1.1 Types of geomembranes with advantages and disadvantages and some hydraulic applications.................................................................................................................. 3

Table 2.1 Molecular weights and effective temperature ranges of antioxidants in the geomembranes................................................................................................................................. 20

Table 2.2 Composition of the geomembranes .................................................................. 21

Table 3.1 Results of Enthalpy, Peak Melting Temperature, and Crystallinity for unaged geomembrane .......................................................................................................................... 29

Table 3.2 Results of Enthalpy, Peak Melting Temperature, and Crystallinity for 3 months aged geomembrane .................................................................................................................. 29

Table 3.3 Results of Enthalpy, Peak Melting Temperature, and Crystallinity for 6 months aged geomembrane .................................................................................................................. 29

Table 3.4 The tensile results of unaged and aged GM 1 thin samples.............................. 33

Table 3.5 The values of the carbonyl index (I) for the geomembrane samples at the days of 0, 45, 60, 90, 135 and 180 days ........................................................................................................... 37

Table 3.6 FTIR peaks values, possible assignments and references .................................. 40

Table 3.7 Surface compositions of the surface of unaged and 6 months aged geomembranes with EDS ................................................................................................................................. 44

Table 3.8 The approximate results of high-resolution carbon 1s XPS analyses (%) ........... 45

Table 3.9 TGA results for unaged and aged geomembranes ................................................ 49
List of Figures

Figure 1.1 Schematic of crystallites in semi-crystalline polymers ............................................. 12

Figure 1.2 The expected chemical groups in the carbon black ....................................................... 14

Figure 1.3 Oxidation cycle for geomembranes .................................................................................. 17

Figure 2.1 The structure of (a) Irganox 1330 (b) Irfagos 168 and (c) Chimassorb 944 ............ 19

Figure 2.2 TA DSC 2500 (TA Instrument, USA) ............................................................................ 22

Figure 3.1 The DSC curves for (a) unaged (b) 6 months aged geomembranes .......................... 28

Figure 3.2 The applying stress in the machine direction (a), the applying stress in the cross-section direction (b) ........................................................................................................... 31

Figure 3.3 The shape of geomembrane samples before tensile tests (a) and geomembrane sample after the break (b) ................................................................................................................. 34

Figure 3.4 The peaks for unaged geomembranes .............................................................................. 36

Figure 3.5 The absorption peaks of 1732 cm\(^{-1}\) for 6 months aged geomembranes, ............ 36

Figure 3.6 The peak intensities of 2850 cm\(^{-1}\) for (a) unaged samples (b) 6 months aged samples ........................................................................................................................... 38

Figure 3.7 The absorbance of the geomembranes after 6 months .................................................. 39

Figure 3.8 GM surface for unaged sample (a), GM surface after 6 months aging (b), the particulars on the GM surface (c) ........................................................................................................ 43

Figure 3.9 The high-resolution C 1s spectrum of the GM 1 thin (a) before and (b) after thermal aging at 85 °C in air for 6 months ................................................................................................ 45

Figure 3.10 TGA results for unaged geomembranes (a) at a temperature between 0 and 600°C (b) at a temperature between 400 to 500°C ............................................................ 47

Figure 3.11 TGA results for aged geomembranes (a) at a temperature between 0 and 600°C (b) at a temperature between 400 to 500°C ............................................................ 48
Abstract

High density polyethylene (HDPE) geomembrane is most common geomembrane which is mainly used for civil engineering applications. However, HDPE geomembrane loses its properties under oxidative degradation progress. This study aims to assess geomembranes which have different percentage of phenolic antioxidant and hindered amine light stabilizer (HALS) with under the six months of the thermal-oxidative degradation. The interactions between phenolic antioxidant, HALS and carbon black can affect the mechanical, physical and chemical properties. To monitor these properties, Differential Scanning Calorimetry (DSC), Fourier-transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM/EDX), Melt Index tests, X-ray Photoelectron Spectroscopy (XPS) and Tensile tests are evaluated for geomembrane samples.

The study has shown that the performance of geomembrane changes positively and negatively depending on the percentage of antioxidants and size of carbon black. The increase in the percentage of antioxidants inversely has affected the performance of geomembranes. The small size particles of carbon black with antioxidants have shown appreciable yield, break strength and elongation whereas the carbon black has shown antagonistic effects with phenolic antioxidant and HALS based materials.
Chapter 1 Introduction and Background

1.1 Introduction

It is predicted that two billion people in 2040 will not be able to access freshwater. According to this estimation, water should be transferred without leakage from water sources to cities and villages. The low permeable liner systems which are concrete, bitumen, soil amendments, compacted soils, clay or geosynthetics, can be utilized to transfer or store water. These liner materials have different properties in terms of the level of impermeability, constructability, cost, and durability. In developing countries, geosynthetic materials such as geomembranes can provide cost-effective solutions to prevent fresh drinkable water (Blond et al., 2019). According to ASTM D4439, a geomembrane is defined as “a thin, continuous synthetic and impermeable liner or barrier to control liquid and/or gas migration in man-made project, structure or system” (Koerner, 2012). In addition, especially geomembranes are more impermeable than geotextiles, soils and clay soils which are used as barriers because geomembranes are effective in limiting the transport of liquids, contaminants, vapors and diffusion of ions (Ewais, 2014; Koerner, 2012). Besides, Koerner (2012) mentioned that according to results of water-vapour transmission tests, values of permeabilities for geomembranes are between $1 \times 10^{-12}$ and $1 \times 10^{-15}$ m/s which are three to six orders of magnitude lower than the values of typical clay liners (Koerner, 2012). Therefore, geomembranes are effective alternative methods to carry water without leakage throughout long distances via canals and to store water in dams and reservoirs instead of traditional lining methods such as concrete and compacted soils (Stark & Hynes, 2009).
Novak et al. (2007) claimed that geomembranes have great potential to resolve durability problems in these applications and they also have been used not only for new construction but also for rehabilitation projects (as cited by Stark & Hynes, 2009). Geomembranes have been used as fluid barriers for different kinds of civil engineering and agricultural applications such as landfills, wastewater lagoons, dams, canals and reservoirs since the 1970s (Rowe & Sangam, 2002; Koerner & Hsuan, 2003; Peggs, 2006; Stark & Hynes, 2009; Ewais, 2014; Blond et al., 2019). In addition, in some countries, geosynthetic materials can be defined as a “must”, with strict regulatory necessities for their usage in the applications of transportation and environment, and they are also considered as one of the novel materials to permit sustainability for constructions. Therefore, this geosynthetic industry that reaches more than 5 billion dollars as annual sales in these days, has grown about 10% each per year since the 1970s. (Blond et al., 2019).

Polyolefins, the most common synthetic commercial geomembranes, are produced by the polymerization of olefins such as ethylene, propylene and α-olefins (Li, 2005; Ugbolue, 2017; Lohse, 2000 and Mueller & Jakob, 2003). Also, polyolefin geomembranes which are semicrystalline thermoplastic polymers such as polyethylene (PE) and polypropylene (PP), have been increasingly and effectively used for different kinds of applications (Ugbolue, 2017; Li, 2005; Koerner, 1998). Table 1.1 shows several kinds of geomembranes that have different properties in terms of installation procedures, durability, lifespan, and overall performance. These geomembranes are chosen for their mechanical properties (such as elastic modulus, yield strength, puncture/tear resistance), lifespan, cost and chemical and weathering resistance concerning specific applications (Scheirs, 2009). Among all these geomembranes, high-density polyethylene (HDPE) geomembrane (GM) has been used as the most common geomembrane because HDPE
GM has high strength, high chemical resistance and low commercial cost (Scheirs, 2009; Ewais, 2014).

Table 1.1 Types of geomembranes with advantages and disadvantages and some hydraulic applications

<table>
<thead>
<tr>
<th>Geomembrane</th>
<th>Type of Polymer</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Some Hydraulic Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>thermoplastic</td>
<td>- excellent UV resistance (Derek &amp; Justin, 2018)</td>
<td>- High thermal expansion</td>
<td>- San Isidro reservoir (Noval et al., 2014)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Good and broad chemical resistance</td>
<td>- Low point puncture resistance</td>
<td>Bitburg dam, Germany (Zornberg, 2005).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Good properties at low temperatures</td>
<td>- Poor multiaxial strain properties (Scheirs, 2009)</td>
<td>2003 Toshka Canal (Stark &amp; Hynes, 2009)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- good weld strength (Scheirs, 2009)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC</td>
<td>thermoplastic</td>
<td>- Good point puncture resistance (Morrison &amp; Comer 1995)</td>
<td>- not good performance at high and low temperature</td>
<td>1960 Terzaghi Dam, (Jansen, 2012)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Good flexibility at all temperatures (Derek &amp; Justin, 2018)</td>
<td>- poor resistance for UV and weathering</td>
<td>1991-93 Fullerton Canal (Morrison &amp; Comer 1995)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- easy to seam (Scheirs, 2009)</td>
<td>- Cannot be thermally welded after aging (Scheirs, 2009)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- excellent elongation properties (Derek &amp; Justin, 2018)</td>
<td>- less UV and chemical resistance than HDPE (Scheirs, 2009)</td>
<td></td>
</tr>
<tr>
<td>CSPE</td>
<td>Thermoplastic rubber</td>
<td>Excellent resistance to UV and ozone. Good performance at low temperature (Scheirs, 2009).</td>
<td>- difficult to repair because of vulcanizations (Derek &amp; Justin, 2018)</td>
<td>Kohlbrein dam, Austria (Zornberg, 2005).</td>
</tr>
</tbody>
</table>
**Table 1.1 (continued)**

<table>
<thead>
<tr>
<th>Geomembrane</th>
<th>Type of Polymer</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Some Hydraulic Applications</th>
</tr>
</thead>
</table>
| EPDM        | Thermoset       | - Low thermal expansion  
- Good performance at low temperature  
- Shows high strength properties (Scheirs, 2009). | - Seams can be difficult  
- Seam quality is low (Scheirs, 2009). | Ochoco Main Canal Section O-3 (Stark & Hynes, 2009) |
| fPP         | Thermoplastic   | - Easy to install (USBR, 2018)  
Excellent multiaxial properties (Scheirs, 2009) | - Not well-known service life  
- Limited resistance to hydrocarbons and chlorinated water (Scheirs, 2009) | FPP pond liners for natural swimming pool in Grosskirchheim/Austria (FPP pond liner, 2015) |

In addition, geomembranes are usually produced as thin and continuous polymeric sheets (Koerner, 2012). Hsuan & Koerner (1995) mentioned that high-density geomembranes are consist of 96–97.5% of resin, 2–3% of carbon black and 0.5–1.0% of antioxidants and stabilizers. Hsuan & Koerner (1998) identified that the density range of the resin for HDPE GM is between 0.932 and 0.940 g/cm³. According to ASTM D883, this density range is defined as medium density polyethylene. Also, adding a different size and percentage of carbon black and antioxidants increases density. According to ASTM D883, this increased density of geomembrane can be more than 0.941 g/cm³ and it is defined as HDPE geomembrane.

