

Ageing of HDPE geomembranes in jet fuel A-1

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ABSTRACT: The latest findings regarding the ageing of high-density polyethylene (HDPE) geomembrane (GM) exposed to jet fuel are presented. Data from std-OIT and HP-OIT tests both indicate that some component(s) of the antioxidant package are readily leached into the jet fuel but once this component is removed the OIT values remain relatively stable for up to at least 4 years. The std-OIT depletion rates for the readily leachable component of the antioxidant package are estimated from the available data. Based on the jet fuel immersion test at 23°C the depletion time to reach the residual standard oxidative induction time (OIT) is 1.6 years for 1.5 mm thick conventional GM and 5.5 years for the 1.5 mm fluorinated GM. Thus fluorination had a significantly beneficial effect in terms of slowing antioxidant depletion. Arrhenius modelling based on data at three temperatures (23, 9 and -22°C) is used to predict std-OIT depletion times at a temperature (-1°C) applicable to containment of jet fuel spill at Brevoort Island in the Arctic. The estimated depletion time ranged from 14–24 years for 1.5 mm thick untreated GM, 22–33 years for 2 mm untreated GM, and 26–33 years for 1.5 mm fluorinated GM. For GMs with a similar composition, the OIT depletion rate decreased approximately with the square of GM thickness. At 23°C the depletion rate in the diffusion test was only about one-quarter of that in an immersion test. Tensile elongation at yield increased with time of immersion in jet fuel. Tensile yield properties and initial tear resistance of the GM were lower when the GM was wet with jet fuel than when dry. However, no significant change in dry initial tear resistance was observed. No significant change in crystallinity was observed in GM exposed to jet fuel. The immersion data suggest that the 1.5 mm f-HDPE GM liner used to containing the hydrocarbon spill on Brevoort Island is likely to perform well for a period well in excess of 25 years at the average field temperature (-1°C). Based on the findings from the diffusion tests with jet fuel on one side and water on the other (i.e. similar exposure conditions to that in the field), the time to antioxidant depletion is likely to about four times longer than when immersed in jet fuel and so the depletion time in the field under these conditions is projected to be in excess of 100 years. These tests will need to be run for a much longer period of time to allow a better estimate to be made of the depletion rate of remaining antioxidants and service life of GM exposed to jet fuel.

KEYWORDS: Geosynthetics, Geomembrane, Jet fuel, Hydrocarbons, Durability, Ageing, Antioxidants, Fluorination

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1. INTRODUCTION

High-density polyethylene (HDPE) geomembranes (GMs) can play an important role in barrier systems designed to minimize contaminant migration from both landfills (e.g. Brachman and Gudina 2008a, b; El-Zein and Rowe 2008; Saidi *et al.* 2008) and hydrocarbon spills. For example, in 2001, a composite liner comprised of a fluorinated high-density polyethylene (f-HDPE) GM and geosynthetic clay liner (GCL) was used to control the advective and diffusive migration of a jet fuel spill on Brevoort Island in the Canadian Arctic (Bathurst *et al.* 2006). Jet fuel is

composed of many hydrocarbons including paraffins, naphthenes and aromatics (Chevron 2000). These compounds pose a threat to the ground and surface water at many hydrocarbon-contaminated sites worldwide and the problem can be especially severe when the spill is near an environmentally sensitive body of water that could be contaminated (such as in the Arctic). When exposed to jet fuel, GMs may experience a change in properties with time and so some estimate is required of the service life of the GM used at the hydrocarbon-contaminated sites where the hydrocarbons are being effectively contained

and hence clean-up is delayed while higher priority contaminated sites are remediated. Thus there is a need to investigate the effects of interaction of GM with jet fuel and the impact of the climatic conditions in the Arctic on the performance of GMs.

The effect of GM immersion in air, water, municipal solid waste leachate, industrial waste leachate, acid mine drainage leachate and some hydrocarbons on the ageing and physical properties of HDPE GM have all been investigated (e.g., see Rowe *et al.* 2004; Gulec *et al.* 2004; Koerner 2005; Müller 2007; Rowe and Rimal 2008a, b; Rowe *et al.* 2008; Rimal and Rowe 2009; Rowe *et al.* 2009). However, there is a paucity of information concerning the long-term performance of GMs immersed in jet fuel.

Antioxidants are added to the GM to inhibit oxidative degradation and improve GM service life. After depletion of antioxidants the GM becomes susceptible to oxidative degradation (Grassie and Scott 1985). Preliminary laboratory investigations have provided some insight regarding antioxidant depletion and the change in the tensile properties of the HDPE and f-HDPE GMs (Rimal *et al.* 2004; Rowe *et al.* 2007) when immersed in jet fuel for about 1 year at room temperature. The f-HDPE GM exhibited slower antioxidant depletion than the conventional HDPE GM. No significant changes in tensile properties were observed in that 1 year period. This is consistent with the finding of Cazzuffi and Cantarelli (2006) who conducted HDPE GM immersion test in diesel fuel for a period of 8 months and reported negligible change in tensile properties and tear resistance during that period.

The objectives of this study were five-fold: (1) to improve the estimates of the antioxidant depletion time for HDPE and f-HDPE immersed in jet fuel at room temperature based on 4 years of data; (2) to use data obtained at three different temperatures to allow estimates to be made of likely antioxidant depletion rates at field temperature for the containment application at Breevoort Island and provide data that can be used at different locations and temperatures; (3) to examine the effect of GM thickness on antioxidant depletion rates and time for three thicknesses of conventional GM; (4) to examine results of the antioxidant depletion from GM in a diffusion test where there was pure jet fuel on only one side of the GM in order to assess the effect of one-sided exposure; and (5) to assess the effect of immersion in jet fuel (if any) on crystallinity, the tensile properties, and the tear resistance of the GM.

2. BACKGROUND

2.1. Overview of antioxidant depletion mechanisms in GM exposed to liquid chemicals

Antioxidant depletion from a GM occurs through migration and consumption (Müller 2007). Migration involves outward diffusion and volatilization of antioxidants. For a GM immersed in a liquid, outward diffusion is dominant whereas volatilization is more applicable in air exposure (Sangam and Rowe 2002). The consumption process

involves chemical degradation of antioxidants including hydrolytic deterioration of phosphites and phenols, oxidative reaction with oxygen, and/or free radicals and alkyl peroxides (Grassie and Scott 1985; Haider and Karlsson 2002; Bertoldo and Ciardelli 2004).

Most antioxidants with high molecular weight are physically entangled among polyethylene molecules which reduce the ability of chemicals to extract antioxidants. However, the rate of extraction can be accelerated by increasing concentration of chemicals and/or increasing temperature. The GM ageing studies of Sangam and Rowe (2002) have shown that immersion of a GM in synthetic leachate causes faster extraction of antioxidants than when it is immersed in distilled water or air. The main factors affecting loss of antioxidants due to migration are extraction conditions at the GM surface, partitioning coefficient and the diffusion of antioxidants in the polyethylene (Rowe and Rimal 2008b). HDPE is a semicrystalline polymer consisting of amorphous and crystalline regions. Long-term exposure to hydrocarbons for a long period of time may cause swelling of the amorphous region due to sorption (Maisonneuve *et al.* 1997). Amorphous regions can accommodate absorbed liquids without causing major changes in physical and mechanical properties. This can result in a small loss of strength but the effect is more or less reversible by evaporation when the liquid is removed (Koerner *et al.* 1990; Tisinger and Giroud 1993). The swelling of the amorphous region enhances the molecular mobility of antioxidants and hydrocarbon molecules (Maisonneuve *et al.* 1997). Hsuan and Koerner (1998) suggested that, due to the presence of crystalline and amorphous phases within the material, the distribution of antioxidants in HDPE is not uniform. The amorphous region of an HDPE contains the greatest concentration of antioxidants and the mobility of antioxidants in the amorphous phase controls their extractability. The crystallinity of a polymer is a dominant factor in reducing sorption and swelling of polymer in organic liquids (Tisinger *et al.* 1991). A semicrystalline polymer such as HDPE reaches a finite sorption level whereas a completely amorphous polymer will have infinite sorption of a liquid with an identical solubility parameter (Stessel and Garcia-Rubio 1994).

Temperature is an important factor that influences the overall depletion of antioxidants from the GM. An increase in temperature increases the antioxidant depletion rates from the GM (Hsuan and Koerner 1998; Sangam and Rowe 2002). The temperature dependence of antioxidant depletion from GM can be described by the Arrhenius relationship (Koerner *et al.* 1992; Hsuan and Koerner 1998, Sangam and Rowe 2002).

2.2. Fluorinated HDPE GM

A conventional, 'untreated', HDPE GM can be converted to a 'treated' (fluorinated HDPE, or f-HDPE) GM using a process in which elemental fluorine gas (F₂) is applied to both sides of the HDPE GM. The fluorine atoms chemically substitute the hydrogen atoms in the carbon-hydrogen (C-H) polyethylene chain, creating a carbon-fluorine (C-F) covalent bond on the outermost surface of

the HDPE GM. This creates a thin carbon–fluorine layer on the two sides of the GM. The thin carbon–fluorine layer creates a barrier to some hydrocarbons, but the mechanical properties (e.g. tensile, tear) remain relatively unchanged. In a study by Sangam and Rowe (2005), the surface fluorination of GM resulted in a reduction in diffusion and permeation coefficients by factors ranging from 1.5 to 4.5 for some chlorinated and aromatic hydrocarbons. This improved the effectiveness and performance of HDPE GM as a barrier to hydrocarbons. The fluorinated layers are expected to provide additional benefits by reducing the outward diffusion of antioxidants when exposed to hydrocarbons. This improves the service life of the GM.

It is envisaged that the surface fluorination improves the permeation resistance by three synergistic effects (Anand *et al.* 1994): (1) increasing the surface water wettability and consequently decreasing the surface wettability of nonpolar organic liquids; (2) reducing the free volume of the polymer through which the chemical can penetrate; and (3) reducing the segmental mobility of the polymer chains and diffusivity of large molecules due to the crosslinking that accompanies fluorination.

3. EXPERIMENTAL INVESTIGATION

3.1. Series of tests

Four series of GM immersion tests were conducted in jet fuel. In the first (preliminary) series 1.5 mm thick HDPE and f-HDPE GMs were immersed in Jet A-1 at 23°C. This series was intended to provide a direct indication of the effect of fluorination on antioxidant depletion. In the second test series, the 1.5 mm thick HDPE, 1.5 mm thick f-HDPE and 2.0 mm thick HDPE GMs were compared at three different temperatures (23, 9 and –22°C) so as to allow the development of an Arrhenius relationship that could then be used to predict depletion times at temperatures of interest between the temperatures examined. Additionally the experiment was intended to provide initial insight regarding the effect of GM thickness on GM obtained from manufacturer A. The third test series, examined the effect of thickness (1.5, 2.0 and 2.5 mm) on conventional HDPE GMs from manufacturer B to allow some assessment of variability in time to antioxidant depletion with different products. These tests were also performed at three temperatures (23, 9 and –22°C). The fourth series of tests examined the GM samples from manufacturer A retrieved from diffusion tests in jet fuel (Rowe and Mukunoki, personal communication) to allow an assessment of the effect of full immersion versus having Jet A-1 only on one side of the GM (as would be expected in the field).

