

Effect of Texturing on Antioxidant Depletion Rate from HDPE Geomembranes

Effet de texturation sur l'épuisement des antioxydants de polyéthylène haute densité géomembrane

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ABSTRACT: The long term performance of smooth geomembranes has been studied extensively in various geoenvironmental applications. However, the long term performance of textured geomembranes has never been studied. The objective of this study is to explore the effect of texturing on antioxidant depletion from a geomembrane. Textured and smooth high density polyethylene (HDPE) geomembranes made from the same resin and antioxidant package are immersed in a synthetic municipal solid waste leachate at different temperatures. The preliminary results of standard oxidative induction time test suggest that textured geomembranes have 15% shorter time to antioxidant depletion.

RÉSUMÉ : La performance à long terme des géomembranes lisses a été largement étudiée dans diverses applications géoenvironnementales. Cependant, la performance à long terme des géomembranes texturées n'a jamais été étudiée. L'objectif de cette étude est d'explorer l'effet de texturation sur l'épuisement de l'antioxydant de la géomembrane. Dans cette étude, les géomembranes polyéthylène de haute densité texturées et lisses, fabriquées à partir de la même résine et du même ensemble d'antioxydants, sont immergées dans du lixiviat synthétique produit de déchets solides à différentes températures. Les résultats préliminaires de l'essai de temps d'induction oxydatif standard suggèrent que les géomembranes texturées ont 15% plus court temps de l'épuisement des antioxydants.

KEYWORDS: HDPE geomembranes, texturing, antioxidant depletion.

1 INTRODUCTION

Texturing is a technique for roughening the surface of geomembrane (GMB) to increase the interface friction angle between the GMB and the materials in direct contact (Koerner 2005, Müller 2007, Scheirs 2009). Textured GMBs are mostly used in slopes to decrease the risk of sliding of barrier systems down slope although some engineers consider it desirable/convenient to also use textured GMBs on the base as well. There are different methods for texturing GMBs: (a) injection of a blowing agent, (b) structured texturing, and (c) impingement texturing.

Blown film co-extrusion with a blowing agent is a common texturing technique in North America. Physical blowing agents are inert gases injected into polymers without chemical reaction with the polymer. The process of texturing using this technique is: (a) feeding polymer to three co-extrusion dies and injecting a blowing agent (nitrogen) into the outer layer(s) of molten polymer, (b) on extrusion from the die, the nitrogen gas bubbles cool and rupture, and texture is formed (Erickson et al. 2008, Scheirs 2009). This technique has some disadvantages such as, irregular texturing, variability in asperity heights, variable core thickness, and a reduction in mechanical properties of GMB (Scheirs 2009).

Another texturing technique is structured texturing (embossed texturing) where the surface layers are impressed with a roller which creates a structured pattern along the GMB. The advantages of this technique compared to the aforementioned one is that it has a limited effect on the tensile properties of GMB. However, textured GMBs produced by this method have lower interface shear strength at low stress levels compared to the co-extrusion technique (Erickson et al. 2008). The closer the asperities in the structured textured GMBs, the better the interlocking with geotextile (GTX) in contact (Bacas et al. 2015).

The third texturing technique is impingement texturing, where atomized polyethylene is sprayed on base smooth GMB. Smaller and shorter asperities are created by this texturing method in comparison with aforementioned techniques which results in less interface shear resistance (Erickson et al. 2008).

For co-extruded GMBs, the interface shear between textured GMBs and other materials in contact (e.g., GCLs, soils, GTX) is achieved by hook and loop cohesion under the effect of low normal stresses, while the interface shear is frictional under the effect of high normal stresses (Erickson et al. 2008). The texturing degree/asperity height affects the interface shear strength. Laboratory test results show that textured GMBs provide higher interface shear strength compared with smooth GMBs (Stark et al. 1996, Jones et al. 1998). The interface friction of sand with rounded particles is affected by the roughness of the geomembrane surface more than sand with angular grains (Izgin et al. 1998). GMB-GTX peak interface shear stresses are mobilized at larger displacements for textured GMBs compared with smooth GMBs (Jones et al. 1998). The interface shear between textured GMB and NWNP GCL, in direct shear test, increased by 30-35 % as a result of increasing the asperity height by 0.017 mm (0.7 mils; Thiel 2001). The peak shear strength is proportional to the asperity height for an unhydrated GCL and clay-GMB interfaces. If the asperity height is more than a certain value, the large displacement interface shear strength decreases because asperity breakage is easier (Ivy 2003, MaCartney et al. 2005). Increasing the asperity height results in reducing the uniaxial and multiaxial tensile strength and break elongation (Ivy 2003, Erickson et al. 2008). Selection of an appropriate asperity height requires a balance between increasing the interface shear and reducing the tensile properties. Barroso et al. (2008) studied the effect of texturing of the GMB on the transmissivity of a GMB-GCL interface. Their results indicated that the transmissivity of smooth GMB was higher than of the textured GMB until a steady state flow was reached at a point when the texturing had smaller effect on transmissivity. Although, the aforementioned studies investigated the effect of texturing on the interface shear strength, and transmissivity, there are no studies in the literature dealing with the long-term performance of textured GMBs used in different geoenvironmental applications.

