

Oxidative resistance of high-density polyethylene geomembranes

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Abstract

Data are reported from oven aging in air for more than 13 years (!) and from water immersion tests for 6 years at 80 °C on various high-density polyethylene geomembranes (GM) used in landfill lining. The mechanical properties and oxidative induction times (OIT) of the samples were monitored during the long-term testing. Aging behavior in hot air is different from that in hot water. During oven aging a slow, exponential decrease of OIT is observed. Even after 13.6 years there is no indication of an oxidative degradation of the mechanical properties. During immersion in water a strong reduction in OIT occurs within the first year, after which time the curve levels off. Oxidation starts when very low OIT-values are reached after about 5 years at which time the mechanical strength rapidly falls to values below the yield point. We conclude from these data that the service life of HDPE GM's is essentially determined by the slow loss of stabilizers due to migration. The oxidation starts only after the depletion of antioxidants and then quickly leads to brittleness of the sample. However, no complete oxidative deterioration has been observed to date. We estimate by the van't Hoff rule that under normal ambient conditions many centuries will have to pass before the functional mechanical properties of state-of-the-art stabilized HDPE bulk material will be reduced below acceptable limits by oxidative degradation.

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1. Introduction

Research on the long-term behavior of high-density polyethylene geomembranes (HDPE GM) has focused primarily in the past on environmental stress crack resistance. Meanwhile, reliable standard methods of extrapolation of hydrostatic stress rupture data (ISO/DIS 9080) are established, which allow well founded estimates of service life of HDPE materials with respect to stress cracking and of acceptable stresses and deformations. Stress crack resistance of HDPE GMs is generally evaluated and compared by the Notched Constant Tensile Load test (NCTL test, ASTM D 5397–95), which was specifically developed for this purpose. However, along with stress cracking, oxidative degradation can also impair the integrity and/or performance of polyolefin geomembranes. It is generally accepted that oxidative degradation of HDPE GMs is

not a relevant factor with regard to normal geotechnical applications, in which service lives of around 30–50 years are expected and repair work is possible. However, it may become relevant when the geomembranes are integral part of building structures that have to perform over extremely long lifetimes (> 100 years), as is for example, the case for geomembranes in landfill liner systems. Especially in capping systems long-term slope stability may be impaired by oxidative attack [1].

German building authorities have defined two durability categories for materials in landfill lining systems. The durability of a material is classified as long-term, if it can be assumed that no relevant change in the functional engineering properties of the material will occur over “a period of 50–100 years as predicted in accordance with accepted scientific and engineering knowledge and experience”. Durability is classified as permanent, if it can be predicted that no relevant change will occur over “several hundred years”. Landfill lining systems must contain at least one component that is permanent according to this definition. Hsuan and Koerner [2] estimated the typical service lifetimes of

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landfills as follows: regulatory minimum (e.g. post closure) typically 30 years, non hazardous (municipal) waste at least 100 years, hazardous/low level radioactive waste ≥ 1000 years. Accordingly, the service life of HDPE GMs in landfill lining systems is more likely to be in the range of centuries than of decades. For such a large time scale oxidative degradation might substantially contribute to the aging process and failure modes. Often HDPE GMs are classified only as long-term—i.e. not permanent—because of the problem of possible oxidative degradation.

The service lifetime with respect to oxidative degradation of geomembranes made of a certain HDPE-resin was first estimated by Koch et al. [3]. They used hydrostatic burst pressure tests with pipes of the resin used in the GM and measured at 80 and 60 °C the time of the transition from brittle failure due to stress crack to brittle failure due to oxidation. From an Arrhenius diagram they extrapolated a service lifetime of about 700 years at ambient temperature. Hsuan and Koerner studied the aging of a commercially available HDPE geomembrane in an incubation device that simulated the service environment of a geomembrane beneath 30 m of waste [2]. The aging process was accelerated by temperature and mechanical properties and oxidative induction time (OIT) were measured as function of aging time. No oxidative degradation was achieved. However, it was argued that the time of the depletion of antioxidants should be the main part of the service lifetime. This oxidative depletion time was monitored by OIT measurements which led to a lower estimate for the service life at ambient temperature of 200 years. Similar results were obtained by Rowe and Sangam, who emphasized the influence of the immersion liquid on the antioxidant depletion rate [4]. An overview of experimental results is given in Ref. [4].

