

DURABILITY OF FLUORINATED HIGH DENSITY POLYETHYLENE (F-HDPE) GEOMEMBRANE EXPOSED TO HYDROCARBONS IN THE ARCTIC

S. Rimal and R.K. Rowe

GeoEngineering Centre at Queen's-RMC, Civil Engineering Department, Queen's University, Kingston, Ontario, Canada

R.J. Bathurst

GeoEngineering Centre at Queen's-RMC, Civil Engineering Department, Royal Military College of Canada, Kingston, Ontario, Canada



ABSTRACT

A composite barrier comprising of a fluorinated high-density polyethylene (f-HDPE) geomembrane and geosynthetic clay liner (GCL) was used to control the advective and diffusive migration of a hydrocarbon spill in the Canadian Arctic. This paper describes the results of laboratory testing to assess durability of the f-HDPE geomembrane samples retrieved from the field site over the period of 2001 to 2004. The laboratory results indicated that the properties of the buried 1.5 mm thick f-HDPE geomembranes have not changed significantly since installation. The durability of the f-HDPE geomembranes was maintained for well over the original design life of the barrier system.

RÉSUMÉ

Une barrière composée comportant d'un geomembrane à haute densité fluoré de polyéthylène (f-HDPE) et d'un recouvrement geosynthetic d'argile (GCL) a été employée pour commander la migration advective et diffusive d'une flaque d'hydrocarbure dans l'Arctique canadien. Cet article décrit les résultats de l'essai en laboratoire pour évaluer la longévité des échantillons de geomembranes de f-HDPE recherchés de l'emplacement de champ pendant 2001 à 2004. Les résultats de laboratoire ont indiqué que les propriétés des geomembranes épais enterrés de f-HDPE de 1.5 millimètre n'ont pas changé sensiblement depuis l'installation. La longévité des geomembranes de f-HDPE a été bien maintenue au-dessus de la vie de trois ans de conception du système de barrière.

1. INTRODUCTION

High Density Polyethylene geomembranes (HDPE GM) are used as a part of liner systems to limit the migration of contaminants. The HDPE GM should not only have chemical resistance and low permeability to the contaminants but also maintain durability over the design service life. Prior field studies and laboratory tests have shown that HDPE GM age with time (Hsuan et al., 1991; Tisinger et al 1991; Hsuan and Koerner, 1998; Sangam and Rowe, 2002; Rowe et al., 2004; Rimal et al., 2004; Rowe, 2005). The severity of ageing depends on the exposure media (e.g. air, water, leachate, hydrocarbons, acid mine drainage) and temperature (Hsuan and Koerner, 1998; Sangam and Rowe, 2002; Rimal et al., 2004; Gulec et al., 2004).

Application of HDPE GM in hydrocarbon contaminated sites and their long-term performance and durability is of interest. A fluorinated HDPE geomembrane (f-HDPE GM) was selected as the primary liner for an experimental subsurface barrier system at a site with hydrocarbon contaminated ground in the Canadian Arctic. The composite barrier system comprised of the f-HDPE GM as a primary liner to control the advective and diffusive migration of a hydrocarbon spill prior to future site remediation (Li, et al., 2002; Bathurst et al., 2006). The f-

HDPE GM is more resistant to diffusion of aromatic hydrocarbons than the conventional HDPE GM (Sangam et al., 2001, Sangam and Rowe, 2005). Antioxidants are added to the GM to enhance service life. Prior laboratory tests have reported slower antioxidant depletion rates from f-HDPE GM than the conventional HDPE GM (Rimal et al., 2004) when exposed to pure jet fuel.

In the field application under investigation, a key question is the long-term durability of f-HDPE GM. The primary question relates to interaction with the hydrocarbons and the impact of extreme climatic conditions of the Arctic on the durability and service life of the f-HDPE GM. Therefore the objective of this paper is to assess the durability and performance of f-HDPE GM products installed at the field site.

