

Effects of Thickness on the Aging of HDPE Geomembranes

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Abstract: The results of an accelerated aging test program to evaluate the effect of thickness on the depletion of antioxidants from high-density polyethylene (HDPE) geomembranes and subsequent degradation of the physical properties are reported. Three commercially available HDPE geomembranes having nominal thicknesses of 1.5, 2.0, and 2.5 mm were examined. The geomembranes were immersed in a synthetic leachate at 85, 70, 55, and 22°C and tested for oxidative induction time, crystallinity, melt index (MI), tensile properties, and stress-crack resistance. The antioxidant depletion rate for the 1.5 mm geomembrane was faster than for the 2.0 and 2.5 mm geomembranes. Antioxidant depletion time was predicted at representative landfill temperatures of 20–60°C using Arrhenius modeling and was found to increase with geomembrane thickness for the three geomembranes examined. Based on the results of crystallinity, MI, and stress-crack resistance, the degradation of the geomembrane was slowest for the thickest geomembrane. These results suggest that a thicker geomembrane may have a longer service life (other things being equal).

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Introduction

High-density polyethylene (HDPE) geomembranes are extensively used as part of a composite liner in modern landfills because of their excellent capacity for minimizing the leakage of both liquids and gases to the surrounding environment (Rowe et al. 2007; Bouazza et al. 2008; Brachman and Gudina 2008a,b; Saidi et al. 2008). However, several laboratory studies (e.g., Hsuan and Koerner 1998; Sangam and Rowe 2002; Rowe et al. 2008; Rowe and Rimal 2008) and field investigations (e.g., Schmidt et al. 1984; Brady et al. 1994; Rollin et al. 1994; Maisonneuve et al. 1997; Rowe et al. 2003) have shown that an HDPE geomembrane (GM) may experience aging or degradation with time. Furthermore, the studies on the landfill geochemistry and degradation processes suggest that the contaminants in municipal solid waste (MSW) landfills may take hundreds of years to stabilize based on current landfilling practice (Hall et al. 2003; Rowe et al. 2004). Thus, the longevity of HDPE GMs is of major interest as highlighted in a recent U.S. National Academies report (Mitchell et al. 2007).

The required minimum GM thickness as specified in regulations varies from country to country but is usually linked to an implied longer service life for the thicker GM. For example, in Canada, Ontario Regulation 232/98 specifies a 1.5 mm thick GM

for the primary landfill liner and a 2.0 mm thick GM for any secondary landfill liner (MoE 1998) because of the expected longer required service life of a secondary GM liner. The minimum required thickness for an HDPE GM in the United States is 1.0 mm (although 1.5 mm is the most common), while the regulation in Belgium specifies a minimum thickness of 2.5 mm (Arias et al. 1998). It is generally expected that a thicker GM will have greater strength, higher puncture resistance, greater resistance to chemicals, and longer service life, however there is a paucity of published data to validate the assumption of longer service life for thicker GMs. Thus the issue is of considerable interest to geoenvironmental engineers involved in landfill design.

The service life of HDPE GM is normally defined as the length of time the GM acts as an effective hydraulic and diffusive barrier to contaminant migration (Rowe et al. 2004). A well-designed and properly constructed GM is expected to undergo some degree of aging or degradation during its service life. Of the various modes of degradation that may take place in the GM (e.g., oxidation, extraction, ultraviolet (UV) degradation, and thermal degradation), for HDPE GMs used as bottom liners in MSW landfills, oxidative degradation is the primary concern (Hsuan and Koerner 1995; Rowe and Sangam 2002). Oxidation in the polymer increases exponentially with temperature (Hsuan and Koerner 1995; Sangam and Rowe 2002; Rowe and Rimal 2008; Rowe et al. 2008). The result of oxidative degradation causes breakdown in polymer chains and subsequently changes in the physical and mechanical properties of the GM which eventually leads to GM failure in the form of embrittlement. To delay or retard the oxidation reactions, antioxidants (AOs) are added to the HDPE resin during manufacturing of GM in the range of 0.2–0.5% by weight (Grassie and Scott 1985). To protect the GM at temperatures during the extrusion process and throughout the service duration, manufacturers generally add at least one primary and one secondary AO (Hsuan and Koerner 1998). The most commonly used primary and secondary AOs in polyolefins, which include HDPE, are hindered phenols and phosphites, respectively (Thilén and Shishoo 2000; Marcato et al. 2003; Garcia et al.

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Table 1. Properties of the Three GMs Examined

Properties	Method	Unit	Value		
Nominal thickness	ASTM 2008a	mm	1.5	2.0	2.5
Std-OIT	ASTM 2008b	min	135 ± 2.2	150 ± 1.2	136 ± 0.43
HP-OIT	ASTM 2008c	min	244 ± 13	265 ± 10	235 ± 13
Crystallinity	ASTM 2008d	%	47.6 ± 1.4	50.3 ± 0.75	46.6 ± 1.7
MI (21.6 kg/190°C)	ASTM 2008e	g/10 min	14.3 ± 0.8	11.1 ± 0.5	14.5 ± 0.5
Density	ASTM 2008f	g/cc	0.947	0.946	0.946
Single point stress-crack resistance	ASTM 2008g	h	1,432 ± 186	1,252 ± 122	624 ± 61
Tensile properties (machine direction)	ASTM 2008h				
Strength at yield		kN/m	26.7 ± 0.86	38.4 ± 0.48	45.8 ± 1.7
Strength at break		kN/m	46.0 ± 5.3	60.3 ± 4.5	62.3 ± 10.2
Strain at yield		%	23.9 ± 1.7	20.8 ± 0.25	20.3 ± 0.51
Strain at break		%	825 ± 81	788 ± 57	767 ± 58
Tensile properties (cross-machine direction)	ASTM 2008h				
Strength at yield		kN/m	29.0 ± 0.48	39.1 ± 0.75	46.9 ± 0.56
Strength at break		kN/m	43.7 ± 6.1	61.6 ± 3.9	38.5 ± 8.4
Strain at yield		%	18.5 ± 0.40	21.4 ± 0.76	19.4 ± 0.75
Strain at break		%	830 ± 95	785 ± 41	634 ± 143

2004). AOs react with free radicals and hydroperoxides that are generated due to oxidation and convert them into stable molecules (Grassie and Scott 1985). Over the service life of polymers, AOs are depleted due to their chemical reactions with oxygenated free radicals and hydroperoxide and/or physical loss by diffusion, evaporation, or extraction of the AOs from the GM (Gedde et al. 1994; Hsuan and Koerner 1998; Haider and Karlsson 2002; Rowe and Sangam 2002; Garcia et al. 2004). The migration potential for the phosphitic AOs are greater than that of phenolic AOs (Marcato et al. 2003), however no optimum combination and concentration is evident based on the published experimental investigations on the long-term longevity of AOs (Gugumus 1998a,b). AO packages may change from supplier to supplier. For the same supplier, the AO package may vary with different resins or even amongst different batches of the same resin and potentially yield different service lives.