However, in none of these experiments was the depletion process observed to the end and no oxidative degradation was actually achieved, since this requires very long testing times even at high temperatures. Therefore, the depletion rates have to be taken with caution, because they are estimated from short-term experiments, and the assumption that the antioxidant depletion time is the most relevant part of the service lifetime needs experimental justification.

As German certification authority for plastic geomembranes in landfill lining systems [5], the Landfill Engineering Laboratory at the German Federal Institute for Materials Research and Testing (BAM) has performed oven aging and immersion test studies with various HDPE geomembranes since the late 1980s. In this paper, we report our results and try to contribute to answers to the following questions: How long is this service lifetime of HDPE GMs with respect to oxidative degradation at normal service conditions and how does the aging process evolve? What are the best test methods

to select and compare HDPE GM resins with high oxidation stability under normal service conditions?

Polyolefin components used in geosynthetics are often stabilized less than HDPE GMs. They are made of polymers which are more sensitive to oxidative degradation (e.g. PP or LDPE as opposed to HDPE) or have a much higher surface to volume ratio (e.g. fibers or slit films). The oxidative long-term behavior of HDPE GMs should therefore set a time frame for the oxidation stability of geosynthetics and accordingly our results are of significance for the general topic of the oxidative resistance of these products as well.

2. Theory

In the following a simplified picture of oxidation and stabilization is given that we use to analyze our data. A detailed discussion can be found elsewhere ([6–8] and references therein). The oxidative degradation of polyolefin resins is initiated by the formation of free radicals. The formation is due to peroxides, oxygenated compounds (formed during the processing of the polymer) and catalyst residues in combination with oxygen. UV and high-energy radiation also produce free radicals and free radical initiators. Once free radicals are formed and oxygen is available, a chain reaction can start. In each propagation cycle of the chain reaction, hydroperoxides are formed. The decomposition of the hydroperoxides initiates new chain reactions. Eventually each chain reaction is terminated. The termination reaction leads to a decomposition of the polymer chain. To some extent cross linking might occur in the early stage.

After a certain induction period t_1 with no significant changes in the polymer properties, the degradation rate increases rapidly, the molecular weight distribution is shifted towards lower values, the material becomes brittle and loses finally all mechanical resistance. Since the initial reaction rate at ambient temperatures is very low the induction time t_1 can be quite large. Depending on the amount of free radical sources and the sensitivity of the polymer to oxidation, the induction time of the oxidation of an unstabilized polyolefin resin might range from a few years to several decades.

Antioxidants are added to the polymer to protect it from oxidation. These are compounds which either trap free radicals and prevent reaction chain initiation or decompose hydroperoxides, thereby preventing them from forming free radicals as starting point of new reaction chains. Usually a combination of both types of antioxidants is used. Every antioxidant has a temperature range over which it functions most effectively. There are antioxidants which have their effective temperature range at higher temperature and are used as processing stabilizers (e.g. phosphites) and there are others which have their most effective temperature

range at ambient temperature (e.g. HALS) or over a wide temperature (e.g. hindered phenols) range and which are used as long-term stabilizers to provide protection during the low temperature service life. Typically a composition of a phosphite and a hindered phenol is used as the main part of the antioxidant package for most of the HDPE GMs available on the market. Normally carbon black is added as UV stabilizer. The concentration of the antioxidant components is typically in the range of a few thousand ppm (mg/kg).

From pipe pressure tests it is known that under normal conditions (ambient oxygen pressure) antioxidants are not consumed by the very slow oxidation process but are lost by migration, dissolution, evaporation and extraction [9]. These antioxidant depletion processes depend strongly on the environmental conditions. If after a certain induction time t_2 of antioxidant depletion, the antioxidant concentration has fallen below a critical value, the autoxidation with induction time t_1 will start. Therefore, we expect that the service lifetime t_L of a GM might be written as:

$$t_L = t_1 + t_2. \quad (1)$$

The depletion of antioxidant concentration [AO] over time might be approximated more or less by an exponential law:

$$[\text{AO}] = [\text{AO}]_0 e^{-k_{\text{eff}} t}. \quad (2)$$

We call k_{eff} the antioxidant depletion rate and its reciprocal τ_{eff} the depletion time constant. Both are characteristic parameters of the depletion process. The Arrhenius law can often be used to describe the temperature dependence of the depletion rate k_{eff} :

$$k_{\text{eff}} = C e^{-\frac{E}{RT}}, \quad (3)$$

where C is the pre-exponential factor, E the activation energy of the depletion process and R the molar gas constant (8.3145 J/(K mol)).

