

## Degradation of Exposed LLDPE and HDPE Geomembranes: A Review

M. Zahirul Islam<sup>1</sup>, M.ASCE, Ph.D., P.Eng., Beth A. Gross<sup>2</sup>, M.ASCE, Ph.D., P.E.,  
and R. Kerry Rowe<sup>3</sup>, F.ASCE, Ph.D., P.Eng.

<sup>1</sup>Geosyntec Consultants, 3600 Bee Caves Road, Suite 101, Austin, TX 78746; PH (512) 451-4003, e-mail: zislam@geosyntec.com

<sup>2</sup>Geosyntec Consultants, 3600 Bee Caves Road, Suite 101, Austin, TX 78746; PH (512) 451-4003, e-mail: bgross@geosyntec.com

<sup>3</sup>GeoEngineering Centre at Queen's-RMC, Queen's University, Kingston, ON, Canada; PH (613) 533-6933, e-mail: kerry@civil.queensu.ca

### ABSTRACT

The service life of geomembranes varies significantly based on their exposure conditions. For instance, the service life of polymeric geomembranes exposed to atmospheric conditions with solar radiation, high temperatures, and oxygen is anticipated to be shorter than that of buried geomembranes. Both linear low density polyethylene (LLDPE) geomembranes and high density polyethylene (HDPE) geomembranes are used for exposed applications (e.g., landfill covers, pond and canal liners, etc.). LLDPE geomembranes are very flexible, with a higher tensile break elongation than HDPE geomembranes and, therefore, greater ability to maintain their integrity under localized differential settlement without puncturing, tearing, or cracking. On the other hand, HDPE geomembranes have excellent ultraviolet (UV) and chemical resistance; however, they have low puncture resistance and low multi-axial extensibility compared to LLDPE geomembranes. This paper compares the relative performance of exposed LLDPE and HDPE geomembranes based on laboratory test results and field performance data.

### INTRODUCTION

Polyethylene geomembranes have been widely used as barrier to liquids or vapors for many different applications (Rowe 2005). Among the geomembrane materials available in the market [polyvinyl chloride (PVC), chlorinated polyethylene (CPE), chlorosulphonated polyethylene (CSPE), ethylene propylene rubber (EPDM), polypropylene (PP), LLDPE, medium-density polyethylene (MDPE), HDPE, bituminous geomembrane, etc.], LLDPE and HDPE are often selected for geomembranes in exposed applications (e.g., landfill and reservoir covers, pond and canal liners, etc.). The construction costs for exposed geomembranes are less than those of buried geomembranes overlain by soils or other materials.

LLDPE is a considerably linear polymer having significant numbers of short branches. LLDPE is generally made by copolymerization of ethylene with short-chain alpha-olefins (e.g., 1-butane, 1-hexene, and 1-octane) (Scheirs 2009). The

geomembrane generally consists of 94-96% polyethylene resin, 2-3% carbon black, and 0.25-3% antioxidants and stabilizers (Koerner et al. 2005). The density of LLDPE geomembranes varies in the range from 0.915-0.939 g/cm<sup>3</sup>. LLDPE geomembranes are very flexible and have higher tensile break elongation than HDPE geomembranes (Scheirs 2009). Due to their flexibility, LLDPE geomembranes are more likely than HDPE to maintain their integrity under localized differential settlement conditions without puncturing, tearing, or cracking. Also LLDPE does not have the same predisposition to stress cracking as HDPE (Peggs 2003). LLDPE geomembranes are often used in environmental applications, such as landfill covers, where large settlements are anticipated due to long-term compression of waste. LLDPE geomembranes are also used as canal, lagoons, and pond liners.

HDPE has relatively less chain branching than LLDPE and has quite linear molecules which help in producing a highly crystalline polymer (Scheirs 2009). HDPE geomembranes generally consist of 95-98% polyethylene resin, 2-3% carbon black, and 0.25-1% antioxidants and stabilizers (Koerner et al. 2005). The density of the HDPE geomembranes varies in the range from 0.941-0.959 g/cm<sup>3</sup>. The HDPE geomembranes commonly used today actually are manufactured from medium density polyethylene resin (MDPE) to improve stress crack resistance, which decreases with increasing polymer crystallinity, and are only designated as HDPE because the carbon black increases the density sufficiently to move them into this category as defined by ASTM D883. HDPE geomembranes have better UV and chemical resistance than LLDPE geomembranes (Scheirs 2009). HDPE geomembranes have low puncture resistance and low multi-axial extensibility, and are therefore, considered to be disadvantageous in applications where these properties are desirable, for example, in landfill cover applications (Simpson and Siebken 1997; Scheirs 2009).