Also, the resin is basically copolymer polymerized medium density polyethylene (MDPE) with α-olefin under the low pressure and proper catalysts (as cited by Rowe, & Sangam, 2002). These α-olefin co-monomers can cause short chain branches instead of long linear chain molecules of repeating CH₂ groups in the polymer (Hsuan, 2013; Scheirs, 2009). Therefore, Hsuan & Koerner
(1998) explained that adding α-olefin directly decreases polymer density and crystallinity of the resin.

Moreover, 2-3 % of carbon black in the geomembrane provides ideal UV stabilization (Hsuan & Koerner, 1998). Accorsi and Romero 1995 mentioned that more than 3% of carbon black does not improve UV stability (as cited by Hsuan & Koerner, 1998). Besides carbon black, many types of antioxidants are used in the polymer. To increase efficiency, more than one antioxidant in the package is used such as phenolic antioxidants, phosphites and hindered amine light stabilizers (HALS). Indeed, the carbon black is used to protect the polymer from UV degradation during the service life whereas the antioxidants protect polymers from the degradation not only during the processing but also during the service life against the UV lights, chemicals and oxidation (Wong & Hsuan, 2016).

Overall, since 1959, the major question for all kinds of geomembranes has been “How long will they last?”. Therefore, the mechanism and behavior of additives in the geomembranes tremendously affect the performance during the processing and service life. Therefore, the effectiveness and combination of additives are very important in terms of physical, chemical and mechanical properties which can be analyzed by IR, discoloration, molecular weight analysis, melting behavior and tensile experiments. (Celina, 2013; Koerner, Hsuan & Koerner, 2016; Manan, Pitroda & Bhavar, 2015).

1.2 Literature Review

Lodi et al. (2008) studied 84 months of weathering degradation (solar radiation, humidity, wind, rain) for different thicknesses of geomembranes: 0.8 mm and 2.5 mm HDPE; and 1.0 mm and 2.0 mm PVC. Small physical changes were observed after 84 months. As the puncture and tear resistances increased, elasticity decreased for especially PVC geomembranes after 84 months of weathering. Therefore, the aged samples became more rigid.
Vaschetti, Verani, & Cowland (2006) explained the technical details and installation and showed the performance of 2 mm and 2.5 mm thicknesses PVC geomembranes for three different dams in Australia. The dams were constructed in the year 2004 and 2006. From installation, geomembrane systems proved better performance than concrete systems in terms of seepage control, design life and maintenance requirements. The installation of waterproofing geomembrane system at Meander Dam was completed in 6 weeks. Therefore, it can be said that the geomembranes provide faster installation. Besides, the geomembranes at Paradise dam and Eidsvold Weir dam showed very less seepage than concrete systems.

Noval et al., 2014 (a) monitored the properties of 1.5 mm HDPE geomembrane at the San Isidro reservoir which was constructed in 1991 in the Canary Islands and mechanical, physical, chemical and surface properties were assessed to understand the degradation mechanism for 20 years. The more degradation was seen from the north of the reservoir because of higher ultraviolet exposure from the sun because the samples from the north slopes have lower thicknesses, higher crystallinities, more surface cracks than the samples from the south slopes. According to OIT test, the antioxidant will be depleted in 47 years in north slopes and 58 years in south slopes. Overall, HDPE still shows very good performance after 20 years on both slopes. Besides, Blanco et al. (2012) monitored 19 years of properties of PVC-P geomembrane at the “Laguna de Barlovento”. The physical, mechanical, surface and analytical properties were assessed during the 19 years. As the tensile properties changed insignificantly, the noticeable cracks were seen on the exposed side of the reservoir after 19 years. Also, the puncture resistance increased after aging. Overall, PVC-P geomembrane after 19 years showed good performance in especially the non-exposed side. Furthermore, Noval et al., 2014 (b) studied 21 years of properties of EPDM geomembrane in El Boquerton reservoir. After 21 years, the properties of geomembrane are more than the minimum
requirements. Overall, Blanco et al. 2012 (b) compared PVC-P, HDPE, and EPDM geomembranes after about 20 years of field studies and it was found that these three geomembranes are good choices as waterproofing systems in the hydraulic applications.

Cazzufi et al. (1995) carried out aging tests for different kinds of geosynthetic materials such as 2 mm HDPE geomembrane under the natural and laboratory environments. The laboratory weathering tests are performed at 50 °C and 60 °C with UV-B lamps (280–315 nm). After 24 months of aging, tensile strength and modulus decreased around 20% and 10%, respectively. (as cited by Rowe & Sangam, 2001).

Jeon, Bouazza, & Lee (2008) performed 90 days accelerated aging test at 85 °C followed by 50 days incubation in the alkaline and acidic buffer solutions at 40,50 and 60 °C for HDPE in the forced air oven to evaluate antioxidant depletion. They found that the geomembrane still have more than 55% residual value after 90 days of thermal-oxidative aging. It can be said that geomembrane have still enough antioxidants to provide stability. After incubation of alkaline and acidic buffer solutions, they found that geomembrane in the alkaline solution has faster antioxidants depletion than geomembrane in the acidic buffer solutions. Moreover, Arrhenius modeling was used to predict depletion time which was found between 9 years and 107 years depending on the exposure and temperature.

Wong & Hsuan (2014) studied high-density polyethylene (HDPE) pipes with two kinds of antioxidants (Irganox 1010 and Irflagos 168) and carbon black. Indeed, ten different HDPE plaques (between 1.8-2.1 mm thickness) were produced with different compositions of antioxidants with and without carbon black. Samples were exposed to air and water environments. Then, the oxidation behaviors of these HDPE pipes were evaluated using oxidative induction time test (OIT) and FTIR, tensile and melt index tests to see antioxidant depletion and to understand structural and
physical changes. According to results, the composition of 2:1 ratio of Irganox 1010 and Irgafos 168 is less effective against the thermo-oxidation compare with other antioxidant compositions. In addition to this result, the interactions of carbon black and antioxidants have antagonistic effects because oxidative induction time (OIT) value decreased and this caused faster degradation. The carbon black size also affects OIT values.

Phase, Billingham & Bigger (2000) used medium-density polyethylene with different percentages of Irganox 1010, Irfagos 168 and carbon black. As the percentage of carbon black (CB) increases, the OIT value decreases. The optimum percentage of Irganox 1010, Irfagos 168 and CB for the stability of thermal oxidation were found as 1690 ppm, 1580 ppm and 2.5%, respectively. In addition, the result showed that 108 ppm of Irfagos 168 is consumed and the negligible amount of Irganox 1010 is consumed after processing.

Furthermore, Islam (2009) studied accelerated aging tests with different temperatures for 1.5, 2.0 and 2.5 mm thick geomembranes at 55, 70 85°C. It was found that thicker geomembranes are less vulnerable for degradation and can show better service life because the antioxidants in the thick geomembranes have long diffusion path. Also, it was found that thicker geomembranes have longest antioxidant depletion time which was calculated using Arrhenius modeling.

Ewais (2014) examined nine different geomembranes; five of these nine different geomembranes have different thicknesses but the same resin. It was found that the different thicknesses of the geomembranes from the same resin can show different physical and mechanical properties because the properties depend on not only the material but also on the stress and thermal histories during the processing. In addition, these geomembranes were immersed in synthetic leachate, water, and air. After long immersion time at three different elevated temperatures, it was found that thicker geomembranes have longer antioxidant depletion time. In addition,
geomembranes’ initial properties can show good longevity, but it is misleading because geomembranes can degrade chemically even if geomembranes have enough amount of stabilizer and antioxidant.

Hsuan & Koerner (1998) mentioned that there are different kinds of degradation mechanisms for geomembrane which are oxidation, extraction, biological, ultraviolet and thermal degradations. However, Hsuan & Koerner (1995) expressed that the most dangerous degradation mechanism is oxidation for geomembrane.

1.3 Oxidation and Service Life

Oxidation is very harmful to HDPE because of decreasing strength and increasing embrittlement. According to Hsuan et al. 2005, the predicted service life for pristine HDPE is about 35 years at 20°C in air. (as cited by Wong, 2011).