2. BACKGROUND

At a North Warning System long-range radar installation located at 63°20'23"N, 64°08'45"W on Brevoort Island, Nunavut Territory, Arctic diesel (jet fuel) spills and leaks have occurred. The site is located 225 km east of Iqaluit. The site was re-built in 1987 and is now known as BAF-3 (Figure 1). The site has a zone of continuous permafrost at a depth of 1-2 m, which provides a natural barrier to downward migration of contaminants. But the shallow

permafrost depth contributes to lateral spreading of the hydrocarbons, especially after precipitation and infiltration.



Figure 1: The BAF-3 site location (Bathurst et al., 2006)

There are two large petroleum tanks approximately 75 m north of the ocean (Figure 2.). The existing tanks replace older tanks dating back to the original Breevort Island distant early warning line communication site. Contamination due to leaks from corroded tanks or fuel spilled during reconstruction activities was first investigated in 1998 (Bathurst et al., 2006). The presence of hydrocarbons was confirmed in the sloped area between the tanks and the ocean at levels up to 14,000 ppm total petroleum hydrocarbons (TPH). Additional sampling was conducted in 2000 by the Environmental Sciences Group (2001). Laboratory analysis of samples from the site indicated that most of the surface samples were uncontaminated but the samples collected at depths beneath the surface had TPH levels that exceeded the acceptable criteria. It was concluded from the contaminant distribution at the site that the hydrocarbon plume was moving down slope from the site of the decommissioned tanks towards the bay.



Figure 2: The existing tanks (Bathurst et al., 2006)

The Canadian Department of National Defence initiated a cleanup program of the BAF-3 site. Site remediation by excavation and exsitu treatment was planned. However a short-term strategy was needed to contain the hydrocarbon plume until future site remediation. The strategy involved the installation of a subsurface geosynthetic composite barrier system comprised (from bottom up) of a needle-punched GCL, f-HDPE GM, and a needle-punched geotextile protection layer in a trench constructed down-gradient of the plume and excavated to permafrost in 2001 (Li et al., 2002). The contaminant plume was covered with a GM and the surface graded to minimize infiltration. The barrier was designed to intercept the jet fuel contaminant plume. The plume migrates predominantly at the water table as it is less dense than water (a light non-aqueous phase liquid – LNAPL).

During the construction of the barrier system a series of vertical wooden frames supporting coupons of f-HDPE GMs were buried in the backfill immediately upstream of the barrier system (Li et al., 2002) with the objective of allowing the monitoring of changes in the barrier materials with time. Each frame holds six 0.25 x 3.0 m samples (Figure 3). The coupons were extended to reach the permafrost table to ensure contact with contaminants.



Figure 3: The frames supporting f-HDPE GM coupons during installation in 2001

The f-HDPE coupons were retrieved from the frame in summer of 2002 and 2004 and returned to the laboratory for analysis. The behaviour of the material in the harsh Arctic climatic conditions was monitored and quantified to assess their durability and field performance.

3. MATERIALS

The f-HDPE GM installed in the field was 1.5 mm thick. In addition, coupons of two other thicknesses (1.0 mm, and 2.5 mm) were buried. The f-HDPE GM was manufactured by GSE Lining Technology Inc., Houston, Texas, USA and treated at Fluoro-Seal Inc., Texas, USA. This GM was manufactured as smooth black-surfaced untreated HDPE GM that was then treated by the fluorination process. This process involves application of elemental fluorine gas to both sides of the untreated GM. The fluorine atoms chemically substitute the hydrogen atoms in the carbon-hydrogen (C-H) bond in the polyethylene chain to form carbon-fluorine (C-F) covalent

bonds. Thin carbon-fluorine layers of 0.31-0.37 microns (as measured in some of the samples of f-HDPE by Scanning Electron Microscope/Energy Dispersive X-Ray) are created on the two sides of the GM. The properties of the f-HDPE GM are summarized in Table 1.