This paper presents a review of the key relevant literature on the aging of exposed LLDPE and HDPE geomembranes.

## **DEGRADATION MECHANISMS IN EXPOSED GEOMEMBRANES**

Exposed geomembranes are highly susceptible to degradation by UV, oxidative, and thermal mechanisms (Koerner et al. 1990, 2005). At a given time, more than one degradation mechanism can take place and the resulting synergistic effects can accelerate the degradation processes.

Of the degradation mechanisms, UV degradation is the most harmful for an exposed geomembrane (Qureshi et al. 1989). Solar radiation is generally divided into various regions or bands on the basis of wavelengths, for example: infrared region with wavelengths in the range from 780-1400 nm, visible region with wavelengths in the range from 400-780 nm, and UV region with wavelengths in the range from 290-400 nm (Qureshi et al. 1989; Acra et al. 1990; Koerner et al. 1990). The UV portion of the radiation, which accounts for about 4-6% of total global radiation, is mainly responsible for the degradation of polymers (Qureshi et al. 1989; Koerner et al. 1990). According to Suits and Hsuan (2003), photons with similar or higher energy than the energy of the polymer chemical bonds cause a series of reactions to polymers that are exposed to sunlight and liberate free radicals which cause bond scission in the polymeric structure and eventually makes the polymer brittle and susceptible to

environmental stress cracking. For instance, the chemical bond strengths of C-C and C-H bonds are 420 and 340 kJ/mol, respectively. On the other hand, the energies of 300 and 400 nm photons (in the UV range) are 390 and 300 kJ/mol, respectively (Suits and Hsuan 2003). Therefore, UV radiation has adequate energy to break the polymer bonds. To retard the UV degradation, carbon black or other chemical-based light stabilizers are normally added to a polymeric geomembrane. However, the stabilizers in the geomembrane are depleted with increasing exposure time.

Oxidative degradation causes breakdown of polymer chains and subsequently alters the physical and mechanical properties of a geomembrane leading eventually to the failure of the geomembrane. The details of oxidative degradation can be found elsewhere (Grassie and Scott 1985; Hsuan and Koerner 1998; Rowe and Sangam 2002). Oxidative degradation accelerates in exposed polymer due to photo-oxidation reactions. These photo-oxidation reactions result in the formation of several free radicals (Suits and Hsuan 2003):



$$E = h \frac{c}{\lambda} \quad (2)$$

where RH is the polymer chain;  $E$  is the photon energy and is related to Planck's constant ( $h$ ), speed of light ( $c$ ), and wavelength ( $\lambda$ ); and  $\text{R}\bullet$ ,  $\text{ROO}\bullet$ ,  $\text{RO}\bullet$ , and  $\text{OH}\bullet$  are the free radicals. As more and more free radicals are formed, more polymer chains break down and the polymer becomes more vulnerable to environmental stress cracking. Oxidation reactions in polymer also accelerate due to the effect of elevated temperatures (Hsuan and Koerner 1995; Sangam and Rowe 2002; Rowe and Rimal 2008; Rowe et al. 2008, 2010; Islam 2009). To retard the oxidation reactions, antioxidants are added to the polymer resin during formulation (Grassie and Scott 1985).

Thermal degradation causes change in physical, mechanical, or chemical properties of geomembranes (Koerner 2005). Elevated temperature accelerates both ultraviolet and oxidative degradations. The thermal effects allow accelerated aging tests to be conducted at elevated temperature. However, sufficient care should be taken in selecting the maximum temperature for aging studies because the melt temperature of geomembranes may be relatively low. Maximum aging temperature was suggested to be in the range of 80 to 90°C for polyethylenes (Gugumus 1999; Ding et al. 2001), although temperatures up to 105°C have been used (Viebke et al. 1994). On the other hand, the melt temperature of HDPE geomembrane is on the order of 120 to 130°C, and the melt temperature of LLDPE geomembranes is on the order of 105 to 115°C.

## LABORATORY AGING STUDIES ON THE DURABILITY OF EXPOSED LLDPE AND HDPE GEOMEMBRANES

The existing literature on the durability and service life predictions of geomembranes is entirely focused on buried applications. However, there are a few studies that investigated the degradation of exposed LLDPE and HDPE

geomembranes in the laboratory. A brief description on the current degradation studies on the exposed LLDPE and HDPE geomembranes is presented below.