As the initial part of a broader study of the effect of texturing on GMB long-term performance, the objective of this paper is to compare antioxidant depletion for a textured and a smooth GMB made with the same Chevron K306 resin, antioxidant package, and nominal thickness.

2 EXPERIMENTAL INVESTIGATION

2.1 Accelerating aging and incubation media

The accelerating aging of the GMBs was investigated by immersion of 190 x 95 mm GMB coupons in 4-liter glass jars filled with the synthetic municipal solid waste (MSW) leachate (Tables 1a & 1b). The jars were incubated in forced air ovens at temperatures of 40, 55, 75, and 85°C. GMBs were incubated at the higher temperatures to allow an estimate of the antioxidant depletion rate and time and subsequent geomembrane degradation in a shorter incubation period than is possible at lower temperatures.

The synthetic MSW leachate used in this study (pH=7.04±0.22) has components similar to those found in leachate samples collected from the Keele Valley landfill in Ontario, Canada (Rowe et al. 2008). The leachate's components are (Table 1a): inorganic/organic nutrients, surfactant, and inorganic trace metal solutions (Table 1b). Industrial surfactant (IGEPAL ® CA720) is used to simulate the aggressive effect of detergents found in the MSW. The leachate is reduced by sodium sulphide at a concentration 3% w/v to simulate the reduced anaerobic leachate (Eh= -120 mV) in MSW landfills (Rowe et al. 2008). Sulfuric acid of concentration 5 ml/L of water is used to adjust the pH of leachate to 7. This leachate is considered to be a relatively aggressive MSW leachate with respect to the long-term performance of GMBs and antioxidant depletion and degradation may be slower in less aggressive solutions (Abdelal et al. 2014).

Table 1a. Chemical composition of leachate used in this study.

| Component | Formula | Amount |
|--------------------------------------|--------------------------------------|--------|
| Inorganic/organic nutrients | | |
| Sodium hydrogen carbonate (g/L) | NaHCO ₃ | 3.012 |
| Calcium chloride dehydrate (g/L) | CaCl ₂ | 2.882 |
| Magnesium chloride (g/L) | MgCl ₂ •6H ₂ O | 3.114 |
| Magnesium sulfate heptahydrate (g/L) | MgSO ₄ •7H ₂ O | 0.319 |
| Ammonium hydrogen carbonate (g/L) | NH ₄ HCO ₃ | 2.439 |
| Urea (g/L) | CO(NH ₂) ₂ | 0.695 |
| Sodium nitrate (g/L) | NaNO ₃ | 0.05 |
| Potassium carbonate (g/L) | K ₂ CO ₃ | 0.324 |
| Potassium hydrogen carbonate (g/L) | KHCO ₃ | 0.312 |
| Potassium dihydrogenphosphate (g/L) | K ₂ HPO ₄ | 0.03 |
| Trace metal solution (ml/L) | -- | 1 |
| Surfactant (ml/L) | -- | 5 |
| Sodium sulphide nonahydrate (ml/L) | -- | 0.91 |
| Sulfuric acid (ml/L) | H ₂ SO ₄ | 0.7 |

2.2 GMB examined

The textured black HDPE GMB was manufactured in 2015. The resin was textured using blown film co-extrusion with a blowing agent texturing technique. Textured GMB rolls have a major textured portion and minor smooth edge for welding. ASTM index tests were conducted to estimate the initial properties of the textured and smooth portion of the GMB from the same roll (Table 2). Differential scanning calorimetry detected the oxidative induction time (OIT) of the GMB in terms of