The oxidation stability at high temperatures (above the melting point) can be directly measured using thermoanalytical methods. The thermoanalytical measurement determines the time interval (OIT) to the onset of exothermic oxidation of a polymer at a specified OIT testing temperature T_m in a specified oxygen atmosphere. For some stabilizer packages the change in OIT values of a given HDPE GM sample during aging can be used to monitor the change in the level of stabilization and to estimate the induction time due to antioxidant depletion t_2 of the sample. Especially for the earlier mentioned stabilizer package the OIT increases monotonously with antioxidant concentration [10–12]. Therefore, it is possible to approximate the oxidative induction time OIT roughly as linear function of the antioxidant concentration

[AO] within a broad medium concentration range excluding the sectors of low and very high concentration values. We may assume:

$$\text{OIT} = \alpha \cdot [\text{AO}] + \beta, \quad (4)$$

where $\alpha > 0$. α and β strongly depend on the specific properties of the resin, the nature of the stabilizer package and the OIT measurement conditions used. Normally negative values have to be attributed to β to interpolate measured relations between OIT and antioxidant concentration [11,12], because zero OIT value might be achieved at high OIT testing temperature even with a certain amount of stabilizer present. However, at very low OIT testing temperature a high oxidation stability of the unstabilized material might come into play, which would lead to an offset in the OIT-value even at zero stabilizer content. In this case, β might also become positive. Inserting Eq. (4) into Eq. (2) we expect that the change in OIT during aging, $\text{OIT}(t)$, might be fitted by an exponential decline with amplitude A and offset B , with both parameters differing significantly for the different materials and measurement conditions, and a depletion rate k_{eff} which is characteristic for the depletion process:

$$\text{OIT}(t) = A e^{-k_{\text{eff}} t} + B. \quad (5)$$

3. Experimental

Nine commercially available HDPE GMs [samples 1 and 48 (same resin, same GM manufacturer but several years difference in dates of manufacturing), 12 and 136 (ditto), 82, 123, 139, 146, 257] made of seven different resins from five GM manufacturers were tested. The GMs are widely used for example, in landfill lining systems. The tested samples were 2.5 mm thick. In all cases the UV stabilization was effected by carbon black with a typical content of 2–2.5 wt.%. Table 1 shows the specifications for melt flow rate (MFR) and density of the GMs. Added are the ratio between the MFR (190/5) and MFR (190/21,6), which reflects the width of the molecular weight distribution, and the type of copolymer. The copolymer content is normally relatively low, i.e. < 10 wt.%. Most of the resins used for HDPE GMs are actually ethylene- α -olefin-copolymers and should therefore rather be classified as linear low density or as linear medium density. Although only the carbon black additive places them formally in the high density range, the geosynthetic community customarily refers to them as HDPE GMs. All resins were stabilized at least with a few thousand ppm of phenolic and phosphite antioxidants. However, there are considerable differences in the initial OIT-values (Table 2) due to the details of the

Table 1
Resin specifications of the HDPE GMs studied

Sample	Specification			Copolymer
	MFR (190/5) g/10 min	MFR Ratio (190/21.6)/ (190/5) (–)	Density (GM) (g/cm ³)	
1	0.85±0.15	19	0.946±0.002	?
48				
12	1.6±0.2	9	0.942±0.003	Butene
136				
82	23±3 ^a	18	0.947±0.003	Hexene
123	(0.5)	(26)	(0.950)	Hexene
139	2.5±0.4	9	0.943±0.002	Octene
146	0.80±0.15	23	0.950±0.005	Hexene
257	(1.7)	(9)	(0.940)	Blend

Values measured at the samples were all within the specifications. Values stated in parentheses are measured values, i.e. no specification was available.