Commonly, the oxidative degradation of HDPE GMs is considered as a three-stage process: the depletion of AOs (Stage 1), induction time to onset of polymer degradation (Stage 2), and degradation to failure (Stage 3) (Viebke et al. 1994; Hsuan and Koerner 1998). The service life of a GM is taken as the sum of the duration of the three stages. Stage III is characterized by significant changes to the physical and mechanical properties which will eventually lead to GM failure. Failure in this context refers to a decrease in an engineering property (e.g., stress-crack resistance, tensile break stress, and tensile break strain) to a specified value. Since the most likely mechanism for failure is cracking of the GM at location of elevated tensile stress, the writers consider stress-crack resistance to be the most important physical characteristic. The value defining the end of Stage III is somewhat subjective and engineers may select different definitions depending on circumstances. The two most commonly used approaches correspond to 50% of the initial property (Hsuan and Koerner 1998) or 50% of the specified property value (Rowe et al. 2009). The latter approach is fairer for products whose initial value of a property significantly exceeds the minimum specified value.

Typically the depletion of AOs from GMs is examined by incubating the GM in the environment of interest [e.g., air, water, simulated landfill leachate, acid mine drainage, etc.—see Hsuan and Koerner (1998); Sangam and Rowe (2002); Müller and Jacob

(2003); Gulec et al. (2004); Rowe et al. (2008); Rowe and Rimal (2008)]. These studies have provided insight regarding the effect of the interaction between different leachates and GMs with respect to the depletion of AOs. However, the effect of thickness with respect to the service life of GMs has received very little attention in the literature. Lopes et al. (1998) conducted accelerated aging tests using 1.0 and 2.0 mm GMs at 60°C by immersing the GMs in landfill leachate for 7 months. Results showed that the tensile strength and stiffness decreased more for the 1.0 mm GM than for the 2.0 mm GM. However, Lopes and coworkers did not explicitly examine the effect of GM thickness on the depletion of AOs in their study. Thus there is a paucity of published research in the literature relating to the effect of thickness on the depletion of AOs and so the objective of this study is to examine the effects of thickness on the depletion of AOs from HDPE GMs.

Experimental Investigation

Materials

Three commercially available HDPE GMs (manufactured by Solmax International, Varennes, Quebec) having nominal thicknesses of 1.5, 2.0, and 2.5 mm were tested. Table 1 shows the key properties of the GMs. The types of AOs used in the GMs were not provided by the manufacturer. However, an analysis of AOs done at a commercial analytical testing laboratory showed that the AOs package used in the GMs were hindered phenol (primary group) and phosphites (secondary group). No hindered amine light stabilizers (HALSs), another commonly used AO grouping, were detected.

Exposure Conditions

GM samples were cut into 190 by 100 mm coupons and were immersed in 4 L glass containers filled with synthetic leachate. To ensure that there was leachate on both sides of coupons, 5 mm diameter glass rods were placed as separators between coupons. The containers were placed in ovens at temperatures of 85, 70, 55, and 22°C. The synthetic leachate was produced by mixing

Table 2. Composition of Synthetic Leachate

Component	Concentration (mg/L) (except where noted)
Trace metal solution ^{a, b} (ml/L)	1
Surfactant, Igepal CA720 (ml/L)	5
E_h (adjusted by $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) (mV)	~ -120
$\text{FeSO}_4\cdot 7\text{H}_2\text{O}$	2000
H_3BO_3	50
$\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$	50
$\text{CuSO}_4\cdot 5\text{H}_2\text{O}$	40
$\text{MnSO}_4\cdot \text{H}_2\text{O}$	500
$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$	50
$\text{Al}_2(\text{SO}_4)_3\cdot 16\text{H}_2\text{O}$	30
$\text{CoSO}_4\cdot 7\text{H}_2\text{O}$	150
$\text{NiSO}_4\cdot 6\text{H}_2\text{O}$	500
H_2SO_4 (ml/l)	1

^aComposition of trace metal solution – 1 ml/L in synthetic leachate.

^bModified from Hrapovic (2001).

trace metals, surfactant, and reducing agents in distilled water (Table 2) and replaced every two weeks to prevent the buildup of AOs in the leachate. The leachate used in this study was considered to be the most appropriate with respect to a real leachate for evaluating the potential degradation of HDPE GMs based on a study that examined the effect of different synthetic leachate compositions on AO depletion (Rowe et al. 2008). HDPE GM samples were retrieved at specified time intervals and tested for oxidative induction time (OIT), crystallinity, melt index (MI), tensile properties, and stress-crack resistance as described in the following sections.

Test Methods

Oxidative Induction Time Test

The OIT is considered to be a good index for evaluating the amount of AO present in the GM (Surmann et al. 1995; Hsuan and Koerner 1995,1998; Maisonneuve et al. 1997; Sangam and Rowe 2002; Müller and Jacob 2003; Gulec et al. 2004; Rimal et al. 2004; Rowe and Rimal 2008; Rowe et al. 2008). Both standard OIT (Std-OIT) [ASTM D3895 (ASTM 2008b)] and high pressure OIT (HP-OIT) [ASTM D5885 (ASTM 2008c)] tests were carried out in this study; however, most of the tests were conducted using the Std-OIT method. The Std-OIT tests were conducted using a TA Instruments Q-100 series differential scanning calorimeter (DSC) equipped with an auto sampler. A 6–10 mg specimen was heated from room temperature to 200°C at a rate of 20°C/min in nitrogen environment with a gas flow rate of 50 mL/min. After reaching 200°C the flow of nitrogen gas was maintained for 5 minutes and then the gas flow was changed from nitrogen to oxygen at isothermal condition and 35 kPa pressure. Tests were terminated when an exothermal peak was detected. The HP-OIT tests were conducted using a TA Instruments 2910 DSC equipped with a pressure cell capable of withstanding up to 7,000 kPa pressure. The procedure for the HP-OIT tests were the same as the Std-OIT tests except the temperature and pressure were 150°C and 3,500 kPa, respectively. For both types of tests, the duration between the start of oxygen flow and the onset of exothermal peak was reported as the OIT in minutes. At any specific sampling event, at least five samples (taken from both the edge and the centre of the coupon) were tested and the average and standard deviation are reported.