Table 1: Properties of f-HDPE GM examined

Property	ASTM Method	f-HDPE GM		
		1 mm	1.5 mm	2.5 mm
OIT (min)	D3895	128 (2.4)	118 (1.7)	125 (2.6)
Crystallinity (%)	E794	59 (0.72)	63 (1.3)	44 (16)
Melt Flow index (g/10 min.)	D1238	0.098 (7.3)	0.017 (11)	0.365 (3.1)
Tensile strength at yield (kN/m)	D6693	16.8 (1.5)	28.6 (1.3)	48.3 (1.7)
Tensile strain at yield (%)	D6693	18.1 (0.83)	21.0 (1.4)	20.5 (0.78)
Tensile strength at break (kN/m)	D6693	29.9 (1.8)	50.0 (2.0)	71.2 (1.5)
Tensile-strain at break (%)	D6693	795 (3.1)	831 (5.0)	751 (4.6)

Note: Average values are presented. Bracketed values are coefficient of variation (COV %)

4. TEST METHODS

4.1 Analytical Testing Methods

4.1.1 Oxidative Induction Time (OIT)

The OIT test provides an index measure of the amount of antioxidant present in the GM. 0.5 to 1% of antioxidants and additives are added to the polyethylene resin used to manufacture HDPE GM. They are added to minimize oxidative degradation of the polymer and hence extend the service life of the GM. The OIT test is useful in monitoring the depletion of antioxidants from the GM. Many prior studies have used OIT as an indicator of the amount of antioxidant in the GM (Hsuan and Koerner, 1995; Hsuan and Koerner, 1998; Sangam and Rowe, 2002; Müller and Jakob, 2003; Rimal et al., 2004; Gulec et al., 2004, Rowe, 2005). Standard OIT tests were carried out following ASTM D3895 with differential scanning calorimeters (DSC): TA Instruments 2910 and Q100. For the evaluation of OIT the testing temperature of 200°C was used at a pressure of 35 kPa and flow of ultra high pure nitrogen and oxygen of 50 ml/min.

4.1.2 Degree of Crystallinity

Degree of crystallinity provides an indication of amount of crystalline region in the polymer with respect to amorphous content. HDPE GM is semicrystalline polymer. Degree of crystallinity influences some of the important physical and mechanical properties such as yield stress, elastic modulus, density, impact resistance, melting point, and permeability (Kong and Hay, 2002; Sperling, 1992). Crystallinity tests were performed according to ASTM E794 using a differential scanning calorimeter. The GM specimen was heated at the rate of

20°C/min. to 200°C in nitrogen atmosphere. The percentage crystallinity was calculated by dividing the measured heat of fusion with the heat of fusion of 100% crystalline HDPE, 290 J/g (Flory and Vrij, 1963).

4.2 Mechanical Testing Methods

4.2.1 Melt Flow Index (MFI)

The MFI is useful in examining the changes in molecular weights of the polymer. Oxidative degradation of polymer results in either a cross linking or chain scission reaction. Cross linking increases the molecular weight and chain scission decreases the molecular weight (Peacock, 2000).

MFI is an index measure of the ease of flow of the polymer melt. MFI can be generally defined as the weight of polymer in grams flowing in 10 minutes through a capillary of specific diameter and length, under specific temperature and loading conditions. MFI is inversely proportional to molecular weight (Shah, 2002). The MFI test was conducted in accordance with ASTM D1238 for condition E at 190°C at a load of 2.16 kg.

4.2.2 Tensile Properties

Changes in tensile properties are a useful means to assess the durability of the GM. Elongation at break is more sensitive to polymer degradation than tensile strength (Hamid et al., 1992). The tensile properties of the GM were obtained in accordance with ASTM D6693 using universal testing machines: Instron Model 3396 and Zwick Roell equipped with load cell, crosshead measurements, and self aligning wedge grips. Dumbbell shaped specimens (ASTM 693 Type IV) were tested at a speed of 50mm/min. Tensile properties at yield and break were evaluated.