Grassie & Scott (1998) simplified six free radical reactions for the oxidation of polyethylene. The first step is without oxygen and it can happen during the processing (equation 1). Then, free radicals react with polyethylene chains under the presence of oxygen and produce peroxide radicals (Equation 2). This peroxide radical reacts with hydrogen atoms and form hydroperoxide and other free radicals (Equation 3). The hydroperoxide can decompose with energy and form RO• and OH• (Equation 4). These forming RO• and OH• can produce more free radicals in the polymer (Equation 5 & 6). These equations can be seen in Figure 1.3. Once free radicals are initiated, the oxidation becomes auto catalytic and the reaction rate increase exponentially with time. (as cited by Wong, 2011).

\[ \text{RH} \rightarrow \text{R} \cdot + \text{H} \cdot \] (Equation 1)

\[ \text{R} \cdot + \text{O}_2 \rightarrow \text{ROO} \cdot \] (Equation 2)

\[ \text{ROO} \cdot + \text{RH} \rightarrow \text{ROOH} + \text{R} \cdot \] (Equation 3)

\[ \text{ROOH} \rightarrow \text{RO} \cdot + \text{OH} \cdot \] (aided by energy) (Equation 4)
RO• + RH → ROH + R• (Equation 5)

OH• + RH → H₂O + R• (Equation 6) (Wong, 2011).

In addition, Hsuan & Koerner (1998) stated that service life for the high-density polyethylene (HDPE GM) can be divided into three stages; Stage I: antioxidant depletion, Stage II: induction time, Stage III: the time when the mechanical and physical properties of geomembranes is reduced due to polymer degradation (Rimal, 2009). In order to decrease the degradation rate and increase service life, 0.5-1% of antioxidants/stabilizers and carbon black can be used. In addition, for Stage I, the rate of antioxidant depletion from geomembranes can affect long term performance. Therefore, most of the literatures (Hsuan & Koerner 1998; Sangam & Rowe 2002; Gulec et al. 2004; Rimal et al. 2004) have intensively studied Stage I of the geomembrane under the environment of air, water, leachate and hydrocarbons (as cited by Rimal, 2009). According to Hsuan & Koerner (1995), oxidative degradation is called the most harmful degradation because oxygen can deteriorate polymer chains and decrease mechanical and physical properties. In addition, free radicals are formed due to oxidation chain reactions and these free radicals can deteriorate polymer chains and can decrease molecular weight and these can make the polymer more brittle and susceptible. When the free radicals and hydroperoxides react with antioxidants, stable molecules are formed (Islam, 2009). However, Gugumus 1998 (a) and (b) mentioned that no optimum combination and concentration are evident from the published experimental studies on the long-term longevity of antioxidants in the geomembranes (as cited by Islam, 2009). Also, different types and amount of antioxidant packages can be used by companies. In terms of commercial geomembrane, the manufacturer cannot give information about types and amounts of antioxidants/ stabilizers in the geomembrane.
In addition, field conditions can take long time to learn the results of geomembranes which have different types of antioxidants and stabilizers. Therefore, most of the studies used laboratory accelerated aging test to predict the service life of geomembranes.

1.4 Polyethylene

Polyethylene which simply has long chains of linear repeating units of \((\text{CH}_2)_n\), is the most extensively used polymer as a resin to produce geomembranes (Scheirs, 2009; Wong, 2011). There are different densities of polyethylene resins which are high density, medium density, linear low density, low density and very low density. These can be used as a resin in the geomembranes having density in the range of 0.850 to 0.960 g/cm\(^3\). In addition, the molecular weight, molecular weight distribution and density of the resin are very important for durability of geomembranes (Scheirs, 2009). This research is focused on the durability of HDPE geomembrane. As mentioned above, MDPE resin (0.932-0.940 g/cm\(^3\)) is used for HDPE geomembrane (ASTM D-883) because the high-density polyethylene has tendency of environmental stress cracking. The MDPE resin in the geomembrane has a widely linear polymer with high frequency of short chain branching. The short chain branching is mainly coming from the ethylene copolymerization by adding short chain alpha-olefin (Scheirs, 2009).

1.5 Morphology of HDPE Geomembranes

Lustiger & Markham (1983) explained that HDPE geomembrane is semi crystalline polyethylene consists of crystal and amorphous phases (as cited by Ewais, 2014). Wong, (2011) explained that “Polymer crystals are formed by a molecular chain which folds itself into a long thin ribbon. These crystals, also called lamella, continue to grow to form spherulites.”. In addition, two adjacent lamellas are connected via tie molecules through a small amorphous region. Figure 1.1 shows a folded polymer chain in the crystal region and tie molecules in the amorphous structure. In addition, the oxidation reaction can break tie molecules in the amorphous region and
these broken molecules can slightly cause higher crystallinity. The amorphous region in the polyethylene tends to oxidative degradation because oxygen can diffuse easier in the amorphous phase (Scheirs, 2009). Also, antioxidants in the semi-crystalline materials can reside in the amorphous region to protect polymer because the crystalline region is too dense to diffuse for not only antioxidants but also oxygen. Therefore, increasing the amorphous region can increase the potential of the degradation and this large volume of the amorphous region should be protected by the antioxidants.

![Schematic of crystallites in semi-crystalline polymers](image)

Figure 1.1 Schematic of crystallites in semi-crystalline polymers

When it comes to crystallization during the processing, the high-density polyethylene starts to crystallize as spherulites below the melting temperature. There are many tiny spherical objects which consist of spherulite centers and rod-like fibrils. These rod-like fibrils which spread in all directions from the center of spherical objects, are the smallest noticeable morphological structures and consist of small crystallites called lamella. As mentioned above, the two adjacent lamellas are interconnected via tie molecules through a small amorphous region.
1.6 Function of Additives

1.6.1 Carbon Black

According to Allen et al. 1998, carbon black can be produced via the combustion method or thermal decomposition methods. There are different types and sizes of carbon black for the manufacturing processes. These carbon blacks are furnace black (17-70nm), impingement black (10-27 nm), thermal black (150-500nm), lamp black (50-90nm) and acetylene black (35-50nm) (as cited by Wong, 2011). Also, the small particle size of carbon black is expensive than the coarse particle size of carbon black (Scheirs, 2009).

In addition, 2-3% of carbon black (17-70 nm) in the geomembrane is used to provide UV protection but the efficiency of protection depends on the particle sizes, dispersion of CB, aggregate size/structure, surface chemistry and concentration of the oxygen containing functional groups in the polymer (Wong, 2011 & Pena et al., 2001). Also, the smaller particle size of carbon black can be more durable under the UV lights while for the small size of carbon black, not only the dispersion in the polymer is difficult but also effectiveness in the polymer can also decrease because of the absorption and immobilization of the antioxidants (Pena et al., 2001). In addition, both high structure (high branch chain) and large aggregate size can cause less UV resistance (Wong, 2011). Moreover, some chemical groups and structures can link with the carbon black surface during the processing and some kind of additional treatments such as liquid-phase oxidation (Wypych, 2000). These expected chemical groups and structures can be seen in Figure 1.2. Especially, some oxygenated groups (-OH or -COOH) are attached on the surface of carbon black (Hawkins, 1984). Kovacs & Wolkober (1976) proved that these groups on the particle surface can react with harmful free radicals. Indeed, both combining these oxygenated groups on the
particle surface and unpaired electrons within the structure can trap these radicals. That is to say, carbon black acts as a radical scavenger.

Hawkins et. al., (1959) explained that 3 wt% the small size of carbon black in the polymer can inhibit photo-oxidation and also can behave as mild antioxidants against accelerated test conditions. However, some organic inhibitors are much stronger than carbon black during the processing and service conditions. Therefore, the carbon black, and polymer additives such as phenol and amine antioxidants are added together to able to increase stability under the thermal and photo-oxidation. However, carbon black and antioxidants can also reduce potential performance. Hawkins et al. (1959a) and Kovacs & Wolkober (1976) express that “the quinone active sites on the CB surface are stringer acceptors than free radicals.” Therefore, antioxidants react with the quinone active sites instead of free radicals (as cited in Wong & Hsuan, 2014). This reaction can reduce the efficiency of the performance of the antioxidants and carbon black.
1.6.2 Antioxidants/ Stabilizers

Polymers are susceptible to degradation against thermal and photo-oxidation without proper antioxidants. During the processing, storage, service life, different combinations of antioxidants can stop or retard decomposition and provide good mechanical properties during all processing, storage and service life (Beißmann et al., 2014).

Geomembranes have been used for different kinds of civil engineering applications such as landfill, reservoir, dam and canal (Rowe & Sangam, 2002; Koerner & Hsuan, 2003; Peggs, 2006; Stark & Hynes, 2009; Ewais, 2014; Blond et. al., 2019). Therefore, AO packages can be adjusted for the specific environments. Scheirs (2009) suggested several packages of antioxidants for different applications. One of these packages has been used as a combination of 3000 ppm Irganox 1010 (hindered phenolic), 1500 ppm Irgafos 168 (hindered phosphite) and Chimassorb 944 (hindered amine) for geomembranes in potable water contact applications. The second package has been employed for non-potable applications, consists of Irganox 1010 (hindered phenolic), Irgafos 168 (hindered phosphite), Chimmassorb 944 (a high molecular weight hindered amine), and Tinuvin 770 (a low molecular hindered amine).

Many studied focused on the interaction between different types of primary and secondary antioxidants to improve performance for a specific environment such as atmosphere and leachate environment (Wong & Hsuan, 2011). Grassie & Scott, (1985); Yachigo, (1992) explained that the mechanism of primary antioxidants is trapping the peroxy radical formed in the presence of oxygen (as cited by Sangam & Rowe, 2002) while the secondary antioxidants react with hydroperoxides then decompose to create suitable esters, alcohols and protect chain branching during the oxidative reactions. (Pena et al., 2001). Types and the total amount of antioxidants, combinations, and temperature affect antioxidants performances.
Chirinos-Padron, 1989; Chirinos-Padron, 1987; Pospisil, 1988; Minagawa, 1989; Hamid et al., 1992 focused on the interactions between different types of primary and secondary antioxidants, HALS and metal deactivators. To improve the performance and efficiency, more than one compound of antioxidants has been utilized for geomembranes in recent days. Therefore, some synergistic and antagonistic effects between these additives such as HALS/Phenolic AO; HALS/Thiopropionate have been shown (as cited Wong, 2011).