Because LLDPE has a lower density, and hence lower crystallinity than HDPE (i.e., generally about 10% versus about 50%), oxygen can diffuse faster into LLDPE than into HDPE. As a result, it is expected that the antioxidants in LLDPE geomembranes will be depleted faster than the antioxidants in HDPE geomembranes (Koerner et al. 2005). This hypothesis is supported by the work of Gulmine et al. (2003), who conducted accelerated aging test using thin sheets of LLDPE and HDPE pellets. Both LLDPE and HDPE were stabilized with Inganox 1076 and Weston 399 antioxidants. Aging was conducted by exposing the polyethylene sheets under UV-fluorescent or Xenon Arc radiation at 50 and 60°C for time periods of 12 to 1,600 hrs. The results of the testing protocol, including evaluation of carbonyl index and density, indicate that stabilized HDPE is more resistant to photo-oxidative aging than stabilized LLDPE.

Koerner et al. (2008) present the results of an accelerated aging test conducted on samples of 1.5-mm thick HDPE geomembrane and 1.0-mm thick LLDPE geomembrane using a laboratory weatherometer. The samples were exposed to UV-fluorescent radiation at 70°C for about 28,000 hours. After approximately 25,000 hours, which Koerner et al. (2008) compared to 25 years of exposure in Texas, both the HDPE and LLDPE samples appeared to start degrading, based on a loss of tensile strength and elongation, with the LLDPE geomembrane appearing to show somewhat more degradation than the HDPE geomembrane. It is noted that the LLDPE geomembrane tested by Koerner et al. (2008) was thinner than the HDPE geomembrane. All else being equal, a thinner geomembrane would age faster than a thicker geomembrane (Rowe et al. 2010). Taking into consideration the total testing duration of 28,000 hours, the exposed life time of both LLDPE and HDPE geomembranes were calculated to be greater than 28 years for Texan weather conditions. The exposed life time could be shorter or longer based on the site-specific UV/temperature exposure conditions.

Allen et al. (2000) conducted accelerated aging tests to investigate the thermal and photo-oxidative stabilities of additive-free LLDPE and HDPE. Tests were conducted on 100 and 250 micron thick polymer films placed in a hot-air fan oven at 90°C and irradiated with a high pressure mercury fluorescent lamp. The rates of aging were monitored by measuring the evolution of carbonyl index and hydroperoxide concentration. The results showed that HDPE was less stable with respect to thermal and photo-oxidative degradation compared to LLDPE. They concluded that the types and concentrations of vinyl group and the presence of residual metal ions in the polymer may have contributed to the lower stability of HDPE compared to LLDPE.

Corrales et al. (2002) conducted similar thermal and photo-oxidative degradation studies as Allen et al. (2000) using 280-micron thick additive-free LLDPE and HDPE films. Aging was conducted at 90°C in a forced draught oven and the samples were irradiated with light having wavelengths in the range 300-800 nm. Results of thermogravimetric, spectroscopic, differential scanning calorimeter, and chemiluminescence analyses showed that these additive-free HDPE samples were more susceptible to thermal and photo-oxidative degradation than additive-free LLDPE samples.

These studies suggest that while LLDPE loses its antioxidants faster than HDPE, LLDPE may age slower than HDPE after the antioxidants have been depleted from the polymers.

## FIELD PERFORMANCE OF EXPOSED LLDPE AND HDPE GEOMEMBRANES

Case histories of exposed geomembrane applications are limited in the literature. Hullings (2007) reported the performance of exposed LLDPE and HDPE geomembranes as landfill covers for four different landfills in the USA (Table 1). It can be seen from Table 1 that the exposed HDPE geomembranes had been performing their intended function for about 6 to 8 years and exposed LLDPE geomembranes approximately for 5 to 6 years. It should be noted that these geomembranes were still performing well by the end of the reporting period.

**Table 1. Performance of Exposed LLDPE and HDPE Geomembranes as Landfill Covers in the USA (reproduced from Hullings 2007)**

Landfill Name and Location	Geomembrane Type	Year of Built	Status by the Year 2007
Sabine Parish, Phases I and III, Louisiana	1.5 mm green textured HDPE	1999	Approved as final cover
Polk County, Phase 1, Florida	1.5 mm green textured HDPE	2001	Performing well
New River, Cells 1 and 2, Florida	White textured LLDPE	2001	Performing well
Marion Cell III-C, Florida	White textured LLDPE	2002	Performing well

Other examples of exposed geomembranes installed as landfill covers have been published in the literature, e.g., Gleason et al. (1998, 2001) and Germain et al. (2001); however, there is no follow-up information on geomembrane performance after installation. There have been two separate natural weathering studies found in the literature that investigated the degradation of exposed HDPE (Rimal 2009) and LLDPE (Qureshi et al. 1989) geomembranes.