5. RESULTS AND DISCUSSION

OIT test results on virgin and exhumed (in 2002 and 2004) samples of 1.5 mm thick f-HDPE GM are illustrated in Figure 4. The vertical bars represent average OIT value and the error bars represent one standard deviation. The straight dashed line represents the initial OIT of the virgin GM sample. The linear regression analysis and zero slope test were performed for the OIT data for virgin sample and exhumed samples. The p-value obtained for the null hypothesis (H_0 : slope = 0) was 0.31. Thus, there was no statistically significant difference (at 95% confidence level) between the OIT values of the virgin and exhumed f-HDPE GM. Based on these observations there is no significant changes in antioxidant amount in the GM after three years of exposure in the field.

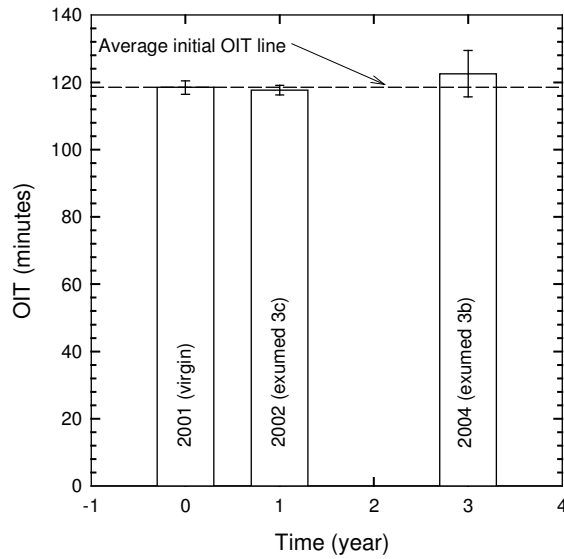


Figure 4. OIT values of virgin and exhumed 1.5 mm thick f-HDPE GM samples. Note: 3-5 specimens per sample, error bars represent ± 1 standard deviation.

The field exposure for three years did not significantly affect the antioxidant formulation in the GM. This result is in contrast with the accelerated laboratory testing in which antioxidants depleted at very high rate. In the laboratory, the f-HDPE GM was directly immersed in pure jet fuel at room temperature (Rimal et al., 2004; Rowe et al., 2007). The results indicated that the exposure to jet fuel significantly affected the depletion of antioxidants. These studies showed that f-HDPE GM immersed in jet fuel was more resistant to antioxidant depletion than the conventional untreated HDPE GM. Moreover, the latest findings for samples tested at sub-zero temperature have shown that the antioxidants depleted at much slower rate than at room temperature (Rowe and Rimal, 2007). The samples buried at the field site were exposed to sub-zero temperature for almost ten months each year. The field samples were also exposed to lower jet fuel hydrocarbon concentrations than the pure jet fuel used in laboratory immersion tests. Hence the better performance of the field exhumed samples with regard to OIT depletion was expected.

The results from OIT tests implied that the concentration of antioxidant in the GM was still intact. The GM is still in the first stage of ageing i.e. (1) the antioxidant depletion time. The other two stages that follow after the depletion of antioxidants are (2) induction time to the onset of polymer degradation and (3) polymer degradation stage as described by Hsuan and Koerner (1998).

Conventional tensile tests were performed on virgin and exhumed f-HDPE GM samples and the results are shown in Figures 5 to 8. The regression analysis and zero slope tests were conducted for the tensile test results. The yield strengths of the GM are plotted in Figure 5 with an initial yield strength line of 29 kN/m. The p-value obtained for

the null hypothesis (H_0 : slope = 0) was 0.95. There was no statistically significant difference between the virgin and exhumed yield strengths of the GM (at 95% confidence level).