Ciba, (1992); Pospisil & Nespurek, (1995) (a),(b) explain that primary antioxidants are used efficiently to protect polymer during the processing and service life as chain-breaking donors whereas they are inefficient during the photodegradation (as cited by Pena et al., 2001). In addition, Gray (1991); Gugumus (1993); Pospisil and Nespurek (1995); Scheirs (2009) showed HALS in polymer provide multi-functional protection against both thermo-oxidation and photo oxidations. On the other hand, HALS in the polymer which is especially used as UV stabilizers provides reproduction of nitroxyl radicals, and the complementarity of the chain breaking donor/acceptor antioxidant mechanism involved (Pena et al., 2001). Moreover, Scheirs 2009 expressed that HALS can trap free radicals, decompose alkyl hydroperoxides (which are unstable intermediates in the oxidation cycle), quench excited states and regenerate its active species. Therefore, HALS additives should be equal to or greater than 5000 ppm (0.5%) to provide more than 20 years of UV stability with 2.5% carbon black.

Primary antioxidants in the polymer can trap and/or deactivate free radicals (1, 2, 4 in Figure 1.3) to create a stable polymer chain. For 2 and 4, primary antioxidants provide electrons to react with ROO, RO, and OH. then ROOH, ROH and H₂O can be formed. Also, primary antioxidants in the location (1), are electron acceptor to convert alkyl free radicals (R.) to the stable polymer. However, secondary antioxidants decompose hydroperoxides (ROOH) to not form free
radicals (3 in Figure 1.4). Therefore, the antioxidants can form stable COH alcohol from hydroperoxides (Hsuan & Koerner, 1998).

Zweifel (2001); Gensler et al. (2000); Gijsman (1994) studied that the environment temperature is very important for performance and diffusion behavior of the antioxidants. Indeed, in a package of antioxidants in geomembrane, phenolic and phosphatic antioxidants are used against oxidation in the high temperatures (200-250°C). However, HALS cannot be used after 150°C (as cited by Muller et al., 2009).

Figure 1.3 Oxidation cycle for geomembranes
1.7 Research Objective

This study aimed to provide information about the accelerated aging of HDPE geomembranes at elevated temperature (85°C) in the forced-air oven. Also, the interactions of different percentages of Irganox 1330 and Chimassorb 944 in the geomembranes and their interactions with carbon black are evaluated during the time period of six months. In addition, the mechanical, physical and chemical properties for these different HDPE geomembranes are monitored via DSC, MI, tensile, FTIR, SEM/EDS, XPS and TGA tests.
Chapter 2 Materials and Experiments

2.1 Materials

As mentioned above, Hsuan & Koerner (1995) mentioned that high-density geomembranes compose of 96–97.5% of resin, 2–3% of carbon black and 0.5–1.0% of antioxidants and stabilizers. Scheirs (2009) suggested the different packages of antioxidants in the geomembrane for the different applications because the interaction of the antioxidants is very important to determine the durability of geomembrane in the specific environment.

Figure 2.1 The structure of (a) Irganox 1330 (b) Irfagos 168 and (c) Chimassorb 944
During the thermal oxidation, the phenolic antioxidant such as Irganox 1010 and Irganox 1330 is responsible to provide long service life. Most of the studies used Irganox 1010 as a phenolic antioxidant (Wong, 2011). However, Pena et al., (2001) explained that Irganox 1330 can be used instead of Irganox 1010 since Irganox 1330 provides low adsorption potential on the carbon black surface and has good resistance against alkaline hydrolysis. Moreover, Irganox 1330 has higher extraction and leaching resistance than Irganox 1010 due to having more rigid and planar molecule structure. In addition, there are some studies that recommended the move away from Irganox 1010 to Irganox 1330 (Scheirs, 2019). Therefore, Irganox 1330 was chosen as a phenolic antioxidant in this study. Besides, Irgafos 168 which is the short-term antioxidant, was chosen to protect geomembrane during the processing because of its low molecular weight and high mobility. Hawkins (1974) explained that the short-term antioxidant should migrate easily to stop initiation reactions throughout the polymer during processing. Also, Chimassorb 944 was chosen as a HALS to protect polymer under the mainly UV degradation. Chimassorb 944 has high molecular weight, low mobility and good extraction resistance to effectively protect geomembrane as a long-term stabilizer. (Scheirs, 2009). Furthermore, as mentioned above, 5000 ppm of HALS can provide more than 20 years of UV stability with 2.5 % carbon black (Scheirs, 2009). Therefore, the minimum 5000 ppm Chimassorb 944 as a percentage was added in the geomembrane. The structure, molecular weight and effective temperature of additives are shown in Figure 2.1 and Table 2.1, respectively.

Table 2.1 Molecular weights and effective temperature ranges of antioxidants in the geomembranes

<table>
<thead>
<tr>
<th>Antioxidants/ Stabilizers</th>
<th>Molecular weight</th>
<th>Effective temperature Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgafos 168 (phosphite)</td>
<td>647</td>
<td>150-300</td>
</tr>
<tr>
<td>Irganox 1330 (phenolic)</td>
<td>775</td>
<td>Up to 300</td>
</tr>
<tr>
<td>Chimassorb 944 (high MW HALS)</td>
<td>2580</td>
<td>Up to 150</td>
</tr>
</tbody>
</table>
To produce the HDPE geomembranes, MDPE resin was used. This resin has 0.938 g/cm$^3$ density and 0.15g/10 minutes melt mass-flow rate (under 190$^\circ$C and 2.16 kg). Polyethylene, Irganox 1330, Irfagos 168, Chimmassorb 944 and carbon black were mixed properly. In addition, carbon black which has a density of 1.139 gm/cm$^3$, was used as a pellet because carbon as a powder is difficult to clean and mix. Then, the mix was put in the 21mm twin Theysohn extruder to obtain polymer sheet in the Polymer Center of Excellence (Charlotte, NC). The molten mix is forced through a flat die and then polished cooling rollers to produce a flat geomembrane sheet. The geomembrane thickness is 1 mm except GM 1 thin (0.5 mm). There are four different compositions to compare efficiency in the geomembrane. The compositions of additives in the geomembrane are given in Table 2.2.

Table 2.2 Composition of the geomembranes

<table>
<thead>
<tr>
<th>Samples/Compositions</th>
<th>Carbon black</th>
<th>Irganox 1330</th>
<th>Irfagos 168</th>
<th>Chimassorb 944</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM 1</td>
<td>2.5%</td>
<td>3500 ppm</td>
<td>500 ppm</td>
<td>5000 ppm</td>
</tr>
<tr>
<td>GM 1 Thin</td>
<td>2.5%</td>
<td>3500 ppm</td>
<td>500 ppm</td>
<td>5000 ppm</td>
</tr>
<tr>
<td>GM 2</td>
<td>2.5%</td>
<td>3500 ppm</td>
<td>500 ppm</td>
<td>7000 ppm</td>
</tr>
<tr>
<td>GM 3</td>
<td>2.5%</td>
<td>5000 ppm</td>
<td>500 ppm</td>
<td>5000 ppm</td>
</tr>
<tr>
<td>GM 4</td>
<td>2.5%</td>
<td>5000 ppm</td>
<td>500 ppm</td>
<td>7000 ppm</td>
</tr>
</tbody>
</table>

2.2 Experiments

2.2.1 Accelerated Aging Tests

The degradation of the geomembranes in the field is very slow for the investigation and so accelerated aging tests in the laboratory have been used to monitor rapid degradation. Accelerated tests have been studied previously by different groups in the leachate, water, air, hydrocarbons and acidic mine drainage at elevated temperatures to provide beneficial information about changing
properties of geomembranes for the field applications (Sangam, 2001; Jeon et al., 2008; Islam, 2009; Wong, 2011; Ewais, 2014; Gulec, 2003). In this work, the geomembrane samples were incubated in the forced air oven (Across International, FO-19070) at 85°C to accelerate degradation. Samples were taken during a period of time to monitor the aging of the samples by using FTIR, DSC, TGA, SEM, EDS, XPS, melt index and tensile test.

2.2.2 Crystallinity Test with Differential Scanning Calorimetry (DSC)

Crystallinity test was performed with a TA DSC 2500 (TA Instrument, USA) in compliance with ASTM E793. This instrument was shown in Figure 2.2. Then, the samples were cut to weight ranges of 5 to 10 mg and sealed in the Tzero pan. Afterward, the samples were heated from 0 to 180°C at the rate of 10°C/min. These tests were run under the 50 mL/min nitrogen gas flow rate. For this study, crystallization temperatures (T_c) and heat of melting were recorded to find the degree of crystallinity (χ_c). The degree of crystallinity can be found using equation 2.1.

\[ \chi_c(\%) = \frac{\Delta H_m}{\Delta H_m^{100\%}} \]

(Equation 2.1.)

Figure 2.2 TA DSC 2500 (TA Instrument, USA)

In equation 2.1, \( \Delta H_m^{100\%} \) which is the theoretical melting enthalpy for 100% of crystallinity HDPE, is 290 J/g. Also, \( \Delta H_m \) is the melting enthalpy which is calculated by the integrated area between the melting curve and arbitrary baseline (Orden et.al., 2015; Ewais, 2014).
2.2.3 Tensile Test

To learn mechanical properties, the tensile tests (ASTM D6693 Type IV) were conducted by Instron 3366 tensile testing machine. The samples were cut in dumbbell-shaped and then the tests were performed with a 50 mm/min (2 inches/minute) elongation rate. For the machine and cross-machine direction, five experiments for each sample were conducted. Then, elongation and stress at yield and break were evaluated.