Rimal (2009) reported results of natural weathering studies conducted in Ontario, Canada using a 2-mm thick HDPE geomembrane. The geomembrane samples were placed on a wooden test frame that was inclined with a slope of 2 horizontal : 1 vertical. The average daily temperature at the site was approximately 33°C during the summer and -27°C during the winter. No measurable change in mechanical properties (e.g., tensile strength and strain, stress crack resistance) was reported within the weathering period of 8.5 yrs. It should be noted that weathering studies of these geomembrane samples are still on-going.

Qureshi et al. (1989) conducted an outdoor natural weathering study using 3-mm thick LLDPE plaques. No UV stabilizer was added to the plaques. The exposure site was located at Dhahran, Saudi Arabia and is representative of a hot, humid, and

subtropical region. The solar radiation received at the testing site (180-220 kLy/year) is comparable to solar radiation in Arizona, USA (190-200 kLy/year). Results showed that both cross-linking and chain scission reactions occurred in the LLDPE due to the photochemical degradation. The tensile strength and strain at break decreased to 50% of the initial value within three months of the exposure time. They concluded that the weather at Dhahran site was highly aggressive to LLDPE. No HDPE was tested by the authors, therefore, no comparison between HDPE and LLDPE was possible.

## CONCLUSION

A review of the relative performance of exposed LLDPE and HDPE geomembranes has been presented in this paper. Based on laboratory accelerated aging test data, antioxidants in stabilized LLDPE geomembranes are expected to be depleted faster than those in stabilized HDPE geomembrane. However, LLDPE may age slower than HDPE after the antioxidants have been depleted from the polymers. Laboratory aging tests indicate that the service life of LLDPE (1.0-mm thick) and HDPE (1.5-mm thick) geomembranes exposed to Texas weather conditions is greater than 28 years. Both exposed LLDPE and HDPE geomembranes have shown to perform their intended function for more than 5 to 8 years in the field, the total durations of the field tests. Given the paucity of research relating to this important topic, more research is required.

## REFERENCES

- ASTM D883 (2008). "Standard terminology relating to plastics." Annual Book of ASTM Standards, Volume 08.01, West Conshohocken, PA.
- Acra, A., Jurdi, M., Mu'Allem, H., Karahagopian, Y., and Raffoul, Z. (1990). *Water disinfection by solar radiation: assessment and application*. International Development Research Centre (IDRC-Canada), Ottawa, Ontario, 75p.
- Allen, N. S., Edge, M., Holdsworth, D., Rahman, A., Catalina, F., Fontan, E., Escalona, A. M., and Sibon, F. F. (2000). "Ageing and spectroscopic properties of polyethylenes: comparison with metallocene polymer." *Polymer Degradation and Stability*, 67(1): 57-67.
- Corrales, T., Catalina, F., Peinado, C., Allen, N. S., Fontan, E. (2002). "Photooxidative and thermal degradation of polyethylenes: interrelationship by chemiluminescence, thermal gravimetric analysis and FTIR data." *J. of Photochemistry and Photobiology A: Chemistry*, 147(3): 213-224.
- Ding, S., Ling, M. T. K., Khare, A., and Woo, L. (2001). "Activation energies of polymer degradation." *Plastic Failure – Analysis and Prevention*, Moalli J. (Editor), William Andrew Publishing/Plastics Design Library: 219-225.
- Germain, A., Houlihan, M., and Richardson, G. (2001). "Exposed geomembrane covers (EGCs): part 3 – geomembrane restraint." *GFR*, 19(1): 20-23.
- Gleason, M. H., Houlihan, M. F., and Giroud, J. P. (1998). "An exposed geomembrane cover system for a landfill." *Proc. 6<sup>th</sup> ICG*, Atlanta, IFAI, 211-218.