^a MFR 190/21.6

Table 2
Initial OIT value of HDPE GMs samples at $T_m=160$ and 180 °C measured in Cu-pans and at $T_m=200$ and 210 °C measured in Al-pans

Sample	OIT (min) at T_m			
	Cu-pan		Al-pan	
	160 °C	180 °C	200 °C	210 °C
1	61	7	–	
48	72	13	11	
12	–	48	79	
82	–	113	81	
123	–	56	102	
136	–	123	138	
139	–	203	81	
146	–	46	70	
257	–	–		41

make-up of the stabilizer package and the intrinsic polymer properties. The exact make-up of the stabilizer package is normally a secret of the resin manufacturer and the information is either not available or must be treated confidential.

The following experimental methods were used to characterize the oxidation stability of the GM:

1. Oven aging (in all but one case: gravity convection).
2. Immersion in hot water.
3. Tensile test, measurement of (MFR) and density.
4. DSC measurement for high temperature OIT values and melting curves.

We give a short description of the experimental procedures:

1. A thermostatically regulated Heraeus T 5110 E oven with gravity convection via a single open air channel and with a working chamber volume of 258 l was used. Technical data concerning the oven's air changes per h are not available. However the number of air changes is substantially lower than 10 per h and therefore, air in the oven is nearly stationary. The temperature variation was about ± 3 °C. To compare the results with other aging conditions, we aged sample 257 in an oven with forced air circulation. A Heraeus UT 6200 oven (working chamber volume 180 l) was used which has an internal air ventilation by a fan. The air change takes place via two open air channels. According to the technical specifications of this oven, there were 47 air changes per h and a fresh air quantity of about 11 m³/h. The temperature variation (with closed flaps) was about ± 1 °C. Rectangular sheets of area 30 · 40 cm² were cut out of the GM samples. These specimens were hung up on grids in the pre-heated oven.
2. For the water immersion test of the GM, tensile test specimens of type 1B according to EN ISO 527–3:1995 were put in closed glass flasks filled with de-ionized water. The flasks were placed in a temperature controlled oven at (80 ± 1) °C. The flasks were opened and shaken every 4 weeks; the water was completely changed every 3 months.
3. The tensile properties of the GM were tested according to EN ISO 527–3. Type 1B specimens were punched out of the sheets that had been taken from the oven and cooled off in standard climate (23 °C/50% r.h.). Fig. 1 shows typical stress–strain diagrams from the tensile test. Using these data the relative value of the elongation at break, $\delta\varepsilon_B(t) = \frac{\varepsilon_B(t)}{\varepsilon_B(0)}$, as a function of the aging time or immersion time t was determined. The melt flow rate and the density were tested according to DIN ISO 1133:1991 and DIN 53479:1976, method A (buoyancy method), using strands from MFR measurements tempered for 1 h in boiling water (ASTM D 2839–69).
4. The procedure for the high temperature OIT measurement by differential scanning calorimetry (DSC) is described in ASTM D 3895–95. A Perkin-Elmer DSC 7 was used. A small cylinder (3 mm diameter) was punched out of the GM. A small plate was cut from the middle section of the cylinder. This plate was used for the OIT measurement. The OIT value was determined using open Al as well as Cu pans. Typically the OIT values at a given OIT testing temperature T_m are roughly by a factor of 5 higher with Al pans than with Cu pans. Cu pans were chosen to accelerate the oxidation: we