2.2.4 Melt Index Test (MI)

Sheny & Saini (1986); Hsuan & Koerner (1998); Hsuan & Guan (1998); Shah (2002) expressed that the MI testing method is a qualitative testing method to evaluate molecular weight and give information about changing polymer structure because of oxidative degradation. Therefore, this method indicates the oxidation of geomembranes. The MI value has inversely correlation with molecular weight. In addition, decreasing MI value represents increasing molecular weight due to cross-linking reactions while increasing MI value shows decreasing molecular weight because of chain scission reactions (as cited by Rowe et. al., 2008). According to Schnabel (1981); Hsuan & Guan (1998); Peacock (2000), the oxidation for polymeric material can give rise to alter molecular weight due to cross-linking or chain scission (as cited by Rimal, 2009). According to ASTM D1238, the melt index test was performed to measure the mass of the molten polymer under test condition of 2.16 kg/190°C using MP 993 Tinius Olsen Extrusion Plastometer / Melt Indexer.

2.2.5 Fourier Transform Infrared (FTIR)

FTIR is utilized to get infrared spectra of compounds or materials. Thanks to obtaining infrared spectra of compounds or materials, specific functional groups can be identified. The peaks for polyethylene structure are at around 2910 to 2850, 1470 to 1460, and 729 to 719 cm\(^{-1}\) which
are related to anti-symmetric and symmetric stretching vibration, scissor vibration, and rocking modes of the CH$_2$ structures (Wong, 2011). It can be seen in Figure 3.4. After the period of thermal-oxidative aging, the common carbonyl compounds such as ketones, aldehydes, carboxylic acids, esters, etc. in the geomembrane can be formed. These compounds can be identified between 1630 cm$^{-1}$ and 1750 cm$^{-1}$ using FTIR. (Wong, 2011; Gulec, 2003). Also, FTIR shows different peaks which can be the synergistic and antagonistic interactions between carbon black and antioxidants.

In addition, the carbonyl index (I) is presumably the most common method to measure the chemical oxidation of polyethylene by finding the ratio of the absorbance of the carbonyl peak (1735 cm$^{-1}$) and the reference peak (2850 cm$^{-1}$) (Equation 2). (Rouillon et al., 2016; Rodriguez-Vazquez et al., 2006). The reference band (2850 cm$^{-1}$) which is the absorbance of the symmetric stretching vibration of CH$_2$ at 2850 cm$^{-1}$ was chosen (Rodriguez-Vazquez et al., 2006; Ewais, 2014). The carbonyl index values were calculated using Equation 2 to monitor the degradation of geomembranes.

$$I = \frac{I_{\text{absorbance @1735 cm}^{-1}}}{I_{\text{ref. absorbance @ 2850 cm}^{-1}}}.$$  
(Equation 2)

Figure 2.3 Thermo Scientific Nicolet iS50 FT-IR Spectrometer

In this study, FTIR-ATR was performed between 400 and 4000 cm$^{-1}$ wavenumber range at 4 cm$^{-1}$ resolution with using Thermo Scientific Nicolet iS50 FT-IR Spectrometer (Figure 2.3)
to monitor changes of chemical compounds for 6 months. Each spectrum was collected from 50 scans in the absorbance mode.

2.2.6 Scanning Electron Microscopy/ Energy Dispersive X-ray Spectroscopy (SEM/EDS)

Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS) was used to analyze the surface of samples which can change significantly. Because of the charging problem, the samples coated with gold before analyzing.

2.2.7 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was utilized to analyze the surface of the unaged and aged GM 1 thin. All elements except hydrogen and helium at sample depths of 7-10 nanometers can be detected by using XPS (Rowe & Sangam, 2008). ULVAC-PHI XPS machine was used for the survey and high-resolution scan analyses which were carried out in the area of 100µ at the energy of 93 and 23 eV, respectively. In addition, to find carbon bonds on the GM surface as a percentage of total carbon can be detected by the high-resolution carbon s1 XPS.

2.2.8 Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) is a method that measure continuous mass weights with increasing temperature. This method can give useful information to determine the amount of moisture, volatiles, carbon black, ash, chemical compounds, quality of compounds and decomposition temperatures in the sample (Lodi & Souza, 2012). Therefore, the thermogravimetric analysis (TGA) is one of the most common methods to determine the quantity of a filler within a polymer. For HDPE GM, the polymer and additives in the inert atmosphere will volatilize at different temperatures until 600°C and the residual mass is carbon black and ash (Lodi & Souza, 2012).
According to ASTM D6370, the 2-10 mg samples in the aluminum pan holder were heated until 600°C at a rate of 20°C/min and under nitrogen gas flow of 100 mL/min with using Metler Toledo TGA / DSC 1 machine (Figure 2.4). The total loss of mass of geomembranes before and after degradation was evaluated and compared. In addition, the temperature ($T_{5\%}$) at which a sample loses 5% of its weight, was used as the onset temperature of thermal decomposition to compare thermal stability.
Chapter 3 Results and Discussion

3.1 Experiments

3.1.1 Accelerated Aging Tests

3.1.2 Crystallinity Test with Differential Scanning Calorimetry

The DSC test was performed to find changes in enthalpy ($\Delta H_m$) and crystallinity ($\chi_c$) due to thermal-oxidative degradation. The dotted lines are the baselines, and the area between the curve and the baseline gives the value of enthalpy ($\Delta H_m$) (Figure 3.1).

First of all, the crystallinity depends on the resin. The copolymerized alpha olefins with polymer resin have low crystallinity by forming short branching because long linear (CH\textsubscript{2}) chains increase the crystallinity (Van Santvoort, 1994). Secondly, the crystallinity also depends on cooling rate, take up ratio during the processing. The high cooling rate decreases crystallinity while high take-up ratio increases crystallinity because of less time for crystallization (Ewais, 2014). In other words, the stress history can affect the crystallization during the processing. Thirdly, during thermal-oxidative degradation, the active mechanisms are chain scission (increase in MI) and/or cross-linking (decrease in MI) can affect crystallinity. When the chain scission mechanism is dominant, the crystallinity can increase, and smaller chains can form (Noval et al., 2014). Also, Petermann et al. 1976; Dörner & Lang 1998 (a), (b) stated that the physical aging can increase crystallinity due to the incubation at a higher temperature which results in re- and/or post crystallization of the material from the chain-scission reaction.
Figure 3.1 The DSC curves for (a) unaged (b) 6 months aged geomembranes

Table 3.1, 3.2 and 3.3 show enthalpies, peak temperatures which are obtained from the DSC curve and crystallinity. Crystallinity was obtained from equation 2.1. The crystallinity of unaged samples is around 49% (Table 3.1). After 3 months of the thermal-oxidation process, the crystallinity increased from around 49% to around 51% for all samples except GM 1 thick (52.7%) (Table 3.2). In addition, these geomembrane samples have almost same crystallinities even if these geomembranes have different thicknesses and different percentages of antioxidants. The chain scission and recrystallization mechanisms can be responsible for this small crystallinity increase.
However, the value of crystallinity slightly decreased after 6 months of aging (Table 3.3). The crosslinking mechanism might be active as much as chain-scission and re-crystallization mechanisms. In addition, it cannot be seen any big differences in the value of the peak melting temperature.

Table 3.1 Results of Enthalpy, Peak Melting Temperature, and Crystallinity for unaged geomembrane

<table>
<thead>
<tr>
<th>Samples</th>
<th>Enthalpy (J/g)</th>
<th>Peak Melting Temperature (°C)</th>
<th>Crystallinity (Equation 2.1) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM 1 Thin</td>
<td>142.34</td>
<td>124.83</td>
<td>49</td>
</tr>
<tr>
<td>GM 1 Thick</td>
<td>143.37</td>
<td>125.68</td>
<td>49.4</td>
</tr>
<tr>
<td>GM2</td>
<td>142.26</td>
<td>126.15</td>
<td>49</td>
</tr>
<tr>
<td>GM 3</td>
<td>142.14</td>
<td>125.67</td>
<td>49</td>
</tr>
<tr>
<td>GM4</td>
<td>142.72</td>
<td>125.53</td>
<td>49.2</td>
</tr>
</tbody>
</table>

Table 3.2 Results of Enthalpy, Peak Melting Temperature, and Crystallinity for 3 months aged geomembrane

<table>
<thead>
<tr>
<th>Samples</th>
<th>Enthalpy (J/g)</th>
<th>Peak Melting Temperature (°C)</th>
<th>Crystallinity (Equation 2.1) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM 1 Thin</td>
<td>148.08</td>
<td>125.60</td>
<td>51</td>
</tr>
<tr>
<td>GM1 Thick</td>
<td>153.20</td>
<td>126.45</td>
<td>52.7</td>
</tr>
<tr>
<td>GM2</td>
<td>148.99</td>
<td>125.85</td>
<td>51.3</td>
</tr>
<tr>
<td>GM3</td>
<td>148.82</td>
<td>127.30</td>
<td>51.3</td>
</tr>
<tr>
<td>GM 4</td>
<td>147.64</td>
<td>125.76</td>
<td>50.9</td>
</tr>
</tbody>
</table>

Table 3.3 Results of Enthalpy, Peak Melting Temperature, and Crystallinity for 6 months aged geomembrane

<table>
<thead>
<tr>
<th>Samples</th>
<th>Enthalpy (J/g)</th>
<th>Peak Melting Temperature (°C)</th>
<th>Crystallinity (Equation 2.1) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM 1 Thin</td>
<td>148.10</td>
<td>125.62</td>
<td>51</td>
</tr>
<tr>
<td>GM1 Thick</td>
<td>144.98</td>
<td>125.12</td>
<td>49.9</td>
</tr>
<tr>
<td>GM2</td>
<td>145.81</td>
<td>127.71</td>
<td>50.2</td>
</tr>
<tr>
<td>GM3</td>
<td>146.91</td>
<td>126.35</td>
<td>50.6</td>
</tr>
<tr>
<td>GM 4</td>
<td>148.96</td>
<td>126.33</td>
<td>51.3</td>
</tr>
</tbody>
</table>
3.1.3 Tensile Test