Std-OIT (ASTM D3895) and HP-OIT (ASTM D5885). The physical and mechanical properties tested were melt flow index (ASTM D1238) and tensile properties (D6693). At least six specimens were tested to estimate the initial properties of the GMB. The texturing resulted in a 32 % and 34 % reduction in the break strength and strain of the GMB, respectively. The asperity height is variable in co-extrusion with a blowing agent because the process of nitrogen gas escape (rupture of bubbles) on cooling is uncontrolled (Ivy 2003). This means that the core thickness is variable across the GMB's roll. In addition, variations in asperity height means uneven stress distribution/concentration in GMB that affect the tensile properties of the GMB. In this paper the textured and smooth portion of the GMB roll are referred as textured and smooth GMB respectively.

Table 1b. Chemical composition of traced metal solution used in this study.

| Component | Formula | Amount |
|---|---|--------|
| Ferrous Sulfate (mg/L) | FeSO ₄ •7H ₂ O | 2000 |
| Boric Acid (mg/L) | H ₃ BO ₃ | 50 |
| Zinc sulfate heptahydrate (mg/L) | ZnSO ₄ •7H ₂ O | 50 |
| Cupric sulfate, Pentahydrate (mg/L) | CuSO ₄ •5H ₂ O | 40 |
| Manganous sulfate monohydrate (mg/L) | MnSO ₄ •H ₂ O | 500 |
| Ammonium Molybdate Tetrahydrate (mg/L) | (NH ₄) ₆ Mo7O ₂₄ •4H ₂ O | 50 |
| Aluminum Sulphate, 16-Hydrate (mg/L) | Al ₂ (SO ₄) ₃ •16H ₂ O | 30 |
| Cobaltous Sulphate, Heptahydrate (mg/L) | CoSO ₄ •7H ₂ O | 150 |
| Nickel (II) Sulfate (mg/L) | NiSO ₄ •6H ₂ O | 500 |
| Sulfuric Acid +96% purity (ml/L) | H ₂ SO ₄ | 1 |

3 BACKGROUND

Polyethylene GMBs can be affected by different degradation mechanisms such as, thermal degradation, photo degradation, radioactive degradation, and oxidative degradation (Rowe and Sangam 2002, Koerner 2005, Müller 2007, Hsuan et al. 2008, Scheirs 2009). Oxidative degradation is considered the most critical degradation mechanism for buried polyethylene geomembranes (Hsuan and Koerner 1995, Hsuan et al. 2008). Antioxidants are added to GMBs to retard the onset of oxidation reactions. Antioxidant depletion depends on type, amount, and distribution of antioxidants in GMB, incubation temperature, and fluid in contact with GMB.

4 RESULTS AND DISCUSSION

Std-OIT tests (ASTM D3895) were performed using a differential scanning calorimeter (DSC). The Std-OIT depletion time was 2.5 months, and 3 months for the textured and smooth GMBs, respectively at 85°C (Figure 1). At a temperature of 75°C, the Std-OIT depletion time was 6 months and 7 months for the textured and smooth GMBs, respectively (Figure 2). Although the regression of normalized Std-OIT vs incubation time curves for textured and smooth GMBs coincide, the

antioxidant depletion time for the textured GMB was shorter than for the smooth GMB. The antioxidant depletion times for the textured GMB were 0.83 and 0.85 times that of smooth GMBs at 85°C and 75°C, respectively. This is attributed to the textured GMB's surface area being greater than that for the smooth GMB which increases the area exposed to fluid and hence antioxidant depletion for the mobile antioxidants detected by the Std-OIT test.

Table 2. Initial properties of tested GMB.

| Property | Method | Textured | Smooth |
|--|------------|-------------|-------------|
| Designator | -- | MxT | MxS |
| Core thickness ^a (mm) | ASTM D5994 | 1.50 | 1.50 |
| Asperity height ^a (mm) | ASTM D7466 | 0.43 | 0.00 |
| Color | -- | Black | Black |
| Resin density ^a (gm/cm ³) | ASTM D1505 | 0.937 | 0.937 |
| GMB density ^a (gm/cm ³) | ASTM D1505 | 0.947 | 0.947 |
| Std-OIT ^a (minutes) | ASTM D3895 | 184.5±9.5 | 184.5±9.5 |
| HP-OIT ^a (minutes) | ASTM D5885 | 1584±94 | 1584±94 |
| HLMI ^b (21.6kg) (g/10min) | ASTM D1238 | 13.3±0.3 | 13.3±0.3 |
| LLMI ^c (2.16kg) (g/10min) | ASTM D1238 | 0.107±0.002 | 0.115±0.002 |
| Flow rate ratio ^d | ASTM D1238 | 124 | 116 |
| Tensile break strength ^a (kN/m) | ASTM D6693 | 40.6±5.1 | 58.9±4.5 |
| Tensile break strain ^a (%) | ASTM D6693 | 502±63.6 | 768±38.9 |