- Gleason, M. H., Houlihan, M. F., and Palutis, J. R. (2001). "Exposed geomembrane cover systems: technology summary." *Proc. Geosynthetics Conference 2001*, Portland, Oregon, February 12-14, IFAI Publ., Roseville, MN, pp. 905-918.
- Grassie, N. and Scott, G. (1985). *Polymer Degradation and Stabilisation*, Cambridge University Press, New York, USA, 222 p.
- Gugumus, F. (1999). "Effect of temperature on the lifetime of stabilized and unstabilized PP films." *Polymer Degradation and Stability*, 63 (1): 41-52.
- Gulmine, J. V., Janissek, P. R., Heise, H. M., and Akcelrud, L. (2003). "Degradation profile of polyethylene after artificial accelerated weathering." *Polymer Degradation and Stability*, 79(3): 385-397.
- Hsuan, Y. and Koerner, R. M. (1995). "Long-term durability of HDPE geomembrane. Part 1: depletion of antioxidant." Geosynthetics Research Institute, Philadelphia, PA, GRI Report 16, 35 p.
- Hsuan, Y. G. and Koerner, R. M. (1998). "Antioxidant depletion lifetime in high density polyethylene geomembranes." *J. of Geotechnical and Geoenvironmental Engrg.* 124(6): 532-541.
- Hullings, D. (2007). "Finalizing exposed geomembranes covers for landfills." *Proc. Geosynthetics 2007*, Washington, DC, IFAI Publication (CD-ROM).
- Islam, M. Z. (2009). Long-term performance of HDPE geomembranes as landfill liners. *PhD Thesis*, Dept. of Civil Engineering, Queen's University, Kingston, Ontario, Canada, 355p.
- Koerner, R. M., Halse, Y. H., and Lord, A. E. Jr. (1990). "Long-term durability and aging of geomembranes." *Waste Containment Systems: Construction, Regulation, and Performance*, Bonaparte, R., Editor, ASCE Geotechnical Special Publication No. 26, New York: 106-134.
- Koerner, R. M., Hsuan, Y. G., and Koerner, G. R. (2005). *Geomembrane lifetime prediction: unexposed and exposed conditions*. GRI White Paper # 6, Geosynthetics Institute, Pennsylvania, USA, 19p.
- Koerner, R. M., Hsuan, Y. G., and Koerner, G. R. (2008). "Freshwater and Geosynthetics; Perfect Marriage." *Proc. GeoAmericas 2008*, Cancun, Mexico: 4-28.
- Peggs, I. D. (2003). "Geomembrane liner durability: contributing factors and the status quo." *1<sup>st</sup> United Kingdom Geosynthetics Symposium*, UK Chapter of IGS, June 2003.
- Qureshi, F. S., Amin, M. B., Maadha, A. G., and Hamid, S. H. (1989). Weather-induced degradation of linear low-density polyethylene: mechanical properties." *Polymer-Plastics Technology and Engrg.* 28(7&8): 649-662.
- Rimal, S. (2009). Ageing of HDPE geomembranes used to contain landfill leachate or hydrocarbon spills. *PhD Thesis*, Dept. of civil Engineering, Queen's University, Kingston, Ontario, Canada, 412p.
- Rowe, R. K. (2005). "Long-term performance of contaminant barrier systems." *Géotechnique*, 55(9): 631-678.
- Rowe, R. K. and Islam, M. Z. (2009). "Impact of landfill liner time-temperature history on the service life of HDPE geomembranes." *Waste Management*, 29(10): 2689-2699.

- 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.
- Rowe, R. K., Islam, M. Z. and Hsuan, Y. G. (2010). "Effects of thickness on the ageing of HDPE geomembranes." *J. of Geotechnical and Geoenvironmental Engrg.* 136(2): 299-309.
- Rowe, R. K. and Rimal, S. (2008). "Depletion of antioxidants from an HDPE geomembrane in a composite liner." *J. of Geotechnical and Geoenvironmental Engrg.* 134(1): 68-78.
- Rowe, R. K. and Sangam, H. P. (2002). "Durability of HDPE geomembranes." *Geotextiles and Geomembranes*, 20(2): 77-95.
- Sangam, H. P. and Rowe, R. K. (2002). "Effects of exposure conditions on the depletion of antioxidants from high-density polyethylene (HDPE) geomembranes." *Canadian Geotechnical J.* 39(6): 1221-1230.
- Scheirs, J. (2009). *A Guide to Polymeric Geomembranes: A Practical Approach*. John Wiley & Sons Ltd., West Sussex, UK, 596p.
- Simpson, M. and Siebken, J. (1997). "A comparison of high density polyethylene (HDPE) and linear low density polyethylene (LLDPE)." In *Geosynthetics Asia 1997: Selected Papers*, Varma, C. V. J., Rao, G. V., Rao, A. R. G., Editors, Taylor & Francis, Inc., Rotterdam, 496p.
- Suits, L. D. and Hsuan, Y. G. (2003). "Assessing the photo-degradation of geosynthetics by outdoor exposure and laboratory weatherometer." *Geotextiles and Geomembranes*, 21(2): 111-122.
- Viebke J., Elble E., Ifwarson M., and Gedde U. W. (1994). "Degradation of unstabilized medium-density polyethylene pipes in hot-water applications." *Polymer Engineering and Science*, 34(17): 1354-1361.