The tensile test was performed to find changes of elongation and stress at yield and break for unaged and aged GM 1 sample. For unaged sample, the stresses and elongation at yield at the cross-machine direction and machine direction have similar values while elongation at the break at cross-machine direction (850%) is much higher than that of machine direction (692%) (Table 3.4). A similar response for both directions can be due to equal crystal orientation (Lu et al., 2001). However, some studies showed that the values of the stresses and elongations at yield and break at cross-machine direction and machine direction are different (Ewais, 2014; Lu et al., 2011; Krishnaswamy & Sukhadia, 2000). The reason can be uniaxial orientation of crystalline lamella. If the crystal orientation is formed perpendicular to machine direction, the soft amorphous phase can be dominant to determine properties of tensile test during applying stress in the machine direction (Figure 3.2.a). Also, the first possible deformation can be the lamellar separation which is limited by the presence of tie molecules in the polymer until yield. After yield, the main deformation mode is chain slip for crystalline phase (Lu et al., 2001). When the stress applies in the cross-section direction, the hard crystal phase can be dominant to determine properties of tensile test (Figure 3.2.b). In addition, lamellar separation, interlamellar shear and lamellar rotation which can be formed in the amorphous phase, can affect very little or nothing (Krishnaswamy & Sukhadia, 2000; Lu et al., 2001). The main mechanisms for crystalline phase are “the break-up of the crystalline lamellae, the pull-out of the chains from the lamella and the transverse slip” (Lu et al., 2001), are dominant in the cross-machine direction. Therefore, the break stress in the cross-machine direction is lower than that of in the machine direction. Also, the strain hardening, is strengthening in the amorphous phase during the large strain deformation, cannot be formed or formed a little in the cross-machine direction. In addition, the film in the cross-machine direction
can yield very small compared with the film in the machine direction (Lu et al., 2001). On the other hand, if the crystalline lamella perpendicular to cross-machine direction, the film in the machine direction can yield very small compared with the film in the cross-machine direction.

Figure 3.2 The applying stress in the machine direction (a), the applying stress in the cross-section direction (b)

In addition, the value of stress at yield and break for GM 1 thin is 16.8 MPa and 30.6 MPa for machine direction and 17.47 MPa and 30.38 MPa for cross-machine direction, respectively. These values of stress at yield and break are higher than literature for 0.5 mm HDPE and the values of similar to 1 mm thickness of HDPE geomembrane (Ewais, 2014; Ewais & Rowe, 2014; Rowe et al., 2010). The main reason can be smaller carbon black size, different antioxidants and production methods. Especially, smaller carbon black size can increase strength.

After 3 months of aging, the value of the elongation and stress at yield and break at both directions increased by around 10% due to re-crystallization. Also, the increasing strength may be
due to increasing crosslinking/chain branching during the especially early stage of aging. (Wong, 2014). The stress and elongation at break at cross-machine direction are also higher than that of machine direction after 3 months (Table 3.4). The differences in the lamella orientation between the cross-machine direction and machine direction can cause different properties in terms of elongation and stress. (Ewais, 2014).

After 6 months aging, especially stress at the break at cross-section direction unexpectedly decreased to 10.28 MPa while the stress at break at machine direction decreased around 10%. This unexpected decrease can be due to heterogenous oxidation or agglomeration. As stated above, HDPE geomembrane consists of amorphous and crystalline phases and the oxidation reaction is mainly into the amorphous phase because oxygen cannot easily diffuse the crystalline phase. Therefore, heterogenous oxidation can cause slight fluctuations for the result of tensile tests (Grassie and Scottt, 1985 as cited in Wong, 2011). In addition, another reason can be the agglomeration because the agglomeration of small size of carbon black can particularly occur in the polymer and this agglomeration can cause untimely (early) failure (Wong, 2011). Also, the elongation at yield for both directions decreased while the elongation at break for both directions increased. The values of elongation at breaks looks not stable, the reason can be crosslinking/branching during the degradation (Wong, 2011) because the mobility of polymer chain in the amorphous phase can be decreased by crosslinking reactions. This decreasing mobility cannot blunt sharp fatigue crack which can easy to propagate (Ries & Pruitt, 2005) That is to say, if there is any small crack, less energy is enough to propagate crack.

Wong (2011) explained that “The strength of polyethylene mainly correlates to the chain drawing of entanglement networks” (pp.34). In addition, the oxidation reaction can affect the changing molecular weight via chain scission and/or crosslinking and changing molecular weight
can significantly affect elongation. Therefore, it can be said that the tensile test can be an indicator of oxidation.

Table 3.4 The tensile results of unaged and aged GM 1 thin samples

<table>
<thead>
<tr>
<th>Tensile Properties (ASTM D6693)</th>
<th>Unaged</th>
<th>3 months aged</th>
<th>6 months aged</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress at a yield at a machine direction</td>
<td>16.8 MPa</td>
<td>18.25 MPa</td>
<td>16.57 MPa</td>
</tr>
<tr>
<td>Elongation at yield at machine direction</td>
<td>10.9 (%)</td>
<td>12.0 (%)</td>
<td>11.5 (%)</td>
</tr>
<tr>
<td>Stress at the break at machine direction</td>
<td>30.6 MPa</td>
<td>30.94 MPa</td>
<td>25.77 MPa</td>
</tr>
<tr>
<td>Elongation at break at machine direction</td>
<td>692.6 (%)</td>
<td>804 (%)</td>
<td>895.38 (%)</td>
</tr>
<tr>
<td>Modulus at machine direction</td>
<td>644 MPa</td>
<td>365 MPa</td>
<td>329 MPa</td>
</tr>
<tr>
<td>Stress at yield at the cross-machine direction</td>
<td>17.47 MPa</td>
<td>18.9 MPa</td>
<td>17.17 MPa</td>
</tr>
<tr>
<td>Elongation at yield at cross-machine direction</td>
<td>10.3%</td>
<td>13.1%</td>
<td>8.8 %</td>
</tr>
<tr>
<td>Stress at break at cross-machine direction</td>
<td>30.38 MPa</td>
<td>34.49 MPa</td>
<td>10.28 MPa</td>
</tr>
<tr>
<td>Elongation at break at cross-machine direction</td>
<td>850 (%)</td>
<td>910.3 (%)</td>
<td>710 (%)</td>
</tr>
<tr>
<td>Modulus at cross-machine direction</td>
<td>756 MPa</td>
<td>405 MPa</td>
<td>631 MPa</td>
</tr>
</tbody>
</table>
Figure 3.3a and b show the geomembrane samples before tensile tests and after the break. Figure 3.1 shows that the material was cut as a shape of a dog bone structure before the tensile test. After running the experiment, it can be easily seen the elongation of geomembrane.

Figure 3.3 The shape of geomembrane samples before tensile tests (a) and geomembrane sample after the break (b)

3.1.4 Melt Index Test

Melt index values provide information on molar mass related phenomena. MFI is a measure of the ability of the material to flow under pressure and relates to melt viscosity. The MFI has an inverse relationship to melt viscosity under the conditions on the test. The viscosity measurement is dependent on the applied force. An increase in the MFI indicates a decrease in the molar mass (due to chain scission reaction) and in the viscosity and hence the material flows easier. In the same way, a decrease in MFI can signify that crosslinking has occurred. The MI value is 0.17 g/10 mi for unaged and aged samples. During the six months of aging, there was not shown any changes in terms of the value of MI.
Park, Khan, & Jeon (2013) studied accelerated UV test for HDPE about 8 months and their Melt index values of virgin and exposed samples were the same. However, According to Wong (2011), the melt index value of geomembrane increased from 0.25 g/10 min to 0.35 g/10 min after 90 days aging in the oven while the values of melt index for geomembranes decreased from 0.25 g/10 min to around 0.13 g/10 min after 3 months of aging in the water incubation. For oven aging, the dominant degradation mechanism is chain scission because surface functional groups on carbon black react with hydroperoxide. After 3 months of water incubation, the crosslinking/branching was the major mechanism. Overall, the types and amounts of the antioxidants and external environment can affect MI values. Ewais (2014) explained that both the crosslinking and chain scission are seen during the oxidation of polyethylene.

In the geomembrane, 0.05% Irganox 168 was used to protect properties during the processing. This percentage can also be enough to help GM to maintain initial properties value of melt flow index test because the values did not change after 6 months of aging.

3.1.5 Fourier Transform Infrared (FTIR)

The peaks for all unaged geomembranes are at around 2914 to 2847, 1472 to 1462, and 729 to 718 which are related to anti-symmetric and symmetric stretching vibration, scissor vibration, and rocking modes of the CH$_2$ structures. This can be seen in Figure 3.4.

After aging, the outputs for polyethylene are the carbonyl compounds such as ketones, aldehydes, carboxylic acids, esters in the range of 1630 and 1750 cm$^{-1}$ (Wong, 2011, pp.21). To elucidate the oxidation degradation on the surface of geomembranes, FTIR was utilized to detect the existence of carbonyl compounds. The absorption peak of 1732 cm$^{-1}$ with C=O stretching and additional peaks of 1252, 1227, 1199, 1120, 1100 1021 945 cm$^{-1}$ with C-O were formed for all geomembrane’s surface.
Figure 3.4 The peaks for unaged geomembranes

Figure 3.5 The absorption peaks of 1732 cm$^{-1}$ for 6 months aged geomembranes,
In addition, to evaluate the extent of oxidation for all samples, the carbonyl index (I) calculated from using equation 2.2. These carbonyl index values from 0 to 180 days are indicated in Table 3.5. It can be seen that as incubation time increases, the value of the carbonyl index increases. In addition, after 180 days (6 months) incubation, the value of the carbonyl index (I) increased from 0.0384 to 0.382 for GM 1 thick; 0.0384 to 0.214 for GM 1 thin; 0.0398 to 0.392 for GM 2; 0.0851 to 0.455 for GM 3; 0.0515 to 0.535 for GM 4. According to these results, the extent of the oxidation is the lowest for thin GM 1 even if the others are thicker and/or have more antioxidants. The reason can be the quality of mixing of additives and the pressure and temperature and before and during the processing, respectively.