^a Provided by GMB manufacturer, ^b High load melt index, ^c Low load melt index, ^d HLMI/LLMI.

5 CONCLUSIONS

The performance of a textured and smooth HDPE GMB made from the same resin and antioxidant package was assessed by immersing the GMBs' samples in synthetic MSW leachate. The results of Std-OIT give a preliminary indication on the effect of texturing on the antioxidant depletion time for the mobile antioxidants detected by the Std-OIT test. Based on the results presented herein, the following preliminary conclusions have been reached:

- The Std-OIT depletion time for the textured GMB was less than for the smooth GMB.
- Texturing of GMB surface results in approximately 15 % reduction of Std-OIT depletion time based on the results presented in this paper at 75°C and 85°C.

This paper has focused on the antioxidants detected by Std-OIT and depletion at temperatures of 75°C and 85°C. Results of Std-OIT depletion with time at lower temperatures is needed to enhance the understanding of the effect of texturing on antioxidant depletion time. In addition, some antioxidants and stabilizers are not detected by the Std-OIT test. To fully

understand the effect of texturing, there is a need to also consider the depletion of the antioxidants and stabilizers detected by the HP-OIT test. These studies are in progress and the depletion of antioxidants at 40 and 55°C based on the Std-OIT test, and the depletion of other antioxidants and stabilizers detected by the HP-OIT test will be reported in a subsequent paper, when available.

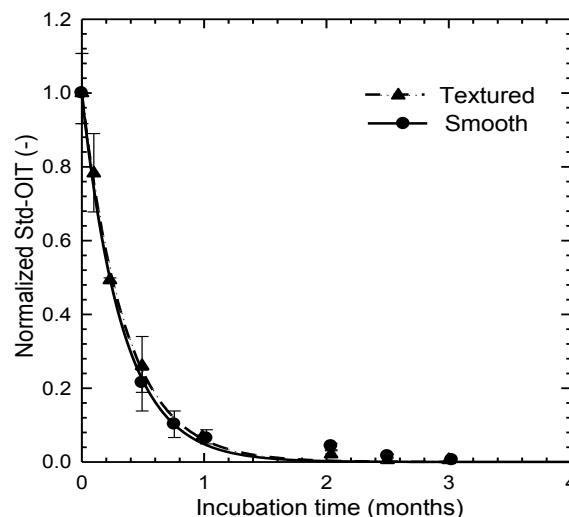


Figure 1. Normalized Std-OIT vs incubation time for textured and smooth GMBs at 85°C.

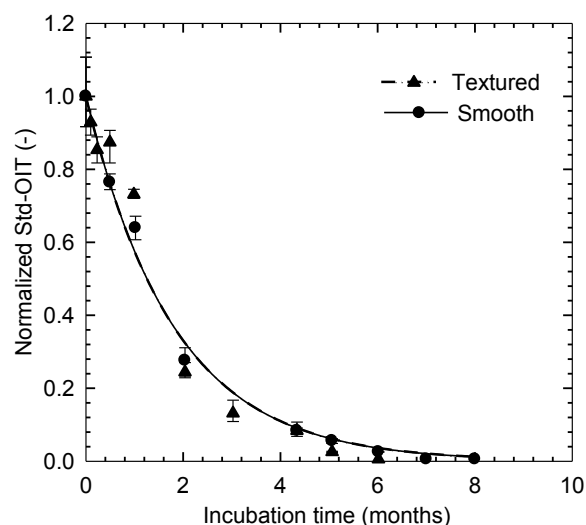


Figure 2. Normalized Std-OIT vs incubation time for textured and smooth GMBs at 75°C.

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6 REFERENCES

Abdelaal F.B., Rowe R.K., and Islam M.Z. 2014. Effect of leachate composition on the long term performance of a HDPE geomembrane. *Geotextiles and Geomembranes* 42(4), 348-362.