3.2. Materials

3.2.1. Jet fuel A-1

All tests were conducted using Jet fuel of grade Jet A-1. This is a colourless to pale yellow liquid with kerosene-like odour. According to the ASTM D1655 the specific gravity of Jet A-1 at 15°C can be between 0.775 to 0.840

(–). It has a freezing point of –47°C, a viscosity at –20°C of 8 mm²/s and a very low solubility in water (5 mg/l; Cheminfo 2001). Jet A-1 is composed of a mixture of many different saturated and unsaturated hydrocarbons. It consists of blends of refined hydrocarbons derived from crude petroleum, naturally occurring gasoline, naturally occurring non-hydrocarbons and additives (ASTM D1655).

Current analytical techniques are not able to separate all of the individual hydrocarbon species present in the jet fuel, but the major hydrocarbons in the jet fuel are members of the paraffin (C_nH_{2n+2}), naphthene (C_nH_{2n}), or aromatic (monocyclic C_nH_{2n-6}; and dicyclic naphthalene C₁₀H₈) classes (Chunshan, *et al.* 2000; Chevron 2000). Jet A-1 is a mixture of aliphatic and aromatic hydrocarbons with carbon number distribution predominantly between about C8 and C16 (Chevron 2000; Cheminfo 2001).

Jet fuel composition and specification is established by ASTM in consultation with manufacturers and aviators. The ASTM D1655 specification for jet fuel is based on performance characteristics and no standard formula exists for Jet A-1. The specification states that the jet fuel composition should not exceed a maximum of aromatic hydrocarbons of 25% by volume, mercaptan sulphur 0.003% by mass, and total sulphur 0.3% by mass (ASTM D1655). The additives in jet fuel may include antioxidants, a metal deactivator and an electrical conductivity additive.

3.2.2. Series I GMs

The investigation was conducted on (1) 1.5 mm thick HDPE GM and (2) 1.5 mm thick f-HDPE GM supplied by manufacturer A. In the following discussions, these GMs will be denoted as 1.5-GM1-A and 1.5-f-GM1-A, respectively, where the first number (1.5) refers to GM thickness, the second number (1 in GM1) to the test series and the final letter (A) to the product manufacturer.

The key properties of these GMs are listed in Table 1. These smooth black-surfaced HDPE GMs were produced from virgin polyethylene resin. As per manufacturer's specifications these GMs contained approximately 97.5% polyethylene and the remaining 2.5% consisted of carbon black, trace amounts of antioxidants and heat stabilizers. The 1.5-GM1-A was surface fluorinated to produce the 1.5-f-GM1-A. This created a thin carbon–fluorine layer on both sides. The thickness of the fluorinated layer was found to range from 0.31 to 0.37 μm measured by scanning electron microscope combined with energy dispersive X-ray. The untreated and fluorinated GM can be distinguished by Fourier transform infrared (FTIR) scans (Figure 1). These scans were obtained using the attenuated total reflectance (ATR) method. The strong carbon hydrogen (C–H) peak at 2850 cm⁻¹ is characteristic of untreated GM and the strong carbon fluorine (C–F) peak at 1100 cm⁻¹ is the result of the presence of C–F bonds in fluorinated GM.

The standard oxidative induction time (OIT) values for the GMs were greater than the minimum value of 100 min required by Geosynthetic Research Institute GM-13 (GRI 1997) and the Ontario Regulation 232/98 of the Environ-

Table 1. Properties of series I and II GMs: manufacturer A

Property	Method (ASTM)	1.5-GM1-A 1.5-GM2-A		1.5-f-GM1-A 1.5-f-GM2-A		2.0-GM2-A	
		Avg.	COV	Avg.	COV	Avg.	COV
Thickness (mm)	As received	1.5	–	1.5	–	2.0	–
Density (g/cm ³)	D1505	0.94	–	0.94	–	0.94	–
std-OIT (min)	D3895	135	1.5	137	0.7	134	1.5
HP-OIT (min)	D5885	227	2.5	175	7.4	707	4.9
Crystallinity (%)	E794	52	2.4	51	2.2	39	7.8
MI (g/10 min)	D1238	0.47	3.7	0.46	3.1	0.44	2.6
Tensile properties	D6693						
Tensile strength at yield (kN/m)		24	3.7	23	2.4	37	1.5
Tensile strength at break (kN/m)		51	11	54	2.8	62	12
Tensile strain at yield (%)		20	1.9	20	2.8	19	1.6
Tensile strain at break (%)		869	12	979	2.8	759	10
Initial tear resistance (N)	D1004	205	3.4	205	1.2	294	0.36
Single point stress crack resistance (h)	D5397 appendix	> 300	–	> 300	–	> 300	–

Avg., average; COV, coefficient of variation (%). For the series II tests, the initial std-OIT of 1.5 mm untreated GM was 148 min (COV = 1.7%) and 1.5 mm fluorinated GM was 146 min (COV = 1.6).

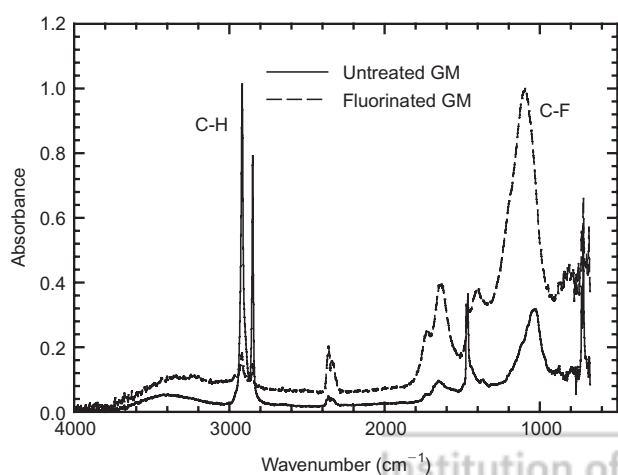


Figure 1. FTIR-ATR scans of untreated and fluorinated GMs. Absorbance for untreated GM is normalized by the C-H peak value, and fluorinated GM is normalized by C-F peak value

mental Protection Act, (MoE 1998). The OIT values for the 1.5-GM1-A (135 min) and 1.5-f-GM1-A. (137 min) GMs were quite similar. The manufacturer would not provide the information on types and amounts of antioxidants in the GMs; however, the virgin GMs were analysed for antioxidants at CIBA[®] Testing services, Tarrytown, New York. Antioxidants and ultraviolet absorbers (UVA) were screened by high-performance liquid chromatography (HPLC). The identified antioxidants (Rimal 2009) were hindered phenols (Irganox 1010 and 1076) and phosphites/phosphates (Igrafos 168). Hindered amine light stabilizers (HALS) were screened by thin layer chromatography (TLC) and gel permeation chromatography (GPC). No HALS were detected. The crystallinity of the two GMs also had similar values of 52 and 51%, respectively.

3.2.3. Series II GMs

Series II tests were conducted using the same 1.5 mm HDPE and f-HDPE GMs as used in series I. These

coupons were taken from different sections of the rolls and had slightly higher initial standard OIT than in series I. In addition, for series II the tests were conducted on a 2.0 mm thick HDPE GM with properties as listed in Table 1. This GM was also produced by manufacturer A but in addition to being thicker it appeared to have been produced from a different resin with lower percentage crystallinity (39% in comparison with 51–52%) and a different antioxidant package as although the OIT was similar (134 min for 2 mm GM versus 146–148 min for series II 1.5 mm GM), the HP-OIT of the 2 mm GM was more than three times higher than for the 1.5 mm thick GMs. In the following discussion these GMs will be denoted as 1.5-GM2-A and 1.5-f-GM2-A and 2.0-GM2-A, respectively. The tensile strength depended on the thickness of GM with higher values for the thicker GM.

3.2.4. Series III GMs

The series III investigation was conducted on three smooth HDPE GMs of thicknesses 1.5, 2.0 and 2.5 mm provided by manufacturer B. In the following discussions, these GMs will be denoted as 1.5-GM3-B, 2.0-GM3-B and 2.5-GM3-B. These GMs were obtained to allow an examination of the effect of thickness for GMs from the same manufacturer and to allow a comparison of the antioxidant depletion for GM of similar thickness from different manufacturers (i.e. by comparing 1.5-GM2-A and 1.5-GM3-B, and 2.0-GM2-A and 2.0-GM3-B).

The typical properties of the series III GMs are listed in Table 2. The initial OIT values of the GMs were above 100 min. The OIT value was lowest at 136 min for the 2.5-GM-III compared with 143 min for 1.5-GM3-B, and 150 min for 2.0-GM3-B. The differences in OIT values were probably due to the fact that the GMs were manufactured from different resin lots at different times. The information on types and amounts of antioxidants in the GMs was not provided by the manufacturer. Analyses for the antioxidants were performed as described above for GMs produced by manufacturer A. The three GMs

Table 2. Properties of series III GMs: manufacturer B

Property	Method (ASTM)	1.5-GM3-B		2.0-GM3-B		2.5-GM3-B	
		Avg.	COV	Avg.	COV	Avg.	COV
Thickness (mm)	As received	1.5	–	2.0	–	2.5	–
Density (g/cm ³)	D1505	0.947	–	0.946	–	0.946	–
std-OIT (min)	D3895	143	1.3	150	0.8	136	0.3
HP-OIT (min)	D5885	245	4.8	268	3.8	239	4.7
Crystallinity (%)	E794	46	10	52	2.7	50	3.7
MI (g/10 min)	D1238	0.09	22	0.06	17	0.10	10
Tensile Properties	D6693						
Tensile-strength at yield (kN/m)		28	2.2	38	1.3	47	1.2
Tensile-strength at break (kN/m)		44	22	60	7.5	48	29
Tensile-strain at yield (%)		24	4.3	21	1.2	19	3.9
Tensile-strain at break (%)		793	19	788	5.2	634	22
Single point stress crack resistance (h)	D5397 Appendix	> 300	–	> 300	–	> 300	–

Avg., average; COV, coefficient of variation (%).

contained the same antioxidants package. The identified antioxidants (Rimal 2009) were hindered phenols (Irganox 1010 and 1076) and phosphites/phosphates (Igrafos 168). No HALS were detected. The crystallinity of the 2.0-GM3-B and 2.5-GM3-B were about the same with 52 and 50%, respectively. The 1.5-GM3-B had a slightly lower average crystallinity value of 46% but with coefficient of variation (COV) of 10.4%.