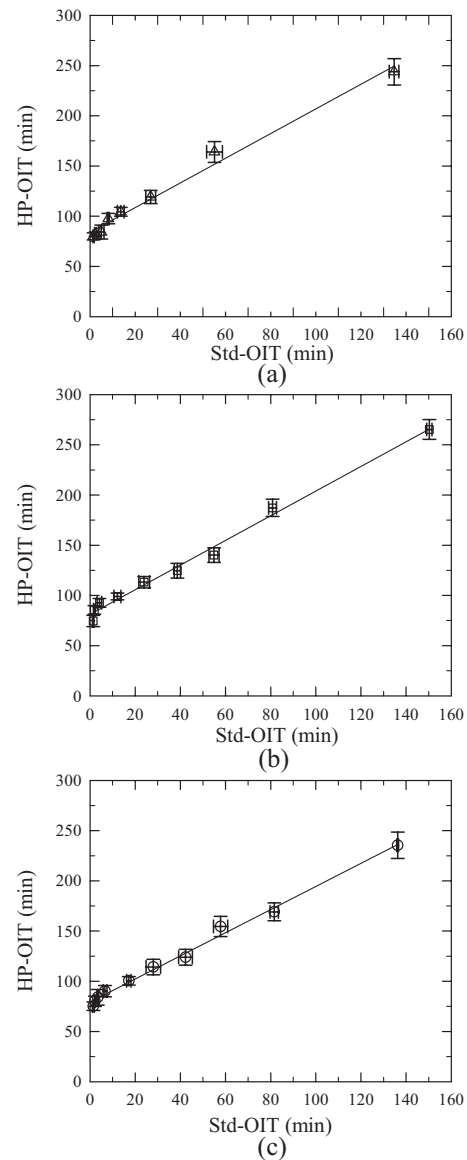


Fig. 1. Relationship between Std-OIT and HP-OIT of 85°C incubated HDPE GM samples: (a) 1.5 mm; (b) 2.0 mm; and (c) 2.5 mm

Crystallinity Test

The crystallinity of a polymer controls some of its physical and mechanical properties, e.g., yield stress, modulus of elasticity, impact resistance, dimensional stability, density, and permeability (Fann et al. 1998; Sperling 1992; Kong and Hay 2002). The degree of crystallinity of the HDPE GMs was measured in accordance with ASTM E794 (ASTM 2008d) using the same DSC as used for the Std-OIT tests. The sampling procedure for the degree of crystallinity test was the same as the OIT test.

Melt Index Test

The MI test is a qualitative test for evaluating the molecular weight of different polymers and is considered to be a good indicator of oxidative degradation (Hsuan and Koerner 1998). Either cross-linking or chain scission reactions can occur in the polymer as a result of oxidation (Hsuan and Koerner 1998; Peacock 2000). A cross-linking reaction leads to a decrease in MI values whereas a chain scission reaction causes an increase in MI values. A low MI value in the polymer represents high molecular weight and vice versa, however this should be considered with reasonable

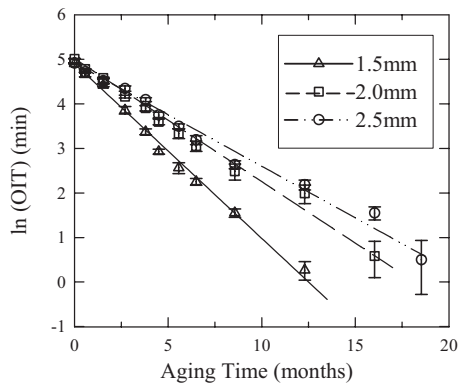


Fig. 2. Variation in ln(OIT) with time at 70°C for the 1.5, 2.0, and 2.5 mm GMs

caution because the long and short chain branching is also considered as a function of molecular weight of the polymer (Wild et al. 1982; Bremner and Rudin 1990). Thus, either an increase or decrease in MI may signal degradation of the polymer. The MI test was performed using a Dynisco Melt Indexer (Model D4002) according to ASTM D1238 (ASTM 2008e) (using a 21.6 kg load and 190°C). The test measures the amount of molten polymer extruded through an orifice of specified diameter and the unit of MI is generally reported as *g/10 min*.

Tensile Test

Tensile tests were performed using a Zwick Roell tensile testing machine (Model Z020) equipped with 20 kN load cell and self aligning wedge grips in accordance with ASTM D6693 (ASTM 2008h) (Type IV) at a strain rate of 50 mm/min. For any specific sampling event, 10 specimens were tested: five along the machine direction and five along the cross-machine direction, and the average and standard deviation in each direction are reported.

Stress-Crack Resistance Test

The stress-crack resistances of the GMs was evaluated according to the single point-notched constant tensile load test [ASTM D5397 (ASTM 2008g)] using dumbbell-shaped specimens immersed in a solution containing 10% Igepal CO630 and 90% water at 50°C. The depth of notch was 20% of the thickness of the GMs. The applied load was 30% of the yield stress of the

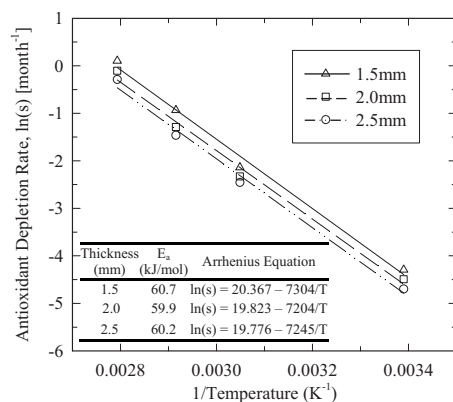


Fig. 3. Arrhenius plot of AO depletion rate for the three thicknesses of GM

Table 3. AO Depletion Rates at Four Different Temperatures for the 1.5, 2.0, and 2.5 mm GMs

Temperature (°C)	Thickness (mm)	AO depletion rate (month ⁻¹)	R^2
85	1.5	1.111	0.931
	2.0	0.902	0.987
	2.5	0.749	0.989
70	1.5	0.392	0.993
	2.0	0.276	0.985
	2.5	0.232	0.984
55	1.5	0.116	0.991
	2.0	0.097	0.991
	2.5	0.085	0.993
22	1.5	0.014	0.987
	2.0	0.011	0.978
	2.5	0.009	0.969

respective GM. At any sampling event three specimens were tested and the average and the standard deviation of the failure time were reported.