Table 3.5 The values of the carbonyl index (I) for the geomembrane samples at the days of 0, 45, 60, 90, 135 and 180 days

<table>
<thead>
<tr>
<th>Samples / Time (days)</th>
<th>0</th>
<th>45</th>
<th>60</th>
<th>90</th>
<th>135</th>
<th>180</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM 1 thick</td>
<td>0.038</td>
<td>0.146</td>
<td>0.211</td>
<td>0.189</td>
<td>0.334</td>
<td>0.382</td>
</tr>
<tr>
<td>GM 1 thin</td>
<td>0.038</td>
<td>0.084</td>
<td>0.126</td>
<td>0.139</td>
<td>0.182</td>
<td>0.217</td>
</tr>
<tr>
<td>GM 2</td>
<td>0.039</td>
<td>0.148</td>
<td>0.147</td>
<td>0.248</td>
<td>0.340</td>
<td>0.392</td>
</tr>
<tr>
<td>GM 3</td>
<td>0.085</td>
<td>0.3639</td>
<td>0.357</td>
<td>0.432</td>
<td>0.436</td>
<td>0.455</td>
</tr>
<tr>
<td>GM 4</td>
<td>0.051</td>
<td>0.1693</td>
<td>0.316</td>
<td>0.320</td>
<td>0.457</td>
<td>0.535</td>
</tr>
</tbody>
</table>

Though the values of the carbonyl index have big differences, there are no noticeable differences in terms of the values of the peak intensities of 1732 cm⁻¹ for 6 months aged geomembranes. It can be seen in Figure 3.5. In addition, the values of the peak intensities of 2850 cm⁻¹ for unaged and 6 months aged geomembranes are very different (Figure 3.6 a & b). The value of the absorbance peak of a methylene group (-CH₂-), symmetric stretching vibration decreased after 6 months. The value of 2850 cm⁻¹ bond decreased from 0.40 to 0.24 for GM 1 thin; from 0.31 to 0.14 for GM 1 thick; from 0.42 to 0.15 for GM 2; from 0.23 to 0.11 for GM 3;
from 0.35 to 0.09 for GM 4. In other words, GM 1 thin still has higher peak value of 2850 cm$^{-1}$ bond. Therefore, this higher peak intensity for GM 1 thin are more stable than other samples.

Figure 3.6 The peak intensities of 2850 cm$^{-1}$ for (a) unaged samples (b) 6 months aged samples
Figure 3.5, and 3.6 (a) and (b) show that there are small differences for the values of the peak intensities of 1732 cm\(^{-1}\) (C=O) while the peak values of 2850 cm\(^{-1}\) (CH\(_2\)) for all geomembranes are distinctive because of interactions of phenolic antioxidants, HALS and carbon black. These can cause to form other bonds. These other bonds which are C-N (1538, 1021 cm\(^{-1}\)), C=N (1567, 1327 cm\(^{-1}\)), N=N (1613 cm\(^{-1}\)), C-C (1567, 1388, 1170, 917 cm\(^{-1}\)), C=C (1613, 1483 cm\(^{-1}\)), C-H (1388, 1360, 1021, 917, 874, 744, 610 cm\(^{-1}\)), C-O-C (1084, 820 cm\(^{-1}\)), C-COOH (1084 cm\(^{-1}\)), CH\(_3\) (2955 cm\(^{-1}\)) and CH\(_2\) (1483, 1456, 1360, 1199, 945 cm\(^{-1}\)) were seen with using the FTIR (Figure 3.7) and these bonds values, assignments and references are given in Table 3.6.

![Figure 3.7 The absorbance of the geomembranes after 6 months](image_url)
<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>Structure</th>
<th>References</th>
<th>Wavenumber</th>
<th>Structure</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(cm(^{-1}))</td>
<td></td>
<td></td>
<td>(cm(^{-1}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1613</td>
<td>C=C stretching</td>
<td>Ghimire et al., 2019</td>
<td>1084</td>
<td>(\nu)C-COOH C-O (COO-) stretching,</td>
<td>Lefèvre, G., Preočanin, T., &amp; Lützenkirchen, J. (2012)</td>
</tr>
<tr>
<td>1483</td>
<td>CH(_2) scissoring</td>
<td>Rajendran, S., 2002</td>
<td>929</td>
<td>-CO stretching</td>
<td>Pang, S. F., Wu, C.</td>
</tr>
<tr>
<td>Wavenumber (cm⁻¹)</td>
<td>Structure</td>
<td>References</td>
<td>Wavenumber (cm⁻¹)</td>
<td>Structure</td>
<td>References</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------</td>
<td>------------</td>
<td>-------------------</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>Wavenumber (cm⁻¹)</td>
<td>Structure</td>
<td>References</td>
<td>Wavenumber (cm⁻¹)</td>
<td>Structure</td>
<td>References</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------</td>
<td>--------------------------</td>
<td>-------------------</td>
<td>------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>1199</td>
<td>CH2 bend</td>
<td>Jung et al. (2018)</td>
<td>508</td>
<td>CC skeletal bending</td>
<td>Bolbasov et al. (2014).</td>
</tr>
<tr>
<td></td>
<td>C-O stretching</td>
<td>Ghorpade et al. (2019)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1120</td>
<td>C-O stretching</td>
<td>Lewis et al. (2010).</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In addition, among these all peaks, it can be seen that three prominent peaks which are 1613, 1567 and 1360 cm⁻¹ were formed after 6 months of aging. Moreover, the absorbance peak of 1613 cm⁻¹ can be C=C (Ghimire et al., 2019; Medina et al., 2017; Sun et al., 2017), C=O (Abnoos et al., 2018; Kailasan et al., 2010); the absorbance peak of 1567 cm⁻¹ can be carboxy-late groups, O=O− (Mitra et al., 2006), C=C (Medupin et al., 2017; Sun et al., 2017) or N-H (Yamina et al., 2018), carbonyl groups of COO− anion (Moini et al., 2019); the absorbance peak of 1360 cm⁻¹ can be CH₂ wagging mode (Ye et al., 2013), C-H deformation mode (Surov et al., 2018). These prominent and other peaks which are mostly formed with carbon bonds can be formed after interaction between carbon black and antioxidants. The antioxidants tend to react with carbon surface instead of free radicals because the surface of carbon black is a strong acceptor (Wong & Hsuan, 2014). Although the low adsorption potential of Irganox 1330 onto carbon black (Scheirs 2009), the negative interactions were seen with an especially higher concentrations of antioxidants.
Therefore, the lower performance can be expected for especially GM 3 and GM 4 because of higher concentrations of phenolic antioxidants and HALS, respectively.

3.1.6 Scanning Electron Microscopy/ Energy Dispersive X-ray Spectroscopy (SEM/EDS)

The SEM images (Figure 3.8) show the surface of unaged and aged geomembranes. The surface of the unaged geomembrane is quite smooth while the roughness increased after 6 months. Also, the fine particulars were seen the first time on the surface of geomembranes after 3 months of degradation. These can be seen in Figure 3.8 (c). It is expected that the percentage of Irganox 1330 (low molecular weight phenolic antioxidant) exceeded the solubility limit of the polymer. Therefore, the super-saturated condition gives rise to blooming and phase separation on the GM surface (Wong, 2014).

![Figure 3.8 GM surface for unaged sample (a), GM surface after 6 months aging (b), the particulars on the GM surface (c)](image-url)
Table 3.7 shows the EDS result of geomembranes. Mostly carbon and oxygen atoms were detected, and the gold element was also detected around 0.1 wt.% because of gold coating for geomembranes before SEM and EDS. It is predicted and seen that the oxygen percentage increased after aging.

Table 3.7 Surface compositions of the surface of unaged and 6 months aged geomembranes with EDS

<table>
<thead>
<tr>
<th>Unaged Geomembranes</th>
<th>Carbon (wt %)</th>
<th>Oxygen (wt %)</th>
<th>6 months aged geomembranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM 1 Thin</td>
<td>98.85</td>
<td>1.15</td>
<td>GM 1 Thin</td>
</tr>
<tr>
<td>GM 1 Thick</td>
<td>96.92</td>
<td>3.08</td>
<td>GM 1 Thick</td>
</tr>
<tr>
<td>GM 2</td>
<td>97.12</td>
<td>2.28</td>
<td>GM 2</td>
</tr>
<tr>
<td>GM 3</td>
<td>95.68</td>
<td>4.32</td>
<td>GM 3</td>
</tr>
<tr>
<td>GM 4</td>
<td>93.4</td>
<td>6.6</td>
<td>GM 4</td>
</tr>
</tbody>
</table>

3.1.7 X-ray Photoelectron Spectroscopy (XPS)

The high-resolution carbon s1 XPS was performed to measure the percentage of C-C, C-O-C and O-C=O bonds on the surface of geomembrane. The mixture of a Gaussian and a Lorentzian and Shirley methods are used to fit C 1s peaks for polymer (Marcondes et al., 2004). The binding energy of 284.4 eV, 285.6 eV and 287.8 eV can be attributed to C-C, C-O and C=O or C-O-C chemical bonds on the surface of the GM 1 thin, respectively (Figure 3.9a and b) (Hamzah et al., 2018). According to Figure 3.9, the increasing C-O and C=O or O-C-O bonds can be seen easily. Also, the area ratio of the peaks can give information about the percentage of carbon bonds on the surface. Therefore, XPS can be at least semi-quantitative analysis (Desimoni & Brunetti, 2015). Table 3.8 shows that single or double bonds between carbon and oxygen on the surface of geomembrane increased significantly due to the degradation.
Figure 3.9 The high-resolution C 1s spectrum of the GM 1 thin (a) before and (b) after thermal aging at 85 °C in air for 6 months

Table 3.8 The approximate results of high-resolution carbon 1s XPS analyses (%)

<table>
<thead>
<tr>
<th>Samples</th>
<th>C-C (%)</th>
<th>C-O (%)</th>
<th>C=O or O-C=O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unaged GM 1 thin</td>
<td>85.8</td>
<td>9.4</td>
<td>4.8</td>
</tr>
<tr>
<td>6 months aged GM 1 thin</td>
<td>67</td>
<td>24.3</td>
<td>8.7</td>
</tr>
</tbody>
</table>
3.1.8 Thermogravimetric Analysis (TGA)

This work presents results from TGA tests conducted in HDPE geomembranes after aging in order to assess the degradation process concerning the total mass loss of geomembranes. Table 3.9 shows polymer, residual mass and onset temperatures for unaged and 6-months aged geomembranes. The polymer and residual mass were obtained by the software of TGA. After 6 months of the aging period, it can be clearly seen that the percentage of residual mass decreased. The decreasing residual mass can be due to forming volatile fragments such as carbonyl groups because of thermal-oxidative degradation (Tisinger & Carraher, 1990). According to Lodi & Bueno (2012), fresh HDPE geomembrane (0.8 and 2.5 mm) and HDPE geomembranes (0.8 and 2.5 mm) that exposed to 30 months of weathering and leachate showed the similar value of the residual mass (carbon black) between 0.08 and 1.72%. These values for geomembranes are quite lower than ASTM standards.