3.2.5. Series IV GMs

Some GM samples from the jet fuel diffusion tests (Rowe and Mukunoki, personal communication) at room temperature (23°C) were also tested after the termination of the tests. The GM used in these diffusion tests was exposed to pure jet fuel on the source side of the GM only. Jet fuel then diffused through the GM to water on the receptor side of the GM (similar to the expected behaviour for intact GM in the field). These samples were tested to infer the depletion of antioxidants when one side is in contact with Jet A-1 and the other is in contact with water. In these tests, the untreated GM denoted as 1.5-GM4-A had an average OIT value of 135 min and crystallinity of 45%. The fluorinated GM denoted as 1.5-f-GM4-A had OIT of 134 min and crystallinity of 44% (Table 3). The difference between the OIT and crystallinity for the series I, II and IV GMs illustrates the variability that can be found for nominally the same product. The laboratory tests were all conducted using the same procedures, equipment and operator.

3.3. Experimental procedure

The GM coupon sizes depended on the interior dimensions of immersion containers and the coupons used were about 19 cm × 19 cm, and 13 cm × 25.5 cm in size. The GM coupons were immersed in a bath filled with jet fuel. They were placed upright and separated from each other using 5 mm diameter glass rods to allow sufficient space for exposure to the jet fuel. As the jet fuel slowly evaporated with time, the level of jet fuel in the bath was maintained by topping up at regular intervals. The jet fuel was completely replaced every few weeks (approximately every 12 to 15 weeks after the initial results of the series I test was available). The rationale behind completely replacing the jet fuel is discussed later in this paper.

A bath was set up inside a fumehood at laboratory temperature of 23°C. Baths were also placed in a special explosion-proof fridge at 9°C and in a freezer at –22°C. Samples were withdrawn for testing at various times. At each sampling period the coupons withdrawn from the bath were cut, rinsed, wiped, and were kept in a fume hood before testing commenced. GM samples for OIT testing were taken from the central portion of the coupons so that the tested specimens, particularly fluorinated GMs, were free from possible depletion of antioxidants from the edges.

3.4. Standard OIT tests

The GM samples exposed to jet fuel were retrieved at various time intervals and the amount of antioxidant

Table 3. Properties of series IV GMs: manufacturer A

Property	Method (ASTM)	1.5-GM4-A		1.5-f-GM4-A	
		Avg.	COV	Avg.	COV
Thickness (mm)	As received	1.5	–	1.5	–
OIT (min)	D3895	135	4.6	134	4.2
HP-OIT (min)	D5885	220	–	178	–
Crystallinity (%)	E794	45	1.5	44	3.4

remaining in the GM was evaluated using standard oxidative induction time (OIT) tests at 200°C and 35 kPa pressure (ASTM D3895). The OIT tests were carried out using TA Instruments 2910 and Q100 differential scanning calorimeters (DSC) which measured the difference in heat flow between a sample and a reference.

The OIT value is an index parameter related to the amount of antioxidant in the GM and is extremely useful for monitoring the depletion of antioxidants in the GM (Hsuan and Koerner 1998; Sangam and Rowe 2002; Müller and Jakob 2003; Rimal *et al.* 2004; Gulec *et al.* 2004). The OIT value of the GM decreases as antioxidants are depleted with time.

3.5. High-pressure OIT tests

High-pressure oxidative induction time tests (HP-OIT) (ASTM D5885) were also utilized to monitor the antioxidant depletion from some samples. A TA Instrument 2910 DSC with a special pressure cell was used to conduct the HP-OIT test. The GM specimen was held isothermally at 150°C and 3500 kPa in an oxygen environment until the exothermic peak was detected. The time to the onset of the exothermic peak was taken as the HP-OIT value.

The HP-OIT test is useful in measuring OIT if antioxidants such as hindered amine light stabilizers (HALS) are present in the GM. HALS lose their effectiveness at 200°C in the std-OIT test (Hsuan and Koerner 1998). Thomas and Ancelet (1993) have demonstrated that hindered amines were active at 150°C in the HP-OIT test. The testing temperature of 150°C in the HP-OIT test also decreases the volatility of these antioxidants during testing and the high pressure increases the concentration of the reacting oxidizing gas (Tikusis *et al.* 1993). HP-OIT provides more accurate OIT results if hindered amines are present in the GM. However, as noted earlier, no HALS were detected in any of the GMs tested.

3.6. Initial tear resistance tests

The initial tear resistance (ITR) is defined as the force required to initiate a tear of the material. The ITR was measured according to ASTM D1004. The test specimens were cut with a die conforming to the ASTM standard with 90° angle at the tearing location. The test was performed in a Zwick Roell universal testing machine at test speed of 51 mm/min as per ASTM. The testing machine comprised a 20 kN load cell to and wedge grips to hold the specimen. The maximum load usually found near the onset of tearing was recorded as the initial tear resistance in newtons.

3.7. Tensile tests

The tensile properties (strength and elongation at yield and break) of the GM was tested in accordance with ASTM D6693. Tensile tests were carried out using the Instron Model 3396 and Zwick Roell universal testing machines with wedge grips. The dumbbell-shaped tensile specimen (ASTM D638 Type IV-shaped specimen) was used. The test was conducted at a speed of 50 mm/min.

3.8. Crystallinity tests

Crystallinity tests were carried out using TA instruments 2910 and Q100 DSCs. The GM specimen of known mass was heated in the DSC in a nitrogen atmosphere to 200°C as per the procedures described in ASTM E794. The percentage crystallinity was obtained as the ratio of measured heat of fusion of GM specimen with the heat of fusion of 100% crystalline polyethylene, 290 J/g (Flory and Vrij 1963).

4. RESULTS AND DISCUSSION

4.1. Antioxidant depletion

The equation for depletion of antioxidant is (Hsuan and Koerner 1998):

$$OIT_t = OIT_o \times e^{(-st)} \quad (1)$$

where s is antioxidant depletion rate (week^{-1}), t is the immersion time (weeks), OIT_t is the OIT value (min) at time t representing the index measure of total antioxidant amount in the GM; and OIT_o is the initial OIT value (min).

If OIT_t is normalized by OIT_o , Equation 1 can be written as

$$\left(\frac{OIT_t}{OIT_o}\right) = e^{-st} \quad (2)$$

Equation 2 may also be written in logarithmic form as

$$\ln\left(\frac{OIT_t}{OIT_o}\right) = -st \quad (3)$$

4.1.1. Antioxidant depletion in series I

In this preliminary series samples of 1.5 mm thick HDPE GM (both untreated 1.5-GM1-A and fluorinated 1.5-f-GM1-A) were immersed in jet fuel. Figure 2 illustrates the change in normalized OIT relative to initial OIT (i.e. OIT_t/OIT_o) plotted against time in the untreated and

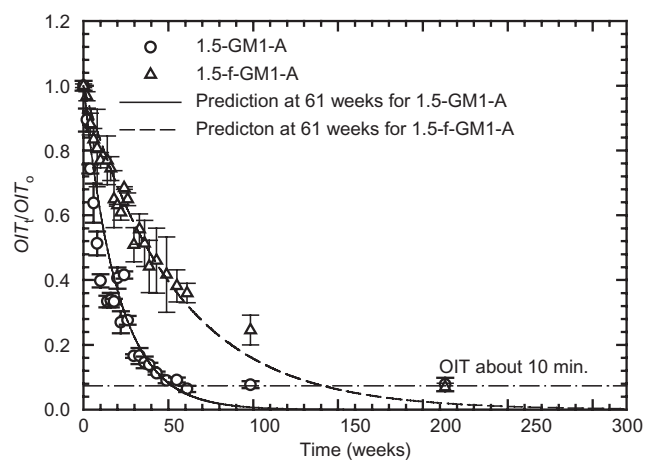


Figure 2. Variation of normalized std-OIT with immersion time for untreated and fluorinated GM exposed to jet fuel at room temperature in series I tests

fluorinated GMs immersed in jet fuel for 4.1 years. At each sampling event three to five replicate specimens were tested and the average value is shown with the vertical bars represent the standard deviation deduced from these tests.

The initial OIT value of the 1.5-GM-Series-I was 135 min. The OIT value gradually reduced with immersion time. From 14 to 26 weeks some scatter was observed in the data. The OIT values did not decrease at the same rate as was observed during the initial 14 weeks of immersion. It was hypothesized that the diffusion of antioxidants from the GM resulted in an increase in their concentration in the jet fuel adjacent to the GM. This would reduce the concentration gradient and further migration of antioxidants from the GM into the jet fuel. Thus after identifying this issue on week 27 the jet fuel in the bath was completely replaced. Afterwards a more rapid decrease in OIT value was observed. This provided some support for the hypothesis. The relationship between OIT and immersion time was exponential according to Equation 2 and as shown in Figure 2. It was observed that antioxidants depleted at a faster rate from untreated GM than fluorinated GM. Immersion in jet fuel substantially accelerated the antioxidant depletion process in comparison with that in water and synthetic leachate as observed in prior studies (Hsuan and Koerner 1998; Sangam and Rowe 2002). Based on early time data, Rowe *et al.* (2007) predicted that the OIT would reach a value of about 0.5 min (typically taken as the value for pure unstabilized HDPE without antioxidants (Hsuan and Koerner 1998) in 2.2 years. It was found (Figure 2), however, that the OIT did not drop below a residual OIT (OIT_r) of about 8–10 min for both GMs and remained there after 4 years of exposure to jet fuel.

It was hypothesized that the measured OIT_r could be due either to the effect of any traces of jet fuel remaining in GM or to a remaining amount of antioxidant in GM that was not readily leached by jet fuel at room temperature. To minimize any possible effect of traces of jet fuel remaining in the GM, the OIT tests were conducted after keeping the sample in air in a fumehood for about 2 weeks (to allow evaporation of any jet fuel), washing and wiping before the test. Furthermore, at the OIT test temperature of 200°C the volatile jet fuel would be expected to evaporate from the specimen prior to the introduction of oxygen. To verify whether jet fuel interfered with the results of the OIT test, virgin untreated and fluorinated GM specimens were immersed in jet fuel for about 24 h and tested for OIT. No significant difference was found in OIT values between the virgin GM and the GM exposed to jet fuel. Furthermore, antioxidant-depleted samples of HDPE GM (archived from another study) were exposed to jet fuel for about 24 h and tested for OIT. No significant difference in OIT values were observed before and after exposing the samples to jet fuel. These results provided evidence that the residual OIT (OIT_r) in the GM is not due to the traces of jet fuel in the GM but rather due to a portion of the OIT package that is not readily leached by the presence of Jet A1.

Based on this finding the data was plotted as illustrated

in Figure 3. The OIT depletion equation is now represented in the following form:

$$\left(\frac{OIT_t - OIT_r}{OIT_o - OIT_r}\right) = e^{-s't} \quad (4)$$

where, s' = antioxidant depletion rate (week^{-1}).