Results and Discussion

Antioxidant Depletion from Std-OIT and HP-OIT Tests

The testing temperature used in the Std-OIT test (i.e., 200°C) may be a concern regarding the volatilization of some AOs (especially HALS) in the GMs (Thomas and Ancelet 1993; Hsuan and Koerner 1998). Although the AO analysis from a commercial analytical testing laboratory did not identify any HALS in the GMs examined, to confirm that the higher test temperature in the Std-OIT test did not volatilize the AOs, HP-OIT tests (at 150°C) were conducted and compared with the results of Std-OIT tests on different samples incubated at 85°C (Fig. 1). The vertical and horizontal bars represent the standard deviation of the data points. A linear relationship was found for all three GMs which imply that either test could be used to predict the depletion of AOs for the GMs examined. According to Hsuan and Koerner (1998), the linear variations provide evidence that there was no thiosynergists or hindered amines whose effective temperature is in the 150–200°C range. This is consistent with the results of AO analysis, which shows that the AOs package used in the GMs were phenolic (Irganox 1010 and Irganox 1076) and phosphitic [Irgafos 168 (PO₃) and Igrafos 168 (PO₄)] (Islam 2009), whose maximum effective temperature is 300°C. Therefore, the results described in the following sections are based on the Std-OIT tests.

The depletion of AO in the leachate is often described by an exponential decay equation (Hsuan and Koerner 1998)

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

or, by taking natural logarithm on both sides

$$\ln(OIT_t) = -st + \ln(OIT_o) \quad (2)$$

where $OIT_t = OIT$ at any time t (min); $OIT_o = \text{initial OIT}$ (min); $s = \text{antioxidant depletion rate}$ (month⁻¹); and $t = \text{time}$ (month).

Fig. 2 shows the variation in ln(OIT) with time for the three GMs at 70°C; similar plots were obtained at other temperatures (Islam 2009). The relationship between ln(OIT) and time can be approximated by a linear relationship indicating that the depletion of AOs can be approximated by a first-order decay pattern with the slope of the regression lines representing the AO depletion

Table 4. AO Depletion Rates in the Literature for Different GMs and Exposure Conditions at Different Temperatures

Exposure condition and reference	Temperature (°C)	AO depletion rate (month ⁻¹)
1.5 mm GM with water saturated sand above and dry sand below with 260 kPa normal stress, initial Std-OIT=80.5 min, HP-OIT=210 min, Hsuan and Koerner (1998)	85	0.140
	75	0.080
	65	0.059
	55	0.022
2.0 mm GM immersed in synthetic MSW leachate, initial Std-OIT=133 min, HP-OIT=380 min, Sangam and Rowe (2002)	85	0.407
	55	0.150
	40	0.089
2.0 mm GM immersed in water, initial Std-OIT=133 min, HP-OIT=380 min, Sangam and Rowe (2002)	22	0.019
	85	0.175
	70	0.105
	55	0.047
1.5 mm GM immersed in synthetic acid mine drainage, initial Std-OIT=208 min, HP-OIT=484 min, Gulec et al. (2004)	40	0.036
	22	0.004
	80	1.206
	60	0.091
1.5 mm GM immersed in synthetic leachate, initial Std-OIT=174 min, HP-OIT=903 min, Rowe et al. (2008)	40	0.048
	20	0.005
	85	1.164
	70	0.299
1.5 mm GM immersed in synthetic MSW leachate, initial Std-OIT=135 min, HP-OIT=660 min, Rowe and Rimal (2008)	55	0.128
	40	0.036
	22	0.013
	85	1.242
1.5 mm GM used in simulated composite liner with top face of the GM exposed to synthetic MSW leachate and the bottom face exposed to hydrated GCL, initial Std-OIT=135 min, HP-OIT=660 min, Rowe and Rimal (2008)	70	0.481
	55	0.118
	26	0.025
	85	0.275
	70	0.212
	55	0.054
	26	0.005

rate. This finding is in accordance with the results obtained by other researchers for different HDPE GMs (Hsuan and Koerner 1995,1998; Hsuan and Guan 1998; Sangam and Rowe 2002; Gulec et al. 2004; Rowe et al. 2008; Rowe and Rimal 2008). Rimal and Rowe (2009) have demonstrated that the systematic deviations from linearity observed by experimentalists is not just experimental scatter but real physical behavior related to the removal of AO by diffusion. Using diffusion theory they obtained a better fit to the data without any systematic deviations. However they also showed that the outward diffusion of AOs can be approximated by a linear relationship between $\ln(\text{OIT})$ and time and hence provided a theoretical basis for the widely adopted empirical approach (adopted also in the present paper). They also indicated that prediction of AO depletion based on a linear (first-order) approximation to only early time data (i.e. before there is substantial AO depletion) will underestimate the actual time to depletion.

The OIT decreased until it reached a residual value of approximately 1.5 min after 4.5, 5.5, and 6.5 months respectively for the 1.5, 2.0, and 2.5 mm GMs at 85°C, and after 12.5, 16.0, and 18.5 months respectively for the 1.5, 2.0, and 2.5 mm GMs at 70°C. At 55 and 22°C the OIT values had not reached the residual value by the end of the testing period (30 months). The AO depletion rate for the 1.5 mm GM was the fastest amongst the three GMs examined while that for the 2.5 mm GM was the slowest (Table 3).

Table 4 lists the AO depletion rates obtained by other research-

ers for different HDPE GMs. The AO depletion rate observed in this study for 1.5 mm GM (e.g., 1.111 month⁻¹ at 85°C) is comparable to what was observed by Gulec et al. (2004) (e.g., 1.206 month⁻¹ at 80°C), Rowe and Rimal (2008) (e.g., 1.242 month⁻¹ at 85°C), and Rowe et al. (2008) (e.g., 1.164 month⁻¹ at 85°C) for 1.5 mm GM. Sangam and Rowe (2002) observed a depletion rate of 0.407 month⁻¹ at 85°C for 2.0 mm GM immersed in MSW leachate at 85°C, which is somewhat less than the depletion rate observed in the current study for the 2.0 mm GM (0.902 month⁻¹ at 85°C). The reason for the difference is probably due to the different AO package used in the two GMs. The GM used in this study had an initial HP-OIT of 265 min compared to the initial HP-OIT of 380 min for the GM used by Sangam and Rowe (2002).