- ASTM 2004. Standard test method for determining tensile properties of nonreinforced polyethylene and nonreinforced flexible polypropylene geomembranes. American Society for Testing and Materials *D6693*, West Conshohocken, PA.
- ASTM 2006. Standard test method for oxidative induction time of polyolefin geosynthetics by high pressure differential scanning calorimetry. American Society for Testing and Materials *D5885*, West Conshohocken, PA.
- ASTM 2007. Standard test method for oxidative induction time of polyolefins by differential scanning calorimetry. American Society for Testing and Materials *D3895*, West Conshohocken, PA.
- ASTM 2010. Standard testing method for density of plastics by density gradient technique. American society for testing and materials *D1505*, West Conshohocken, PA.
- ASTM 2010. Standard test method for measuring core thickness of textured geomembranes. American society for testing and materials *D5994*, West Conshohocken, PA.
- ASTM 2010. Standard test method for measuring asperity height of textured geomembranes. American society for testing and materials *D7466*, West Conshohocken, PA.
- ASTM 2013. Standard test method for melt flow rates of thermoplastics by extrusion plastometer *D1238*, West Conshohocken.
- Bacas M.B., Cañizal J., and Komietzky H. 2015. Shear strength behavior of geotextile/geomembrane interfaces. *Journal of Rock Mechanics and Geotechnical Engineering* 7 (6), 638- 645.
- Barroso M.P., Foltz N.I., and Maubeuge K.V. 2008. Influence of the textured structure of geomembranes on the flow rate through geomembrane-GCL composite liners. *Proceedings of the 4th European conference on geosynthetics*. Edinburgh, Ireland, paper No.86.
- Erickson R.B., Thiel, and R.S., Peters, J. 2008. The ongoing quality issues regarding polyethylene geomembrane material manufacturing and installation. *Proceedings of The First Pan American Geosynthetics Conference and Exhibition*. Cancun, Mexico.
- Hsuan, Y., and Koerner, R. 1995. Long-term durability of HDPE geomembrane. Part 1: Depletion of antioxidant, Geosynthetic Research Institute, Philadelphia, USA, *GRI Report 16*, 35p.
- Hsuan Y.G., Schroeder H.F., Rowe K.R., Müller W., Greenwood J., Cazzuffi, D., and Koerner R.M. 2008. Long term performance and lifetime prediction of geosynthetics. *Proceedings of the 4th European conference on geosynthetics*. Edinburgh, Ireland.
- Ivy N. 2003. Asperity height variability and effects. *GFR* 21(8), 28-29.
- Izgin M., and Wasti Y. 1998. Geomembrane-sand interface frictional properties as determined by inclined board and shear box tests. *Geotextiles and Geomembranes* 16(4), 207-219.
- Jones D.R.V., and Dixon, N. 1998. Shear strength properties of geomembrane/geotextile interfaces. *Geotextiles and Geomembranes* 16 (1), 45-71.
- Koerner, R.M. 2005. *Designing with geosynthetics*. Fifth Ed., Pearson Prentice hall.
- McCartney JS, Zornberg JG, and Swan RH. 2005. Effect of geomembrane texturing on GCL-geomembrane interface shear strength. *Proceedings of GeoFrontiers 2005*. Reston, VA, USA: American Society of Civil Engineers (ASCE), 1-11.
- Müller, W. 2007. *HDPE geomembranes in geotechnics*. Springer-Verlag, Berlin.
- Rowe K.R., and Sangam H. P. 2002. Review article: durability of HDPE geomembranes. *Geotextiles and Geomembranes* 20 (2), 77-95.
- Rowe, R.K., Islam, M.Z., and Hsuan, Y.G. 2008. Leachate chemical composition effects on OIT depletion in an HDPE geomembrane *Geosynthetics International* 15(2), 136-151.
- Scheirs, J. 2009. *A guide to polymeric geomembranes*. John Willey and sons, West Sussex, United Kingdom.
- Stark T.D., Williamson T.A., and Eid H.T. 1996. HDPE geomembrane/geotextile interface shear strength. *Journal of Geotechnical Engineering* 122(3), 197-203.
- Thiel R.S. 2001. Peak vs. Residual Shear Strength for Landfill Bottom Liner Stability Analysis, *15th Annual GRI Conference*. Geosynthetic Institute, Folsom, PA, USA.