Equation 4 may also be written in logarithmic form as,

$$\ln\left(\frac{OIT_t - OIT_r}{OIT_o - OIT_r}\right) = -s't \quad (5)$$

At laboratory temperature the depletion rate, s' , of jet fuel-immersed 1.5-GM1-A was 0.0671 week^{-1} . The depletion rate of 0.0194 week^{-1} for the fluorinated GM (1.5-f-GM1-A) was only 29% of that for the untreated GM.

The time to deplete antioxidant (t_r) to the residual value can be represented by:

$$t_r = \frac{\ln(OIT_o - OIT_r) - \ln(OIT_f - OIT_r)}{s'} \quad (6)$$

where OIT_f is the final OIT value, which is taken as

$$OIT_f = OIT_r + 0.5 \quad (7)$$

For the 1.5-GM1-A the time for depletion to residual, t_r , was 83 weeks (1.6 years), and for 1.5-f-GM1-A it was 286 weeks (5.5 years). The difference in depletion time for untreated and fluorinated GM was 203 weeks (3.9 years). Based on these results the fluorination had beneficial effect and increased the antioxidant depletion time of the GM exposed to jet fuel. The antioxidant depletion times would be expected to be much longer at field temperatures in the Arctic, and so it can be inferred that the 'service life' of the untreated GM will be greater than 1.6 years and for the fluorinated GM it will be well over 5.5 years. The antioxidant depletion time at field temperatures in the Arctic is addressed in the next section. It should also be noted that although a significant amount of antioxidant had depleted by these times, there was still 8–10 min remaining and this could be expected to provide continued protection to the GMs and the additional time to full depletion of antioxidants could be large. Thus the estimates of depletion time presented herein are quite

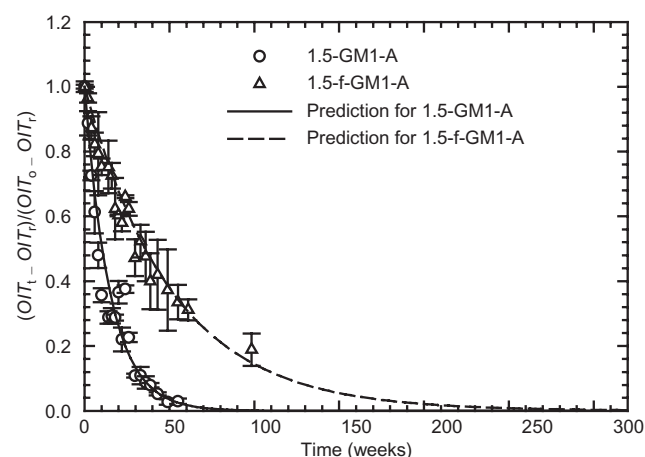


Figure 3. Variation of residual adjusted normalized std-OIT with immersion time for untreated and fluorinated GM exposed to jet fuel at room temperature in series I tests

conservative (i.e. on the low side) but are still useful for making engineering decisions.

4.1.2. Antioxidant depletion in series II

In the following discussion it should be remembered that while the two 1.5 mm GMs had fairly similar HP-OIT values (175 and 227 min), the 2 mm GM had a very different HP-OIT of over 700 min. The high HP-OIT value is often associated with the presence of HALS but there was no HALS detected in antioxidant analysis. Thus while thickness is one important variable, the difference in antioxidant package is another significant variable to be considered when interpreting the test results. Figure 4 shows the variation in the logarithm of standard $(OIT_t - OIT_r)/(OIT_0 - OIT_r)$ with immersion time at three testing temperatures of 23°C, 9°C and -22°C respectively using the same OIT_r as in series I. Each data point is the average of the three replicate samples tested and the vertical bars represent standard deviation. The lines represent the best fit of Equation 5. The values of depletion rates, s' , obtained from the slope of the lines in Figure 4 are listed in Table 4.

At test temperature of 23°C the antioxidant depletion rate, s' , was fastest for 1.5-GM2-A, followed by 2.0-GM2-A and slowest for 1.5-f-GM2-A. Figure 4a shows that the untreated GMs had a greater decrease in the OIT values than the fluorinated GM. The results indicated that the antioxidants detected by the std-OIT tests depleted 3.6 times faster from 1.5-GM2-A than 1.5-f-GM2-A. The s' was 1.6 times faster from 2.0-GM2-A than 1.5-f-GM2-A. Comparing the untreated GMs of two thicknesses the s' from 1.5-GM2-A was 2.2 times faster than the value for 2.0-GM2-A.

At the test temperature of 9°C there was a small difference in s' for the 2.0-GM2-A and 1.5-f-GM2-A (Figure 4b). The depletion rate, s' , was greatest for 1.5-GM2-A. The ratio of depletion rates of 2.0-GM2-A and 1.5-f-GM2-A was 1.04. The s' was 1.38 times faster for 1.5-GM2-A than 2.0-GM2-A and the s' was 1.43 times faster in 1.5-GM2-A than 1.5-f-GM2-A.

At a temperature of -22°C (Figure 4c) the inferred values for s' were very similar for the three GMs. In 2.0-GM2-A and 1.5-f-GM2-A the values of s' were equal. The value of s' was 1.3 times faster from the 1.5-GM2-A than the 2.0-GM2-A or 1.5-f-GM2-A.

Variations in HP-OIT versus immersion time for series II GMs are shown in Figure 5. At 23°C (Figure 5a) the HP-OIT of 2.0-GM2-A did not decrease significantly with time during 57 weeks of testing. In contrast std-OIT had

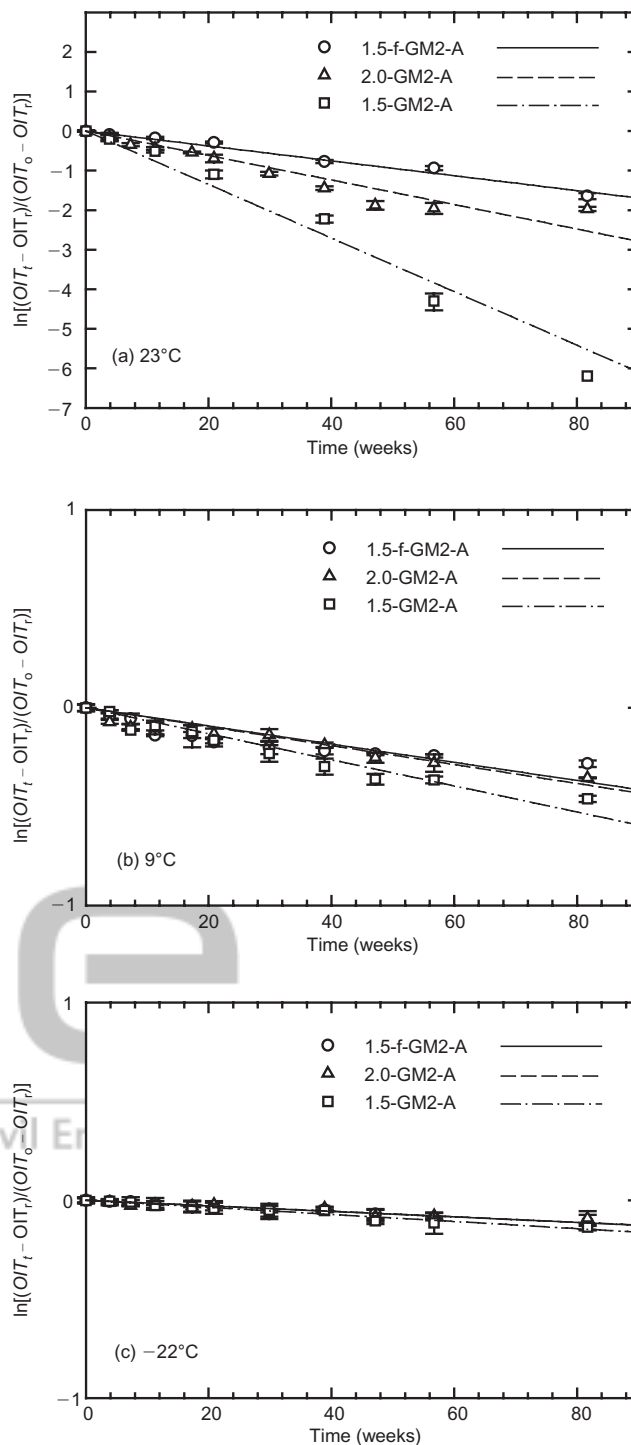


Figure 4. Variation of logarithm of normalized std-OIT with immersion time in series II tests at: (a) 23°C; (b) 9°C; (c) -22°C

Table 4. Std-OIT depletion rates in series II tests

Temperature (°C)	s' (week ⁻¹)		
	1.5-f-GM2-A	2.0-GM2-A	1.5-GM2-A
23	0.0188 (0.98)	0.0310 (0.89)	0.0677 (0.98)
9	0.0046 (0.60)	0.0048 (0.87)	0.0066 (0.92)
-22	0.0014 (0.98)	0.0014 (0.75)	0.0018 (0.95)

The number in parenthesis represents coefficient of determination (R^2).

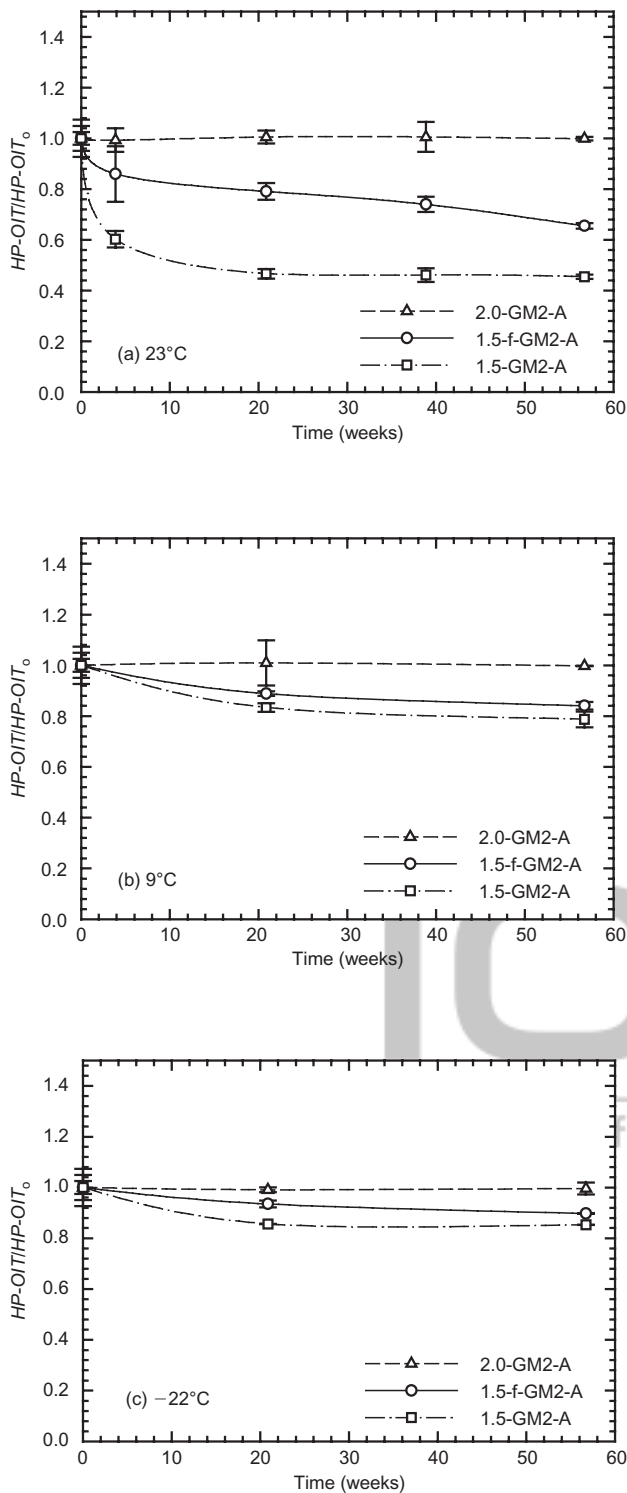


Figure 5. Change in normalized HP-OIT with immersion time in series II tests: (a) 23°C; (b) 9°C; (c) -22°C