Antioxidant Depletion Time Based on Arrhenius Modeling

The AO depletion rate at a temperature of interest is generally evaluated using a time-temperature superposition model commonly known as the Arrhenius model. The Arrhenius equation for AO depletion rate can be written as (Hsuan and Koerner 1998)

$$s = A e^{-[E_a/(RT)]} \quad (3)$$

or, by taking the natural logarithm of both sides

Table 5. Predicted AO Depletion Times at Six Different Temperatures for the 1.5, 2.0, and 2.5 mm GMs

Temperature (°C)	AO depletion time (years)		
	1.5 mm	2.0 mm	2.5 mm
20	45	57	66
30	20	25	29
35	13	17	20
40	9.1	12	14
50	4.4	5.7	6.7
60	2.2	2.9	3.4

$$\ln(s) = \ln(A) - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \quad (4)$$

where s =antioxidant depletion rate (month^{-1}); E_a =activation energy (J mol^{-1}); R =universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); T =absolute temperature (K); and A =a constant often called a collision factor.

Arrhenius plots of AO depletion rates (i.e., plots of $\ln(s)$ versus $1/T$) using Eq. (4) for the three GMs are shown in Fig. 3 which also presents the activation energy and equations of best fit. The AO depletion times (i.e., time to complete Stage 1) for six temperatures (e.g., 60, 50, 40, 35, 30, and 20°C) were calculated from Eq. (1) using the parameters of the Arrhenius equation and are shown in Table 5. The depletion times presented in Table 1 are based on the depletion of OIT values presented in Table 1 to a

final OIT of 0.5 min for a pure HDPE resin without AOs adopted by Hsuan and Koerner (1998). In the present tests, because of the presence of carbon black in the GM tested, the residual OIT value was about 1.5 min. If calculation were performed for the higher residual value (1.5 min) instead of 0.5 min., the depletion times are a little lower than given in Table 5, although the general effect of thickness is the same.

The AO depletion time increases with an increase of GM thickness (Table 5). For instance, the predicted AO depletion times were about 45, 55, and 65 years, respectively for the 1.5, 2.0, and 2.5 mm GMs at 20°C. The effect of thickness on AO depletion time was more significant at lower temperature than at higher temperature. For example, the differences in AO depletion times between the 1.5 and 2.5 mm GMs were 21 years at 20°C and 1.2 years at 60°C. However, the relative difference in AO depletion times was almost the same with respect to the change in landfill temperature [e.g., AO depletion time was about 50% longer for the 2.5 mm GM compared to the 1.5 mm GM at all temperatures considered (Table 5)]. Likewise the depletion time for the 2 mm GM was consistently 30% greater than for 1.5 mm GM. It should be noted that all three GMs were manufactured by the same company but from three different resin lots. The dissimilarity in resins and/or AO packages may have contributed in some extent to the difference in AO depletion times for the three GMs. However, the primary reason for the longer AO depletion time for the thicker GM is considered to be due to the longer diffusion path for AOs in a thick GM than in a thin GM.

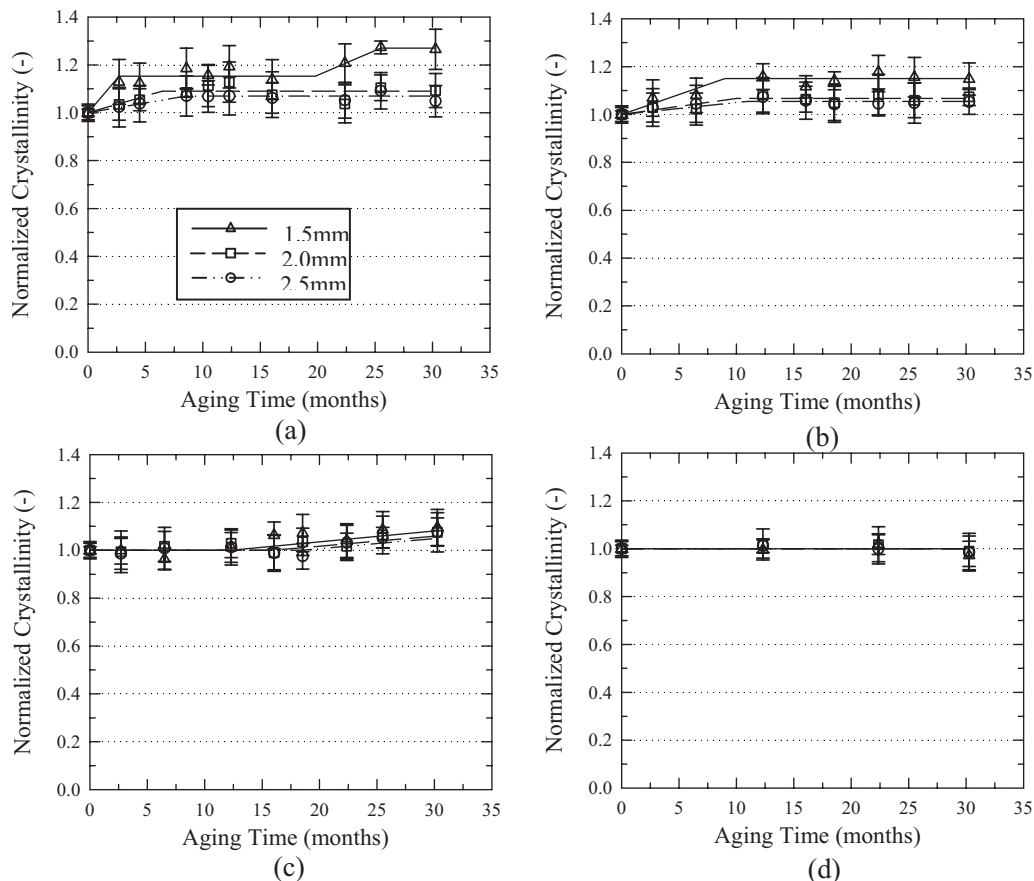


Fig. 4. Variation in crystallinity with time at four different temperatures for the 1.5, 2.0, and 2.5 mm GMs: (a) 85°C; (b) 70°C; (c) 55°C; and (d) 22°C