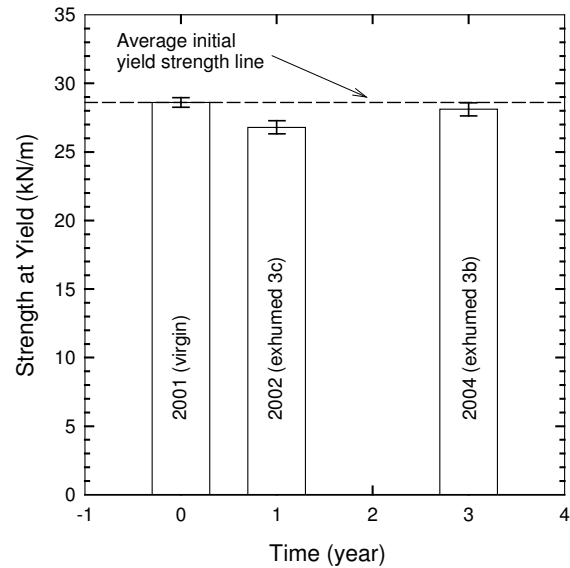


Figure 5. Tensile strength at yield for virgin and exhumed 1.5 mm thick f-HDPE GM. Note: 3-5 specimens per sample, error bars represent ± 1 standard deviation.

The yield strength of polyethylene is closely related to the degree of crystallinity and density (Peacock, 2000). Decrease in polymer crystallinity is typically associated with the decrease in mechanical stiffness. The crystallinity test was carried out on the same GM specimens. No significant changes were noted in the crystallinity of the exhumed GM relative to the virgin GM. The crystallinity and yield strength results are consistent with each other. Strain at yield of the virgin and exhumed f-HDPE GM samples are shown in Figure 6. The p-value of the zero slope test was 0.72. Thus at the 95% confidence level, there was no significant change in the yield strain between the virgin and exhumed f-HDPE GM samples.

The tensile strength at break for the virgin and exhumed f-HDPE GM samples are shown in Figure 7. The p-value for the zero slope test was 0.80. As before, tensile strains at break are plotted in Figure 8. The p-value obtained was 0.64 and so there was no statistically significant difference in the tensile properties at break for the virgin and exhumed f-HDPE GM samples (at the 95% confidence level).

The melt flow index (MFI) test results for the exhumed GM were obtained in the laboratory. It was noted that there was no statistically significant difference between the MFI value of the virgin and exhumed f-HDPE GM samples. This is consistent with the results for tensile properties of the GM. The MFI results imply that there was no change in molecular weight of the material.

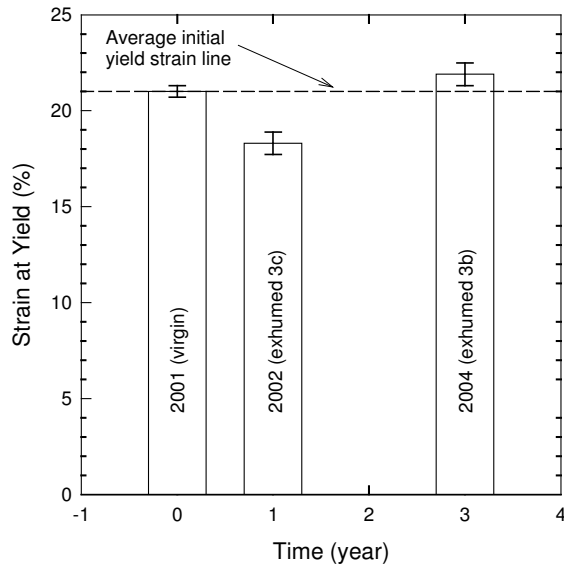


Figure 6. Tensile strain at yield for virgin and exhumed 1.5 mm thick f-HDPE GM. Note: 3-5 specimens per sample, error bars represent ± 1 standard deviation.