reduced to 26 min (about 20% of its original value). The std-OIT results indicated the depletion of some antioxidants originally in the new GM. Whereas the HP-OIT results suggest that a component of the antioxidant package (or other unidentified antioxidant if present) might not have depleted and hence was contributing to the relatively constant HP-OIT value. As noted earlier, no HALS were detected in the CIBA analysis. The decline in HP-OIT was faster in the untreated GM 1.5-GM2-A than the fluorinated GM 1.5-f-GM2-A. In 1.5-GM-f-A the HP-OIT value decreased up to 20 weeks and remained steady up to 57 weeks. At 9°C (Figure 5b) the HP-OIT value had slightly decreased in 1.5-GM2-A and 1.5-f-GM2-A. A greater decline in HP-OIT was observed for 1.5-GM2-A than 1.5-f-GM2-A, whereas the HP-OIT for 2.0-GM2-A remained steady over time. At -22°C (Figure 5c) the HP-OIT value slightly decreased for both the 1.5-GM2-A and 1.5-f-GM2-A, but it did not decrease for the 2.0-GM2-A.

These results suggested that the depletion of antioxidant as observed in the HP-OIT test was quite different to that inferred from the std-OIT test. This highlights the role of the type of antioxidant present in the GM. Thus the results for 2 mm untreated GM suggests that a component of the antioxidant package that was detected by the HP-OIT tests might not have depleted by the exposure to jet fuel. Therefore the std-OIT results should be applied with considerable caution particularly for the 2 mm thick GM for which HP-OIT remained stable.

4.1.3. Antioxidant depletion in series III

Changes in logarithm of standard $(OIT_t - OIT_r) / (OIT_0 - OIT_r)$ versus immersion time for series III GMs at 23, 9 and -22°C were plotted to obtain the s' values listed in Table 5. The plot at 9°C is illustrated in Figure 6. At 23°C, the std-OIT depletion rate, s' , was 1.2 times greater for 1.5-GM3-B than 2.0-GM3-B, and 1.6 times greater for 1.5-GM3-B than 2.5-GM3-B. The s' from 2.0-GM3-B was 1.3 times greater than 2.5-GM3-B. At 9°C the value for s' was 1.3 times greater for 1.5-GM3-B than 2.0-GM3-B and 1.6 times greater for 1.5-GM3-B than 2.5-GM3-B. At -22°C the s' was 1.1 times greater for 1.5-GM3-B than 2.0-GM3-B, and 1.3 times greater for 1.5-GM3-B than 2.5-GM3-B. Results at 23 and -22°C are given by Rimal (2009).

At room temperature the decline in HP-OIT was fastest for 1.5-GM3-B, followed by 2.0-GM3-B and slowest for 2.5-GM3-B. For 1.5-GM3-B the HP-OIT value decreased by about 40% up to 45 weeks and remained steady up to

Table 5. Std-OIT depletion rates in series III test

Temperature (°C)	s' (week ⁻¹)		
	1.5-GM3-B	2.0-GM3-B	2.5-GM3-B
23	0.0483 (0.89)	0.0390 (0.97)	0.0308 (0.98)
9	0.0069 (0.91)	0.0053 (0.93)	0.0044 (0.93)
-22	0.0021 (0.74)	0.0020 (0.77)	0.0016 (0.75)

Note: The number in parenthesis represents coefficient of determination (R^2).

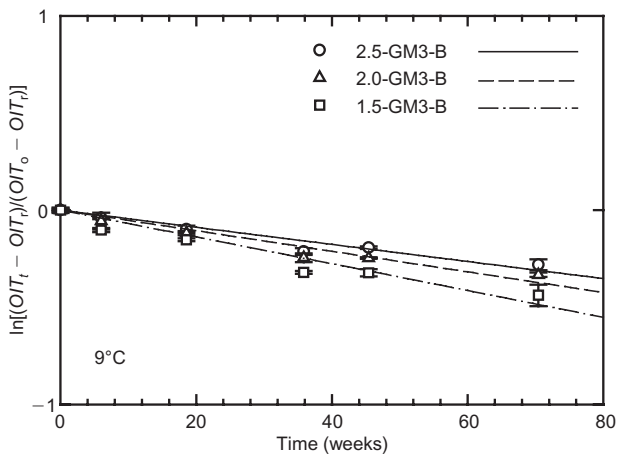


Figure 6. Variation of logarithm of normalized std-OIT with immersion time in series III tests at 9°C

70 weeks (Rimal 2009). At other test temperatures HP-OIT had slightly declined (about 10–19% at 9°C and 5–12% at –22°C in 70 weeks) in all three GM with the greatest depletion in 1.5-GM3-B.

4.1.4. Effect of GM thickness and antioxidant depletion rates

Figure 7 presents the relationship between the thickness of GM and s' in series III tests. It should be noted that each of these GMs from manufacturer B has fairly similar std-OIT and HP-OIT values, and hence likely very similar antioxidant packages, and so the primary variable in this series was GM thickness. Neogi (1996) has shown mathematically that the half-time of mass uptake of solute into the membrane can be approximated by $0.01227L^2/D$, where L is the thickness and D is the diffusion coefficient. Hence it can be expected that the t_r is proportional to the square of the thickness of the GM (other things being equal). Consequently the s' would be related to the inverse square of thickness of the GM. An excellent correlation was obtained between inverse square of thickness and s' at 23 and 9°C. At –22°C the coefficient of determination (R^2) is lower. This is because the values of s' were low and not very sensitive to thickness at –22°C. Thus the

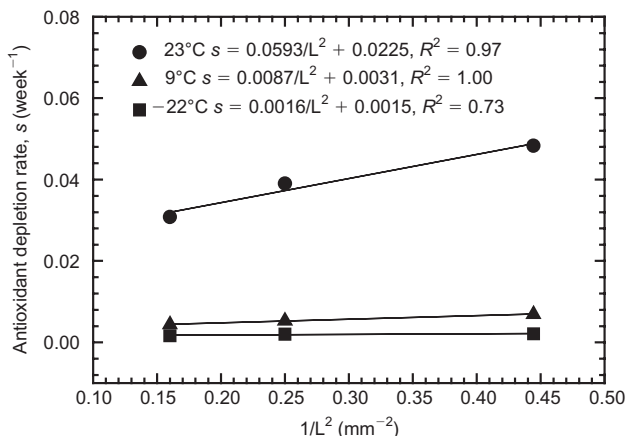


Figure 7. Relationship between thickness and antioxidant depletion rates based on std-OIT for geomembrane B in jet fuel

data shown in Figure 7 confirms that the antioxidant depletion rate depends on the square of GM thickness and hence (other things being equal) a greater GM thickness will provide a longer time for antioxidant depletion. The effect is greatest at 23°C and very small at –22°C.

4.1.5. Antioxidant depletion in series IV

Figure 8 shows the variation in the logarithm of standard $(OIT_t - OIT_r)/(OIT_0 - OIT_r)$ plotted against the time at which the jet fuel diffusion test were terminated at 23°C. The s' for 1.5-GM4-A was 0.0141 week^{-1} and for 1.5-f-GM4-A it was 0.0045 week^{-1} . It was observed that the antioxidant depleted 3.13 times faster from untreated GM than the fluorinated GM. The s' from GM in diffusion tests were lower than in direct immersion tests. For the untreated GM the s' in the diffusion test was only 21% of that in the immersion test. For the fluorinated GM the s' in the diffusion test was 24% of that in the immersion test. At the start of a diffusion test only one face of the GM was exposed to jet fuel. It can be shown that antioxidant depletion is much faster for a GM immersed in Jet A-1 than one immersed in water. If it is hypothesized that for these diffusion tests the depletion is predominantly from the side with jet fuel, one would theoretically expect the depletion rate to be 25% of that in the immersion tests. It can be seen that this is not a bad approximation with the depletion rates being only slightly higher than expected if there was simple one way diffusion. This highlights the fact that most of the depletion occurs to the face with jet fuel and only a small proportion to the face exposed to water. This is generally consistent with the finding at 23°C that the depletion rate, s' , for a 2.0 mm thick untreated GM (manufacturer A) immersed in jet fuel (0.0310 week^{-1}) was about 22 times faster than for a similar GM immersed in water (0.0014 week^{-1} ; calculated at 23°C from results in Rowe *et al.* 2009).

Using Equation 6, the time for std-OIT depletion to residual value, t_r was calculated for the diffusion tests samples. For the untreated GM (1.5-GM4-A) the t_r was 393 weeks (7.6 years) whereas for fluorinated GM (1.5-f-GM4-A) it was 1226 weeks (23.6 years). These results (summarized in Table 6) provide a basis for the assess-

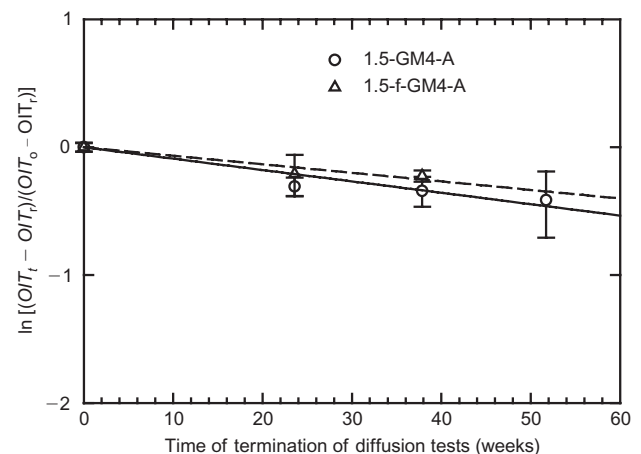


Figure 8. Std-OIT versus time in diffusion test with jet fuel on once side and water on the other at 23°C

Table 6. Comparison of antioxidant depletion from GM in jet fuel immersion test and diffusion tests at 23°C based on std-OIT

Geomembrane	s' (week ⁻¹)			t_r (years)		
	Immersion	Diffusion	Diffusion/Immersion	Immersion	Diffusion	Diffusion/Immersion
1.5 mm untreated	0.0677	0.0141	0.21	1.6	7.6	4.8
1.5 mm fluorinated	0.0188	0.0045	0.24	5.7	23.6	4.1

ment of the effect of full immersion versus having jet fuel only on one side of the GM. One-sided exposure to jet fuel would be expected in containment applications in the field. The results for t_r for one-sided exposure was substantially longer than that for full immersion in jet fuel. It was 6 years longer for the untreated GM and 18 years longer for the fluorinated GM.