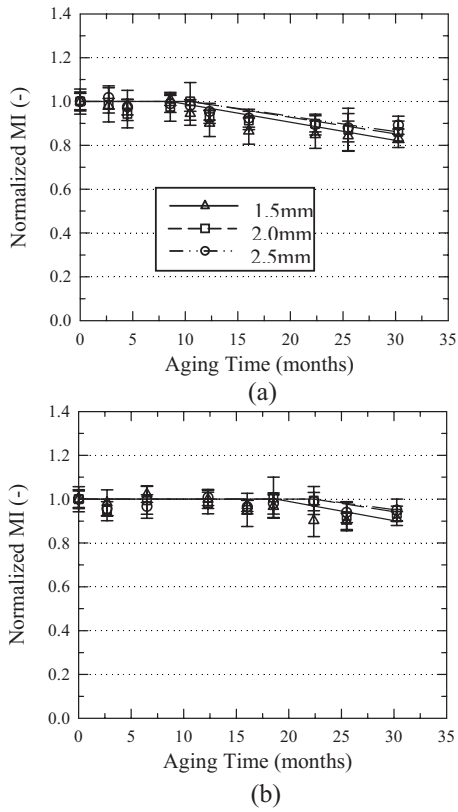


Fig. 5. Variation in MI with time at 85 and 70°C for the 1.5, 2.0, and 2.5 mm GMs: (a) 85°C (b) 70°C

Crystallinity

Fig. 4 shows the variation in crystallinity with time for the three GMs at different temperatures. The vertical bars represent the standard deviation of the data points. The crystallinity of the GM increased initially in all three GMs with time. The crystallinity of the GM increased relatively more for the 1.5 mm GM than for the 2.0 and 2.5 mm GMs. For example for the 1.5 mm GM, the crystallinity increased by approximately 15% after about 2.5 months of aging, whereas for the 2.0 and 2.5 mm GMs the increase was approximately 9 and 7%, respectively at 85°C and the increase was observed after about 7 months. The increase indicates that there was some physical aging due to the incubation at higher temperature which results in re- and/or postcrystallization of the material (Petermann et al. 1976; Dörner and Lang 1998a,b). After the initial increase, the crystallinity of the 2.0 and 2.5 mm GMs remained relatively constant to the end of the testing period at 85 and 70°C. However, for the 1.5 mm GM the crystallinity remained more or less constant for up to 20 months at 85°C, after which time the crystallinity increased again and the total increase was about 27% by the end of the testing period (30 months). The crystallinities of all three GMs began to increase after about 12 months at 55°C, suggesting that some physical aging is in progress. There was no statistically significant change in the degree of crystallinity at 22°C over the duration of the test.

Melt Index

Fig. 5 shows the changes in melt indices with time for the three GMs at 85 and 70°C. The MI values decreased by about 18, 15,

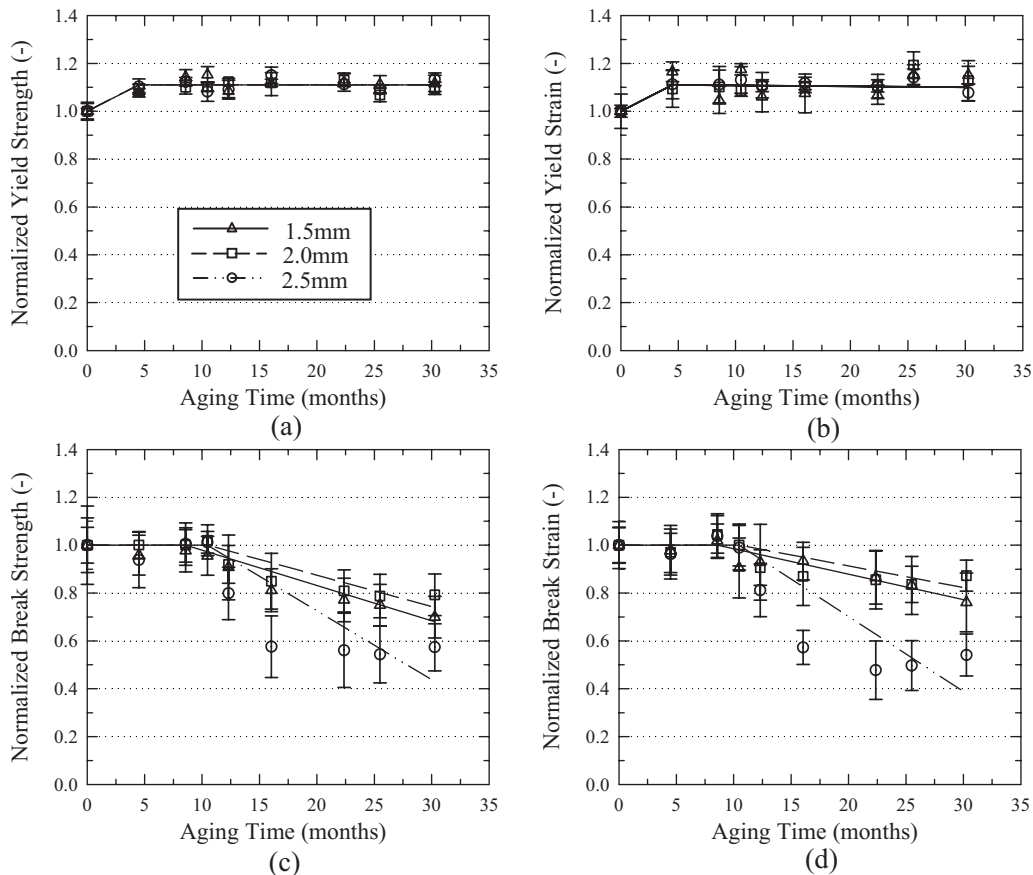


Fig. 6. Variation in tensile properties along machine direction at 85°C for the 1.5, 2.0, and 2.5 mm GMs: (a) yield strength; (b) yield strain; (c) break strength; and (d) break strain