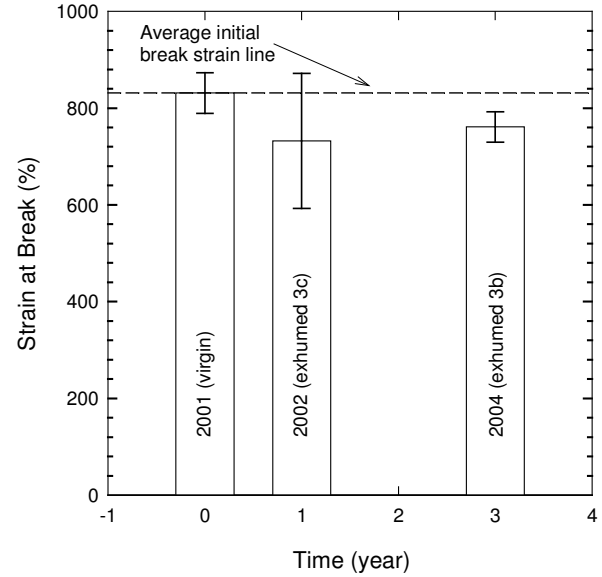


Figure 8. Tensile strain at break for virgin and exhumed 1.5 mm thick f-HDPE GM. Note: 3-5 specimens per sample, error bars represent ± 1 standard deviation.

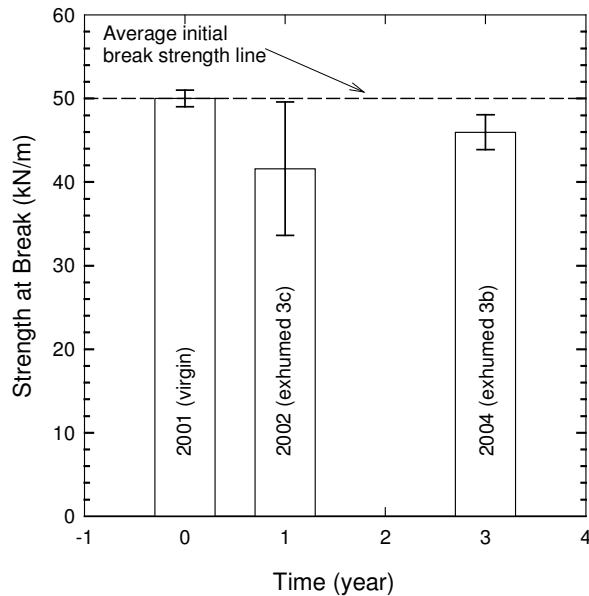


Figure 7. Tensile strength at break for virgin and exhumed 1.5 mm thick f-HDPE GM. Note: 3-5 specimens per sample, error bars represent ± 1 standard deviation.

6. SUMMARY AND CONCLUSIONS

The results of laboratory testing on the f-HDPE GM exposed to cold Arctic climate and hydrocarbons are reported. The fluorine treatment makes the f-HDPE GM more resistant to hydrocarbon diffusion and antioxidant depletion than the conventional untreated HDPE GM. The series of f-HDPE GMs samples buried in the backfill immediately upstream of the barrier system were retrieved in 2002 and 2004. OIT and tensile test results for buried 1.5 mm thick f-HDPE GM samples show that their properties have not changed significantly since installation in 2001. This suggests that the durability of the f-HDPE GM was maintained well beyond the initial 3-year design life of the barrier system. The difference in aging between the field samples and samples immersed in jet fuel in the laboratory at room temperature is attributed to (a) much lower temperatures in the field, and (b) the less extreme exposure conditions in the field with the geomembrane at most only being partly exposed to hydrocarbon given the variable distribution of hydrocarbons (e.g. in part due to variations in water levels adjacent to the geomembrane and in part due to spatial variation in the distribution of hydrocarbons at the site).

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