4.2. Arrhenius modelling and prediction

The relationship between reaction rate and temperature is known as the Arrhenius equation:

$$s = A \cdot e^{-\left(\frac{E_a}{RT}\right)} \quad (8)$$

Taking the natural logarithm and rearranging, Equation 8 can be expressed as

$$\ln(s') = \ln(A) - \left(\frac{E_a}{R}\right) \left(\frac{1}{T}\right) \quad (9)$$

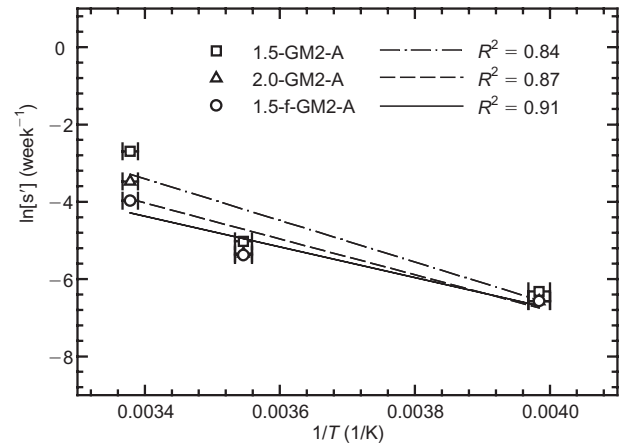
where s' is the antioxidant depletion rate (week⁻¹); A is the constant (week⁻¹); E_a is the activation energy (kJ/mol); R is the universal gas constant (8.31 J/mol per K); and T is the absolute temperature (K).

After establishing Equation 9 from the laboratory results at different test temperatures, s' can be predicted at other site-specific temperatures. The main assumptions associated with the use of Equation 9 to predict s' are: (1) parameter s' is a function of temperature; (2) the value of the constant A is material- and exposure system-dependent although the temperature dependence of A may be neglected; and (3) the activation energy remains relatively constant over the temperature range examined and predicted. Using the predicted values of s' , the t_r can be estimated for series II and III GMs.

4.2.1. Series II GMs

The plot of inverse of temperature, $1/T$ (in K⁻¹) against logarithm s' , $\ln(s')$ (in week⁻¹) is shown in Figure 9. The straight lines were obtained by linear regression. The effect of temperature on s' can be observed from the plot, with higher s' at higher temperature. The Arrhenius equations and the deduced activation energy (slope E_a/R of the regression lines) are listed in Table 7. The activation energy and the intercept for the untreated GMs were higher than the values for the fluorinated GM.

Using the Arrhenius equations listed in Table 7 the s' and t_r values were estimated at average field temperature at BAF-3 (Brevoort Island). Predictions were also made using the linear interpolation of the data between 9 and

**Figure 9. Arrhenius plots of antioxidant depletion rates series II GM. Antioxidant depletion rate based on std-OIT****Table 7. Arrhenius equations and inferred activation energies in based on std-OIT for series II and III tests**

GM exposed to jet fuel	Arrhenius equation	E_a (kJ/mol)
1.5-GM2-A	$\ln(s') = 14.88 - 5379/T$ $R^2 = 0.84$	44.7
2.0-GM2-A	$\ln(s') = 11.78 - 4650/T$ $R^2 = 0.87$	38.7
1.5-f-GM2-A	$\ln(s') = 9.13 - 3971/T$ $R^2 = 0.91$	33.0
1.5-GM3-B	$\ln(s') = 12.30 - 4681/T$ $R^2 = 0.86$	38.9
2.0-GM3-B	$\ln(s') = 10.96 - 4364/T$ $R^2 = 0.81$	36.3
1.5-f-GM3-B	$\ln(s') = 10.75 - 4364/T$ $R^2 = 0.82$	36.3

–22°C since the practical temperature lies in that range. This was done to provide the range of predication from two methods recognizing the uncertainty in the linearity of the Arrhenius equation between 23 and –22°C. Estimates were made at –1°C (the general year long average temperature applicable approximately at all depths at or below 0.5 m) as given in Table 8. Estimates were also made separately at average temperature during summer (July–August) and remaining months. This was done at all measured depths. Weighted average ($s'_{adjusted}$) was used to make predictions using depletion rates in summer (s'_{summer}) and the remaining months of the year (s'_{remain}).

Table 8. Antioxidant depletion time based on std-OIT for Series II GM at (a) -1°C (full year average temperature at most depths) and (b) using weighted average of summer and remaining months temperatures at BAF-3 at 0.5 m below ground surface

GM	Based on linear fit between 23 and -22°C , t_r (years)		Based on linear fit between 23 and -22°C , t_r (years)	
	(a) -1°C	(b) Weighted average temperature	(a) -1°C	(b) Weighted average temperature
2.0-GM2-A	22	21	33	33
1.5-GM2-A	14	14	24	24
1.5-f-GM2-A	26	25	33	33

$$s'_{\text{adjusted}} = \frac{s'_{\text{summer}} + 5s'_{\text{remain}}}{6} \quad (10)$$

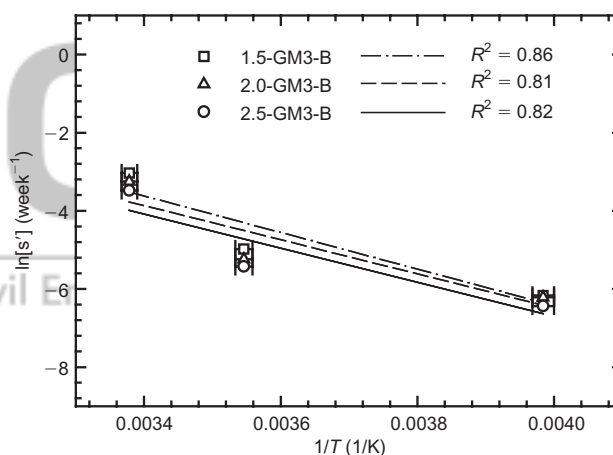
The predicted t_r using s'_{adjusted} at the depth of 0.5 m are also given in Table 8. These predictions yielded similar (to within 1 year) depletion times at all depths to that obtained from s' based on the yearly average temperature of -1°C .

To provide data applicable at different locations and temperatures, predictions were also made at temperatures ranging from -15 to $+15^{\circ}\text{C}$. The predictions were made using Arrhenius equation and linear interpolation of the laboratory data. At temperatures above 9°C the prediction were also made using linear interpolation of data at 9 and 23°C . At temperatures below 9°C the prediction were also made using linear interpolation of data at 9 and -22°C . The predicted times to deplete to the residual std-OIT value based on the two methods are given in Table 9. Within the predicted temperature range of -15 to 15°C the antioxidant depletion times were greatest for the fluorinated GM 1.5-f-GM2-A, followed by the untreated GM 2.0-GM2-A and lowest for the thinner untreated GM 1.5-GM2-A. These predictions assume immersion in the jet fuel. As discussed earlier the depletion rate for a GM with water on one side and jet fuel on the other is likely to only be about 25% of that for immersion and hence the time to depletion under these condition is likely to be upto about four times the values given in Table 9.

4.2.2. Series III GMs

Prediction of s' and t_r was carried out for series III GMs. The Arrhenius plot of s' for series III GM in jet fuel is

shown in Figure 10 (the deduced Arrhenius equations and activation energies are listed in Table 7). The antioxidant depletion times to the residual OIT value are given in Table 9. Within the predicted temperature range the depletion times were greatest for 2.5-GM3-B, followed by 2.0-GM3-B and lowest for 1.5-GM3-B. The predicted s' and time at -1°C are provided in Table 10. The prediction using weighted average of summer and winter months yielded the same predicted times (rounded to nearest year). It was found that the s' was smallest for the thickest GM 2.5-GM3-B followed by the 2.0-GM3-B and lowest for the 1.5-GM3-B.

**Figure 10. Arrhenius plots of std-OIT antioxidant depletion rates series III GM****Table 9. The predicted antioxidant depletion times based on std-OIT at temperatures ranging from -15 to 15°C for immersion in jet fuel (note: as discussed the depletion times are likely to be upto about four times longer if the jet fuel is on one side and water is on the other side of the GM)**

Temperature ($^{\circ}\text{C}$)	Series II t_r (years)			Series III t_r (years)		
	1.5-GM2-A	2.0-GM2-A	1.5-f-GM2-A	1.5-GM3-B	2.0-GM3-B	2.5-GM3-B
-15	42–44*	55–58	57–57	37–37	42–41	51–50
-10	28–35	39–47	42–47	26–30	31–34	37–42
-5	19–28	28–39	32–39	19–25	22–29	27–36
0	13–23	20–32	24–32	14–20	16–25	20–31
5	9.4–19	15–27	19–27	10–17	13–22	15–26
10	6.7–14	11–19	15–21	7.5–13	9.3–17	11–21
15	4.8–5.9	8.4–9.7	11–13	5.6–6	7.1–8	8.7–10

*X–Y: X, derived from Arrhenius equation using data at 23, 9 and -22°C . Y, derived from linear interpolation between data at 23 and 9°C or 9 and -22°C , depending on temperature.