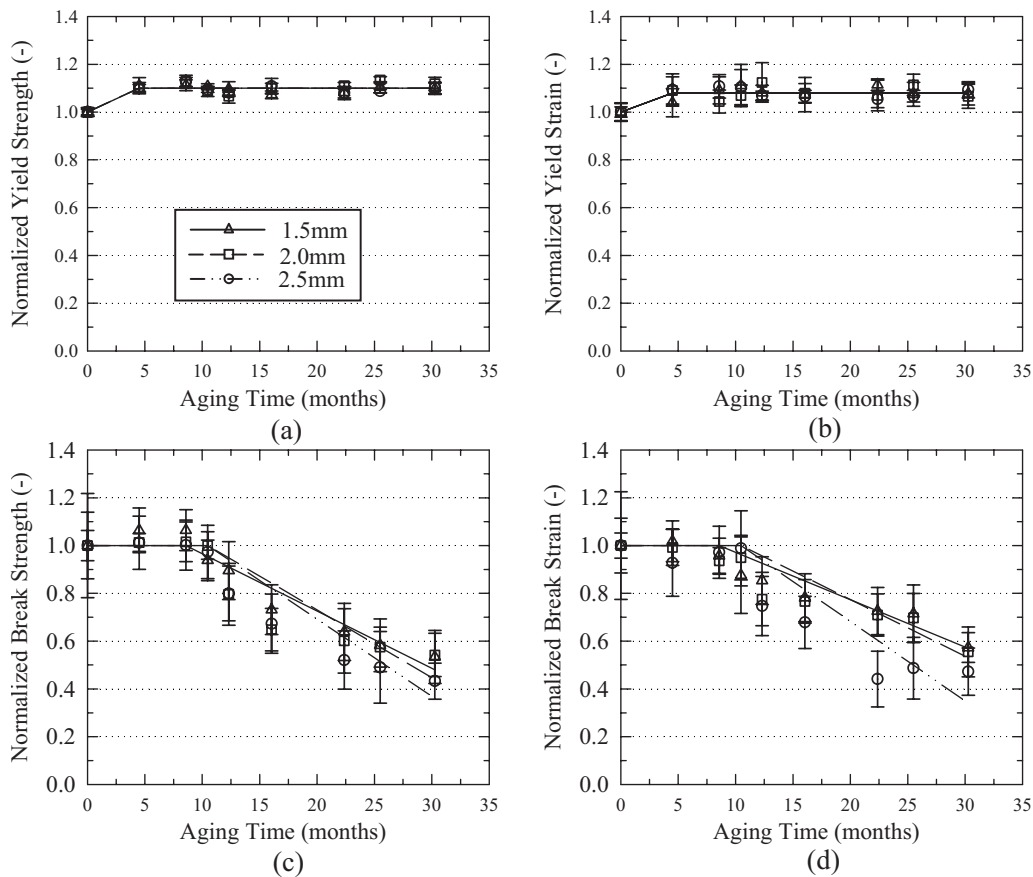


Fig. 7. Variation in tensile properties along cross-machine direction at 85°C for the 1.5, 2.0, and 2.5 mm GMs: (a) yield strength; (b) yield strain; (c) break strength; and (d) break strain

and 14%, respectively for the 1.5, 2.0, and 2.5 mm GMs at 85°C by the end of the testing period (30 months). At 85°C, the decrease in MI values for the 1.5 mm GM was observed after about 8.5 months, whereas for the 2.0 and 2.5 mm GMs the decrease was observed after about 10.5 months of aging. The trends in the change of the MI values at 70°C were more or less the same as for the 85°C, however the change was observed at later times and was slightly lower at 70°C. No statistically significant change in MI values was observed at 55 and 22°C after 30 months of incubation. The decrease of MI at 85 and 70°C suggests that the GMs are in Stage 3 of the three-stage degradation model described by Hsuan and Koerner (1998) at those temperatures.

Tensile Properties

Figs. 6 and 7 present the variations in tensile strength and strain at yield and break with incubation time at 85°C along the machine and cross-machine directions, respectively. The vertical bars represent the standard deviation of the data points. The strength and strain at yield in both directions increased by approximately 10% within the first 5 months and thereafter remained relatively constant until the end of the testing period.

A similar behavior, but relatively lower increase (approximately 7%), was observed at 70°C (Fig. 8). These results are in accordance with the results obtained by other researchers (e.g., Hsuan and Koerner 1998; Rowe et al. 2008; Rowe and Rimal 2008). No specific trend in yield properties was observed with respect to GM thickness.

The break strength and strain at 85°C for the 1.5 mm GM

started decreasing after about 8.5 months in both directions and for the 2.0 and 2.5 mm GMs the decrease was observed after about 10.5 months of aging (Figs. 6 and 7). These results are consistent with the MI results obtained at 85°C (Fig. 5). The break strength and strain decreased more for the cross-machine direction specimens compared to the machine direction specimens for all three GMs at 85°C (Figs. 6 and 7). For example, for the 1.5 mm GM, the tensile break strength decreased by approximately 52 and 33% along cross-machine and machine directions, respectively. The greatest decrease was observed for the 2.5 mm GM in both directions for break strength and break strain. The decrease in tensile break properties suggests that the GMs entered into the Stage 3 of the oxidative degradation. In the cross-machine direction, not only did the tensile strength at break show the greatest decrease for the 2.5 mm GM, it was lower (on an absolute basis) for the 2.5 mm GM than for the other two GMs. This could be important if the break strength is critical to GM service life; however that is unlikely to be the case. Results indicate that the stress-crack resistance is far more significant in assessing the GM service life. The possible reason for the lower break properties in the cross-machine direction is the delamination of the tensile specimen in the postyield strain hardening stage, leading to a premature failure. All cross-machine direction specimens, both aged and unaged, exhibited delamination during failure (Fig. 9). Delamination in the machine direction was observed for only 2.5 mm aged GM. Delamination may be more severe for the thicker GM since the thick GMs are exposed to a greater differential cooling rate during manufacturing than thinner