In addition, the onset (initial degradation) temperatures \( (T_{5\%}) \) for all unaged geomembranes are lower than that of 6-months aged geomembranes. The Table 3.10 and Figure 3.10 and 3.11 show that the range of onset temperatures after 6 months aging slightly increased by between 2\(^{\circ}\)C and 20\(^{\circ}\)C while Lodi & Bueno (2002) measured that the initial degradation of temperature for unaged HDPE geomembranes (0.8 mm) is around 420\(^{\circ}\)C and this value increased to 440 and 480\(^{\circ}\)C after 30 months weathering and under the leachate. The increasing initial degradation temperatures for 6 months aged geomembranes are less than 30 months exposed HDPE and PVC geomembranes in the literature (Lodi & Bueno, 2002) because of different materials, long time period and the different aging processes. During the thermal-oxidative aging, decomposition, crosslinking and generation of low molecular volatile products can be occurred in the polymer (Muller, 2007). Especially, “the beginning of the oxidation, branching and crosslinking of the long polymer chains
dominate.” (Muller 2007, pp. 155). Therefore, the onset temperatures for aged geomembranes can be higher than that of unaged geomembranes. Also, it can be said that the thermal oxidative aging provided better thermal stability (Zhang et al., 2017).

Figure 3.10 TGA results for unaged geomembranes (a) at a temperature between 0 and 600°C (b) at a temperature between 400 to 500°C
Figure 3.10 (b) and 3.11 (b) show TGA results between the temperature of 400 and 500°C to clearly see onset temperatures and decomposition for unaged and aged geomembranes, respectively. In addition, there are not seen any significant differences between unaged geomembranes.

Figure 3.11 TGA results for aged geomembranes (a) at a temperature between 0 and 600°C (b) at a temperature between 400 to 500°C
### Table 3.9 TGA results for unaged and aged geomembranes

<table>
<thead>
<tr>
<th>Unaged Geomembranes</th>
<th>Polymer (%)</th>
<th>Residual mass (%)</th>
<th>Onset Temp. (°C)</th>
<th>6 months aged Geomembranes</th>
<th>Polymer (%)</th>
<th>Residual mass (%)</th>
<th>Onset Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM 1 thin</td>
<td>96.5898</td>
<td>3.41</td>
<td>434</td>
<td>GM 1 thin</td>
<td>97.2384</td>
<td>2.77</td>
<td>436</td>
</tr>
<tr>
<td>GM 1 thick</td>
<td>96.7157</td>
<td>3.29</td>
<td>432</td>
<td>GM 1 thick</td>
<td>97.27</td>
<td>2.73</td>
<td>437</td>
</tr>
<tr>
<td>GM 2</td>
<td>96.5088</td>
<td>3.5</td>
<td>421</td>
<td>GM 2</td>
<td>97.40</td>
<td>2.6</td>
<td>435</td>
</tr>
<tr>
<td>GM 3</td>
<td>94.4896</td>
<td>5.52</td>
<td>430</td>
<td>GM 3</td>
<td>96.782</td>
<td>3.22</td>
<td>440</td>
</tr>
<tr>
<td>GM 4</td>
<td>96.8937</td>
<td>3.11</td>
<td>420</td>
<td>GM 4</td>
<td>97.4884</td>
<td>2.52</td>
<td>439</td>
</tr>
</tbody>
</table>

Although all geomembranes were produced with the same percentage of carbon black, the percentage of residual mass (carbon black and ash) is not the same for unaged geomembranes (Table 3.10) the reason can be the amount of ash or agglomeration because the mixing small size of carbon black is very difficult and carbon black can agglomerate with other carbon black molecules. Therefore, the agglomeration can cause an ununiform structure in the geomembranes.
Chapter 4 Conclusion

This study has focused on chemical, physical and mechanical properties of geomembranes keeping in view of the properties after manufacturing and during and after 6 months of aging processes. Attempts were made to prepare five geomembranes; where two of them had the same compositions but different thicknesses and three of them had different compositions.

The geomembranes were produced with the same percentages of carbon black and hindered phosphite and the different percentages of phenolic antioxidants and HALS. During the processing, the take up ratio and stress histories affected the properties of geomembranes. In addition, different percentage of phenolic antioxidants and HALS interacted with carbon black in the geomembranes during the degradation process. The properties of geomembranes after processing and during and after 6 months of aging were studied.

The crystallinities increased from nearly 49% to around 51% for different thicknesses and compositions of geomembranes. It should not be realized any big differences after manufacturing while there is a small difference after degradation. The dominant mechanisms are recrystallization at elevated temperature and chain scission after 3 months of thermal-oxidative degradation. However, the crystallinities have decreased slightly after 6 months of degradation. The cross-linking after 3 months is also dominant. However, it is imperative that all of the chain-scission, crosslinking and recrystallization are active during the thermal-oxidative degradation in geomembranes.
Melt index values of geomembranes have been unaffected by thickness and stress and thermal histories during manufacturing and 3 months of aging because of enough percentage of hindered phosphite.

Even if the melt index value is shown the same value, the yield and break strengths have increased around 10% for GM 1 thin after 3 months of aging. The increasing strength can be due to the cross-linking and re-crystallization reactions, but the elongation is interestingly increased due to re-crystallization. However, the value of tensile tests for GM 1 thin is dropped sharply and early failure is seen after 6 months of aging because of the possibilities of agglomeration and small crack because of small size of carbon black and increasing crosslinking mechanism.

The value of Carbonyl index number after manufacturing is the same for the same compositions and different thickness but the value of the carbonyl index for GM3 and GM4 are higher than others. The carbonyl value of GM 4 is still higher than other geomembranes because of high concentration of phenolic antioxidants and HALS while GM 1 thin is shown the lowest carbonyl index value after 6 months of degradation. Therefore, GM 1 thin is more stable than other samples.

After 6 months of aging, surfaces of geomembranes have no big differences. However, the blooming is seen after 3 months of aging because the increasing crystallinity can reduce solubility limit and a high percentage of antioxidants can exceed the solubility limit. Also, having low molecular weight of antioxidants can diffuse easily from center to surface.

The onset temperature for geomembranes increased after aging can start to degrade later than unaged geomembranes. That is to say, the thermal stability increased after aging. In addition, after aging, the percentage of residual mass is different because of forming carbonyl groups, some
volatile groups from the oxidative degradation, and the negative interactions between carbon black, phenolic antioxidants and HALS based materials.

The interactions of small carbon black, antioxidants and HALS have provided high strength and elongation while these interactions can be caused forming some additional volatilize compounds and increasing the carbonyl index and carbon-oxygen bonds.

For future studies:

6 months of accelerated aging cannot be enough to evaluate geomembranes in the field conditions because the service life is longer than 100 years. In addition, to estimate service life for geomembranes, HP-OIT and Std-OIT test can be performed.

Different sizes of carbon black and different percentages and kinds of antioxidants can be used to decrease antagonistic effects and increase mechanical properties and service life.

High pressure at low temperature can be used to accelerate oxidation without thermal effects.
References


density nanocluster polyethylene under natural weathering: A spectroscopic investigation.


Lefèvre, G., Preočanin, T., & Lützenkirchen, J. (2012). Attenuated total reflection-infrared spectroscopy applied to the study of mineral-aqueous electrolyte solution interfaces: a general overview and a case study. Infrared spectroscopy-materials science, engineering and technology, 1, 97-122.


Mishra, R., Sapra, B. K., Rout, R. P., & Prajith, R. (2016). Probing the application of Fourier Transform Infrared (FTIR) spectroscopy for assessment of deposited flux of Radon and


Rowe, R. K., Rimal, S., Arneppalli, D. N., & Bathurst, R. J. (2010). Durability of fluorinated high
density polyethylene geomembrane in the Arctic. *Geotextiles and Geomembranes, 28*(1),
100-107.

Rowe, R. K., & Sangam, H. P. (2002). Durability of HDPE geomembranes. *Geotextiles and
Geomembranes, 20*(2), 77-95.


Sangam, H. P., & Rowe, R. K. (2002). Effects of exposure conditions on the depletion of
antioxidants from high-density polyethylene (HDPE) geomembranes. *Canadian
Geotechnical Journal, 39*(6), 1221-1230.


synthesis of MnFe2O4 hollow nanospheres and their photocatalytic degradation of benzene
investigated by in situ FTIR. *Catalysis Communications, 68*, 11-14.

geosynthetics*.

films reinforced by cellulose nanocrystals: Microstructure-properties relationship.
*Carbohydrate polymers, 181*, 489-498.