Table 10. Std-OIT antioxidant depletion rates and time for Series III GM at -1°C (full year average temperature) (note: as discussed the depletion times are likely to be upto about 4 times longer if the jet fuel is on one side and water is on the other side of the GM)

GM	Based on linear fit between 23 and -22°C		Based on linear fit between 9 and -22°C	
	s' (week^{-1})	t_r (years)	s' (week^{-1})	t_r (years)
1.5-GM3-B	0.0074	14	0.0051	21
2.0-GM3-B	0.0063	17	0.0042	26
2.5-GM3-B	0.0051	21	0.0034	31

4.3. Variation in mechanical properties

Variation in tensile properties versus time was monitored for series I GM. The samples for tensile test were kept in air in a fumehood for about 2 weeks to dry the samples prior to testing. This was done to minimize the possible effect of traces of jet fuel remaining in the GM. In order to check the effect of jet fuel in the GM, two identical samples were tested after 76 weeks of exposure: one immediately after taking it out from jet fuel, and one after 2 weeks of drying. The stress–strain curves for ‘wet’ and ‘dry’ conditions are shown for the untreated GM in Figure 11. The tensile properties in these tests are given in Table 11. The t -test results suggested statistically significant difference (at 95% confidence level) in tensile yield

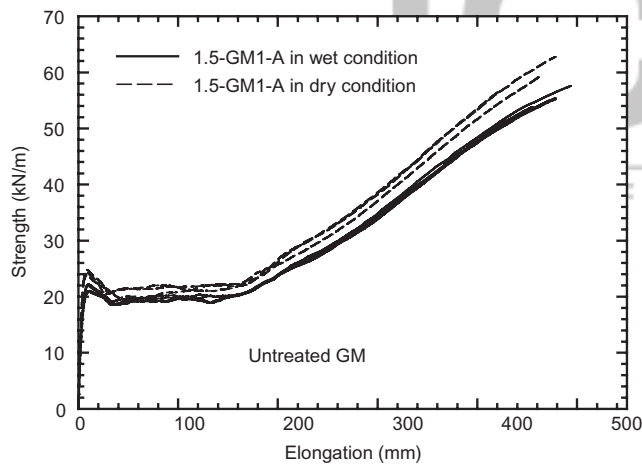


Figure 11. Stress–strain curves for series I GM in wet and dry conditions at 76 weeks of immersion at 23°C

properties between the ‘wet’ and ‘dry’ conditions. For the untreated GM 1.5-GM1-A testing in the ‘wet’ condition gave a yield strain of 38% (SD = 2.9) whereas in the ‘dry’ condition the yield strain was 28% (SD = 0.85). Similar observations were made for the fluorinated GM 1.5-f-GM-A. Higher yield strain was obtained in the ‘wet’ condition due to the softening effect of the jet fuel sorbed in the GMs. The yield strength of the GMs were lower in the ‘wet’ condition. No statistically significant difference (at 95% confidence level) was found in tensile break properties.

The variation of tensile properties with respect to immersion time for the series I GM is given in Figure 12. Similar variations in elongation at yield (Figure 12a) were observed in both 1.5-GM1-A and 1.5-f-GM1-A over the test period when tested in the ‘dry’ condition. After 11 weeks of exposure, the elongation at yield increased from 19.4% (SD = 0.31) for the untreated GM to 22.5% (SD = 0.40). There was a statistically significant difference (at 95% confidence level) in elongation at yield between the virgin and the exposed GM. The increase in yield strain can be attributed to softening of the GM by jet fuel. The elongation at yield gradually increased over time. At the final testing time of 213 weeks the elongation at yield had increased to 29.2% (SD = 0.39). Similarly for the fluorinated GM, the elongation at yield had increased from the initial value of 19.4% (SD = 0.31) to 29.2% (SD = 0.65) in 213 weeks.

For the untreated GM, yield strength (Figure 12b) did not change significantly over the testing period. The yield strength of the jet fuel-exposed fluorinated GM remained slightly higher than that of the virgin GM, although data remained scattered over the testing period. After 213 weeks of immersion in jet fuel there was no statistically

Table 11. Tensile properties of GMs in wet and dry conditions at 76 weeks of immersion at 23°C

	Yield		Break	
	Strength (kN/m)	Elongation (%)	Strength (kN/m)	Elongation (%)
1.5-GM1-A wet	22 ± 0.6	38 ± 2.9	56 ± 1.9	952 ± 39
1.5-GM1-A dry	24 ± 0.5	28 ± 0.9	60 ± 3.0	913 ± 55
1.5-f-GM1-A wet	22 ± 0.6	38 ± 2.7	54 ± 2.7	910 ± 86
1.5-f-GM1-A dry	25 ± 0.6	28 ± 0.6	52 ± 2.7	806 ± 22

Error values represent standard deviations.

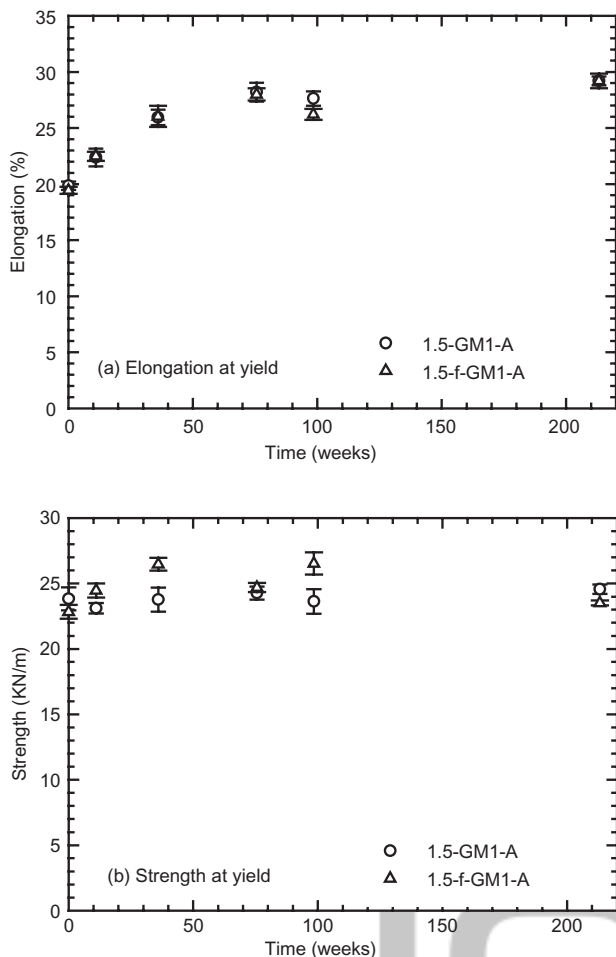


Figure 12. Variation of tensile properties (machine direction) with respect to immersion time for series I GM: (a) elongation at yield; (b) strength at yield

significant difference in the yield strength of the virgin and exposed fluorinated GM.

Figure 13 illustrates the tensile break properties. For the untreated GM the elongation at break (Figure 13a) remained similar during the test period with some scatter in the data. With the fluorinated GM the elongation at break for the exposed GM were slightly lower than the virgin GM. However elongation at break remained scattered over the study period.

The strength at break (Figure 13b) also remained unchanged. The break strength value for the virgin untreated GM was 50.9 kN/m (SD = 5.4) and remained similar at 51.3 kN/m (SD = 6.9) after 213 weeks of immersion in jet fuel. Similarly for the fluorinated GM the initial value of break strength was 54.2 kN/m (SD = 1.5) and remained similar with a value of 53.9 kN/m (SD = 0.72) after 213 weeks.

Variation in crystallinity of series I GMs versus immersion time is shown in Figure 14. No significant changes (at 95% confidence level) in crystallinity were observed over the testing period of 213 weeks for either GM. For 1.5-GM1-A the initial crystallinity was 52% (SD = 1.3) and at 213 weeks it was 49% (SD = 0.25). For 1.5-f-GM1-A the initial crystallinity was 51% (SD = 1.2) and at 213 weeks it was 51% (SD = 0.53). The change in

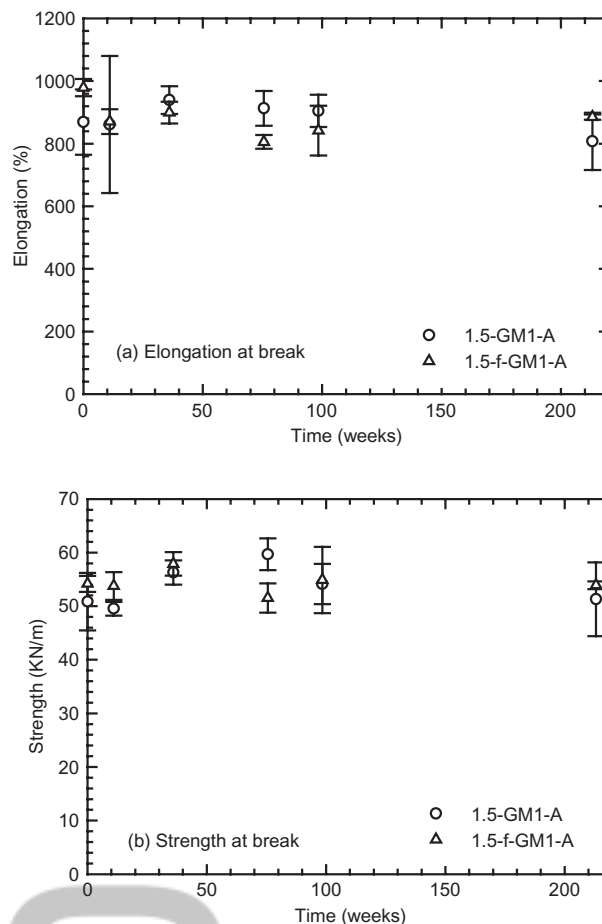


Figure 13. Variation of tensile break properties (machine direction) with respect to immersion time for series I GM: (a) elongation at break; (b) strength at break

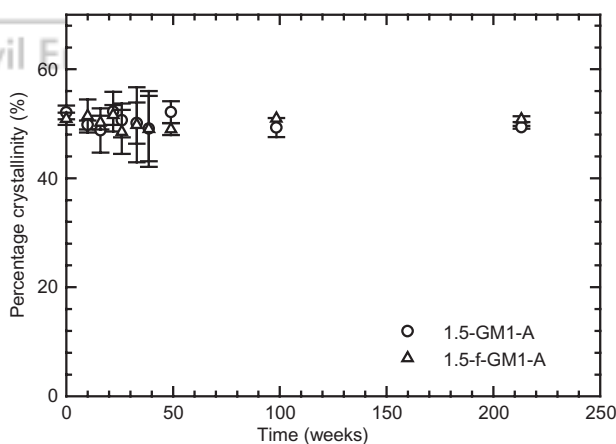


Figure 14. Percentage crystallinity plotted against time for series I 1.5 mm GM at 23°C

crystallinity of series II GM 2.0-GM2-A at 23°C is illustrated in Figure 15. No significant changes in crystallinity were observed for all three series II GMs at 23, 9 and -22°C up to 57 weeks of testing. For series IV GM no significant change in percentage crystallinity for both untreated and fluorinated GMs were observed after 52 weeks of the diffusion test.