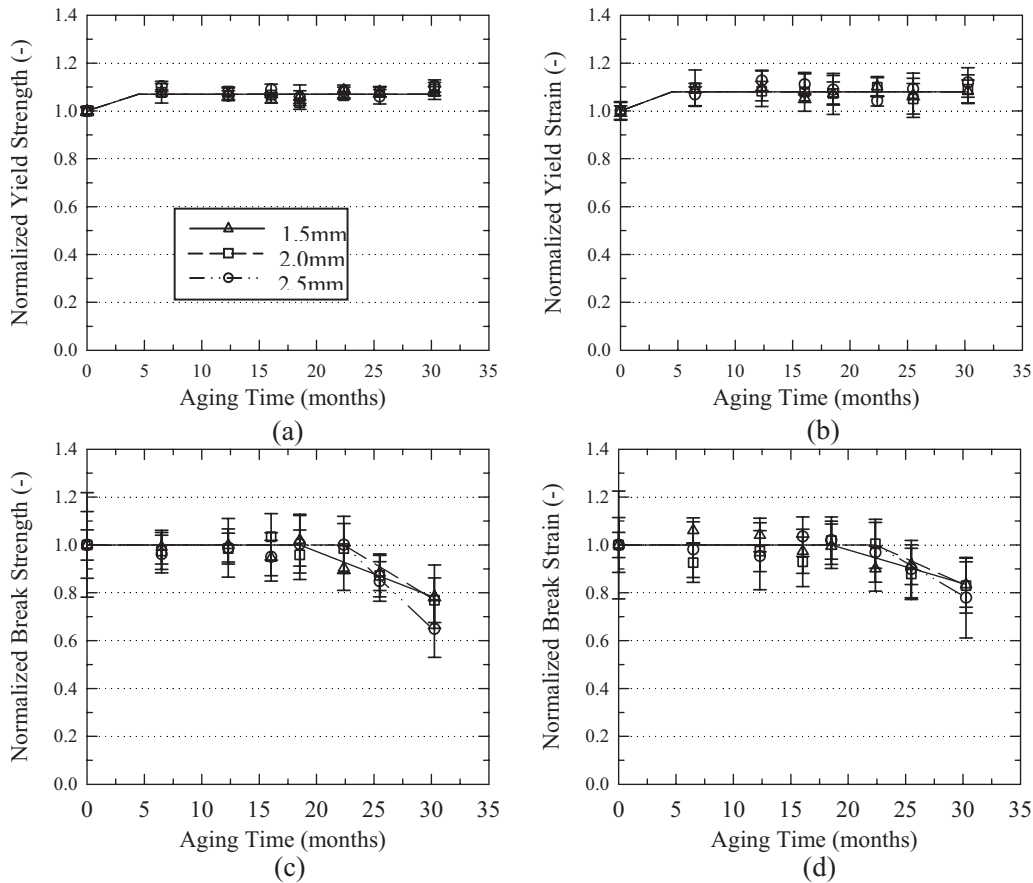


Fig. 8. Variation in tensile properties along cross-machine direction at 70°C for the 1.5, 2.0, and 2.5 mm GMs: (a) yield strength; (b) yield strain; (c) break strength; and (d) break strain

GMs. Because of the delamination behavior, the greater decrease in break strength and strain for the 2.5 mm GM does not necessarily indicate that this GM degraded more compared to the 1.5 and 2.0 mm GMs. The results of the MI and stress-crack resistance (described in the later section), which are generally considered as good indicators of oxidative degradation, suggest that the 2.5 mm GM indeed degraded less compared to the 1.5 and 2.0 mm GMs.

The tensile break strength and strain for the 1.5 and 2.0 mm GMs and the tensile break strength for the 2.5 mm GM along cross-machine direction decreased by approximately 20% at 70°C (Fig. 8). The tensile break strain for the 2.5 mm GM along cross-machine direction decreased by approximately 38%. For the 1.5 mm GM, the decrease was observed after about 18.5 months and for the 2.0 and 2.5 mm GMs the decrease was observed after about 22 months. The observed decrease in tensile break properties are in accordance with the MI results at 70°C (Fig. 5). There was statistically no significant change over the duration of the test in tensile break strength and strain along machine direction at 70°C and in both directions at 55 and 22°C.

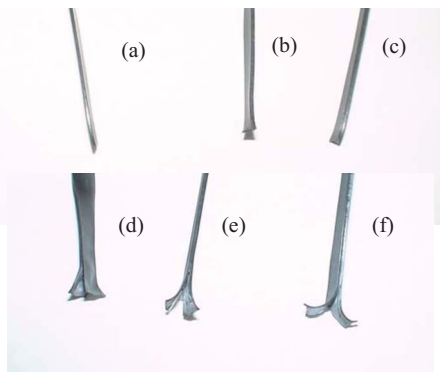


Fig. 9. Photograph of typical failed specimens of tensile tests on unaged GMs: (a) 1.5 mm machine direction; (b) 2.0 mm machine direction; (c) 2.5 mm machine direction; (d) 1.5 mm cross-machine direction; (e) 2.0 mm cross-machine direction; and (f) 2.5 mm cross-machine direction

Stress-Crack Resistance

Fig. 10 shows the variations in average stress-crack resistance with the aging time at 85°C for the three GMs. The average failure times are plotted as the normalized failure time relative to the failure times of the unaged GMs. The failure times decreased by approximately 75, 65, and 35%, respectively, for the 1.5, 2.0, and 2.5 mm GMs by the end of the incubation period. The decrease in failure times for the 1.5, 2.0, and 2.5 mm GMs were observed after about 8.5, 10.5, and 10.5 months, respectively. These results suggest that the rate of decrease in stress-crack resistance of the GMs followed the order (highest to lowest) 1.5 mm > 2.0 mm > 2.5 mm. There was no statistically significant change in stress-crack resistance compared to the initial

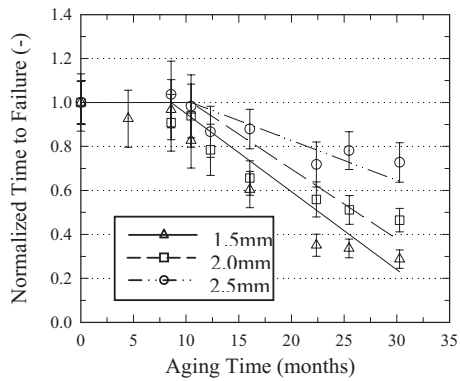


Fig. 10. Variation in time to failure (plotted as normalized failure time to the initial value) versus aging time during stress-crack resistance tests at 85°C for the 1.5, 2.0, and 2.5 mm GMs

stress-crack resistance of the GMs at other temperatures (e.g., 70, 55, and 22°C) over the period of incubation suggesting that they have not yet entered Stage 3 of degradation.

Conclusions

This study describes the results of an accelerated aging test program on the depletion of AOs from three commercially available HDPE GMs having nominal thicknesses of 1.5, 2.0, and 2.5 mm. Tests were conducted at 85, 70, 55, and 22°C by immersing the GMs in a synthetic leachate. Results show that the thickness of the GM has a significant effect on the depletion of AOs with the thicker GM giving the longest AO depletion time (by about 50% at all temperatures examined). The results of crystallinity, MI, and stress-crack resistance suggest that a thinner GM is more susceptible to degradation than a thicker GM. All three GMs exhibited delamination behavior in tensile testing. The delamination behavior was more severe for the thicker GM than the thinner GM. The tensile break properties have shown to decrease more for the thicker GM than the thinner GM which is mainly due to the delamination behavior and does not necessarily reflect on the service life of the GM. The MI and stress-crack resistance are believed by the writers to be better measures of likely long-term performance than the tensile properties for these GMs. It is expected that for many applications a 1.5 mm GM that meets the GRI GM-13 (GRI 1997) specifications will provide adequate performance. However, it also appears (other things being similar) that the thicker GM is likely to have a longer service life than the thinner GM and may be more appropriate when the 1.5 mm GM cannot provide adequate service life, thereby supporting the choice of a thicker GM for secondary liners required to have a longer service life than primary liners as indicated in some regulations (e.g., MoE 1998). However it should be emphasized that the nature of the resin and the AO package used may also have a significant effect on the service life of the GM and this also needs to be considered in the selection of the GM for a given application.

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