The initial tear resistance test was examined in the

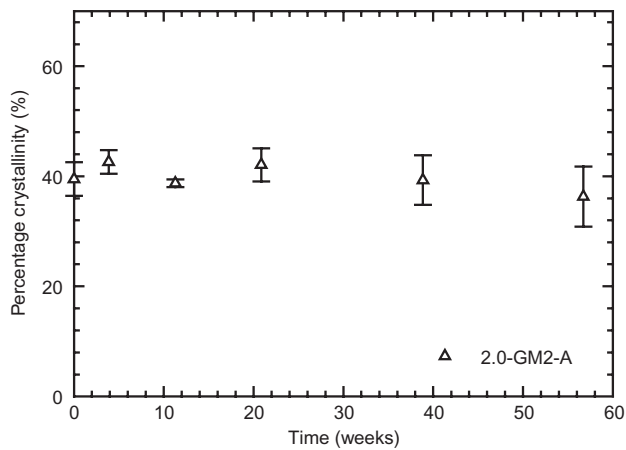


Figure 15. Percentage crystallinity plotted against time for 2.0-GM2-A at 23°C

series II testing because it is much faster to conduct than the tensile test while still indicating if there has been a change in the physical properties of the GM. The changes in initial tear resistance of series II GMs immersed in jet fuel at 23°C is illustrated for 2.0-GM2-A (Figure 16). The GMs were immediately tested after removal from the bath (wet conditions). They were also tested after allowing the jet fuel to evaporate by keeping them in the fumehood for about 15 days prior to testing (dry conditions). The results showed that the initial tear resistance of the GMs were less for the wet conditions. The exposure to jet fuel over a period of time had decreased the initial tear resistance of all three GMs when tested in wet conditions. However after letting the GM dry, no statistically significant (at the 95% confidence level) change in initial tear resistance was observed. Hence the decrease in initial tear resistance when tested in the wet condition was due to the presence of absorbed jet fuel in the GM. To check the short-term effect on initial tear resistance the 2.0-GM2-A was immersed in jet fuel at 23°C for 27 hours. When tested in the wet condition the initial tear resistance decreased from 294 N (SD = 1.06) to 276 N (SD = 2.24).

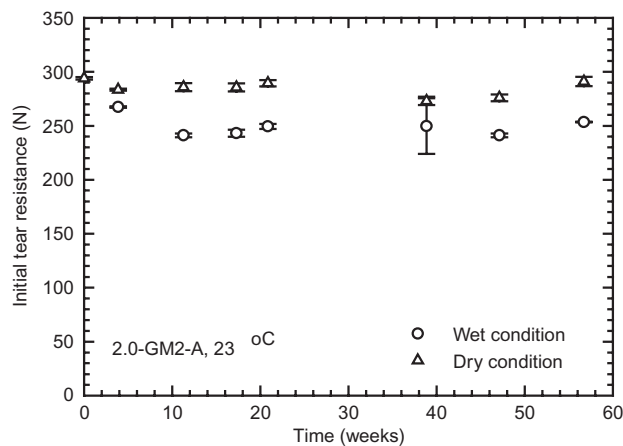


Figure 16. Initial tear resistance for 2.0-GM2-A immersed in jet fuel at 23°C

5. SUMMARY AND CONCLUSIONS

The findings from a series of studies on ageing of GMs in jet fuel have been presented. Based on the GMs tested and presently available data, the following conclusions have been reached.

Estimates of the antioxidant depletion time for untreated and fluorinated GM immersed in jet fuel at room temperature were obtained based on 4 years data.

- Immersion in jet fuel substantially accelerated the standard OIT (std-OIT) depletion rate relative to that observed in water or synthetic leachate.
- Fluorination of the HDPE GM provided a significant beneficial effect and the antioxidants depleted much faster from the untreated GM than the fluorinated GM.
- Although there was relatively rapid depletion of std-OIT it did not deplete to the value expected for pure unstabilized HDPE. Rather, there was residual OIT of about 8 min in the both the fluorinated and untreated GMs after 4 years of exposure to jet fuel. The residual OIT was attributed to antioxidants in the GMs that could not be readily leached by immersion in jet fuel. These residual antioxidants will likely result in total depletion times substantially greater than estimated below.
- The antioxidant depletion rate for the fluorinated GM was about 30% of that for the untreated GM.
- The std-OIT depletion time to reach the residual OIT value was estimated to be 1.6 years for the untreated GM and 5.5 years for the fluorinated GM at 23°C.

Data obtained at three different temperatures for the GM from manufacturer A can be used to conservatively estimate the antioxidant depletion rates at field temperature for containment applications such as that at Brevoort Island.

- At 23°C the antioxidant depletion rate based on std-OIT was found to be greatest for the 1.5 mm untreated GM, followed by 2 mm untreated GM, and slowest in 1.5 mm fluorinated GM. At 9°C similar observations were made. However there was only a small difference in depletion rates for the 1.5 mm fluorinated GM and 2 mm untreated GM. At a temperature of -22°C the inferred depletion rates were similar for the 1.5 mm fluorinated GM and 2 mm untreated GM. The 1.5 mm untreated GM had the greatest depletion rate.
- At all three temperatures the predominant antioxidant detected by the HP-OIT test for the 2 mm untreated GM did not significantly deplete over the testing period resulting in an almost constant HP-OIT value with time. This GM had a substantially higher initial HP-OIT (about 700 min), and hence a substantially different antioxidant package, to that of the 1.5 mm GMs (HP-OIT about 200 min). The HP-OIT for the 1.5 mm untreated GM decreased faster than for the 1.5 mm fluorinated GM. However, for both 1.5 mm

GMs the decline in HP-OIT was slower than that observed in the std-OIT test. This general trend was observed in all temperatures for the 1.5 mm untreated and fluorinated GM. Therefore the predicted times to std-OIT depletion may be very conservative for these GMs.

- Laboratory data obtained at three different temperatures was used to predict the std-OIT depletion time at the annual average barrier temperature of -1°C at the Brevoort Island. The predicted time for std-OIT to deplete to the residual value ranged from 14–24 years for 1.5 mm untreated GM, 22–33 years for 2 mm untreated GM, and 26–33 years for 1.5 mm fluorinated GM used in the barrier at BAF-3. These estimates are for samples immersed in jet fuel. As discussed below the times could be up to about four times longer for samples with jet fuel on one side and water on the other (as expected in the field).

Jet fuel immersion tests on three conventional GMs of different thicknesses (obtained from manufacturer B) at three temperatures indicated the following properties.

- At all three test temperatures (23, 9 and -22°C) the std-OIT antioxidant depletion rate was greatest for the 1.5 mm GM, followed by 2.0 mm GM and slowest in 2.5 mm GM.
- There was an excellent correlation between inverse square of thickness and std-OIT antioxidant depletion rates at all three temperatures.
- The predicted std-OIT depletion time at the annual average field temperature for the barrier at Brevoort Island for the three untreated GMs from manufacturer B ranged from 14 to 21 years for 1.5 mm GM, 17 to 26 years for 2.0 mm GM and 21 to 31 years for the 2.5 mm GM. Again, these estimates are for samples immersed in jet fuel. The times could be up to about four times longer for samples with jet fuel on one side and water on the other.

With one-sided exposure to jet fuel in diffusion tests (as expected in the field) the following observations were noted.

- The antioxidant depletion rate was much lower than for two-sided exposure (immersion test). The std-OIT antioxidant depletion rate for the 1.5 mm untreated GM in the diffusion test was about 0.21 times that for the same GM in the immersion test. For the 1.5 mm fluorinated GM the depletion rate was about 0.24 times that in the immersion test.
- The depletion rates of untreated GM was three times faster than for the fluorinated GM in the diffusion tests.
- The time for depletion of std-OIT to the residual value (at 23°C) was 7.6 years for untreated GM and 23.6 years for fluorinated GM (compared to 1.6 and 5.7 years in immersion tests).

The effect of immersion in jet fuel on the tensile,

crystallinity and tear properties of the GM were examined and the following conclusions were drawn.

- A higher yield strain and lower yield strength were observed for the GMs tested wet than when tested dry but there was no significant difference in tensile break properties.
- The tensile strain at yield increased with the time of immersion in jet fuel due to softening of GM by jet fuel. With over 4 years of immersion in jet fuel, the elongation at yield increased from about 19 to 29%. The tensile yield strength did not change significantly over the testing period. The tensile break properties were not adversely affected by the exposure to jet fuel.
- There was no significant change in the crystallinity of the GMs with over 4 years of immersion at 23°C .
- No significant change in the crystallinity was observed over the period of 57 weeks of testing at 23, 9 and -22°C .
- The initial tear resistance of the GM was lower when the GM was wet with jet fuel than when dry and this is attributed to the effect of the absorbed jet fuel in the GM.
- No significant changes in dry tear resistance were observed for GM immersed in jet fuel for up to 57 weeks.

In summary, the data from std-OIT and HP-OIT tests both indicate that some component(s) of the antioxidant package were leached into the jet fuel relatively rapidly but that once this component was removed the OIT values remained relatively stable over the remainder of the test period (4 years for series I and about 1 year for series II and III). The std-OIT depletion rates for the readily leachable component of the antioxidant package given above could be estimated from the available data. These tests will need to be run for a much longer period of time to allow an estimate to be made of the depletion rate for the remaining antioxidants. Thus the estimates of depletion times given above are quite conservative but nevertheless provide a lower-bound on the antioxidant depletion time and suggest that the 1.5 mm f-HDPE GM used to contain a hydrocarbon spill on Brevoort Island is likely to perform well for a period in excess of 25 years at the average field temperature (-1°C) based on full immersion in jet fuel. Based on the findings from the diffusion tests with jet fuel on one side of the GM and water on the other (i.e. similar to the conditions in the field), the time to antioxidant depletion is likely to be about four times longer than when immersed in jet fuel and so the depletion time in the field under these conditions is projected to be in excess of 100 years based on the available data. With the acquisition of more data it is likely that this estimate will be increased (possibly quite substantially).

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NOTATIONS

Basic SI notations are given in parenthesis.

A	pre-exponential factor (constant) (1/s)
COV	coefficient of variation (dimensionless)
E_a	activation energy (kJ/mol)
OIT_t	OIT value at time t (s)
OIT_o	initial OIT value (s)
OIT_r	residual OIT value (s)
OIT_f	final OIT value (s)
R	universal gas constant (8.31 J/mol per K)
s	antioxidant depletion rate (1/s)
s'	antioxidant depletion rate (1/s).
$s'_{adjusted}$	weighted average antioxidant depletion rate (1/s)
s'_{summer}	depletion rate in summer months (1/s)
s'_{remain}	depletion rate in remaining months (1/s)
t	immersion time (s)
T	absolute temperature (K)
t_r	time to deplete antioxidant to a residual OIT value (s)

ABBREVIATIONS

ATR	attenuated total reflectance
COV	coefficient of variation
DSC	differential scanning calorimeter
f-HDPE	fluorinated high density polyethylene
FTIR	Fourier transform infrared
GCL	geosynthetic clay liner
GM	geomembrane
GPC	gel permeation chromatography
HALS	hindered amine light stabilizers
HDPE	high-density polyethylene
HPLC	high-performance liquid chromatography

HP-OIT	high-pressure oxidative induction time
OIT	oxidative induction time
std-OIT	standard oxidative induction time
TLC	thin layer chromatography
UVA	ultra violet absorbers

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