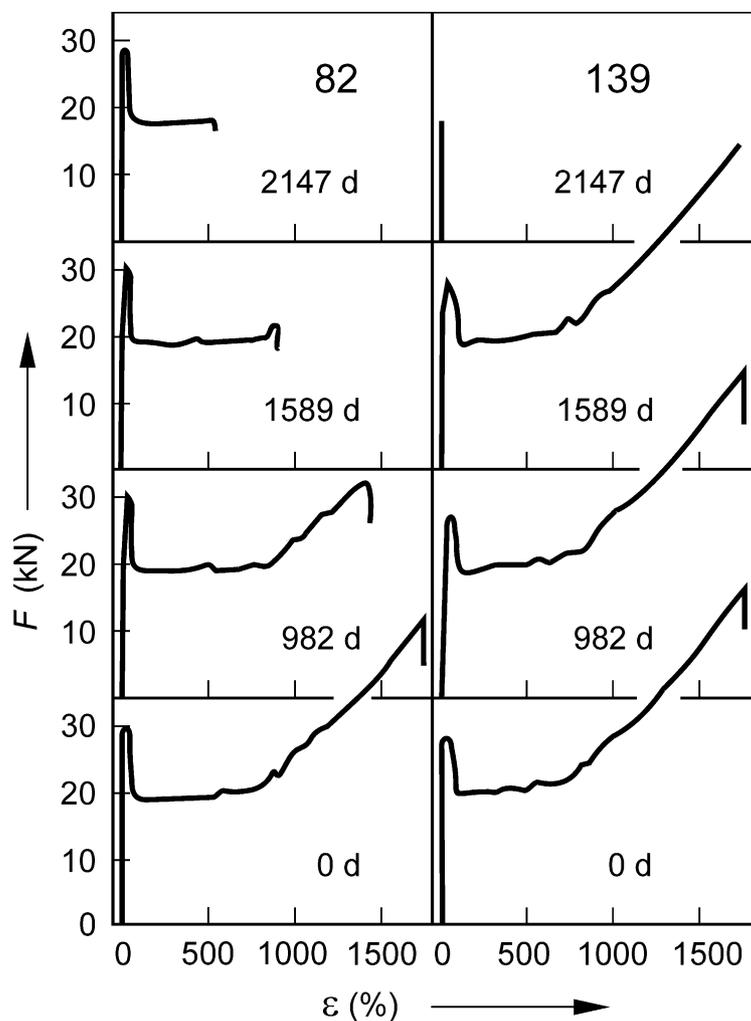


Fig. 1. Examples of tensile force (F) versus strain (ϵ) diagrams from tensile tests on sample 82 and 139 after immersion in hot water. The immersion times are indicated.

wanted to achieve an OIT testing temperature T_m as close to the melting temperature as possible with OIT values short enough to be practicable in the experiment. Fig. 2 shows some examples of measured OIT curves (difference of heat flow ΔQ versus measuring time t_m). The OIT value was determined as the difference between the time of the change to oxygen atmosphere and the time, when ΔQ exceeded a threshold value of 0.01 W/g.

The detection limit of the DSC apparatus is about 1–1.5 min, which is the length of the period to reach a steady state after switching to oxygen-atmosphere (Fig. 2). In most cases the given OIT-value is the average of three single measurements and the standard deviation is typically 10–15%. The OIT value of a sample was set to zero at a given T_m , when it was below the detection limit. From these measurements the relative OIT value, $\delta\text{OIT}(t) = \frac{\text{OIT}(t)}{\text{OIT}(0)}$, as a function of the aging time or immersion time t was obtained.

4. Results

4.1. Oven aging

First we consider the oven aging data. Fig. 3 shows the change in relative OIT values, δOIT , of GM samples 1 and 48, sample 12 and sample 139 during the air oven aging at 80 °C with gravity convection and of GM sample 257 during oven aging in forced air circulation. The corresponding measured OIT values can be calculated using the initial values given in Table 2. The relative OIT values of all samples slowly decreases. After 13.6 years of aging in air the OIT values are very low: 6 min at $T_m = 140$ °C with Cu-pans for sample 1 and about 2 min at $T_m = 200$ °C with Al pans for sample 12.

So far none of the samples show any significant change in the tensile properties during air-oven aging. However, for the specimens of samples 1 and 12, which were aged for the whole period of 13.6 years, a reduction in the melt flow rate is observed (Table 3). The MFR(190/5) and MFR(190/21.6) after an aging time of

4978 days are 0.5 and 14 g/10 min for sample 1 and 1.2 and 12 g/10min for sample 12 respectively. The overall crystallinity changed only slightly (Table 4). But recrystallization led to a small but distinct second peak in the melting curve, known as memory peak attributable to the heat treatment at 80 °C.

At low OIT testing temperatures the OIT values become very large. Still, for the oven aged specimen of sample 48, the OIT value could be determined even at $T_m = 140$ °C. The initial OIT value of sample 48 measured at 200, 180 and 160 °C was used to extrapolate its initial OIT value at 140 °C (Fig. 4). The data (closed circles) follow clearly an Arrhenius law. Using the result of 381 min for $T = 140$ °C the relative OIT value could be calculated and was added to Fig. 3. With all data included, Fig. 3 illustrates the experimental finding that the relative OIT values show roughly a common decline as a function of aging time, independent of the resin or the OIT testing temperature. The decline versus time is actually a superposition of two exponential declines, as

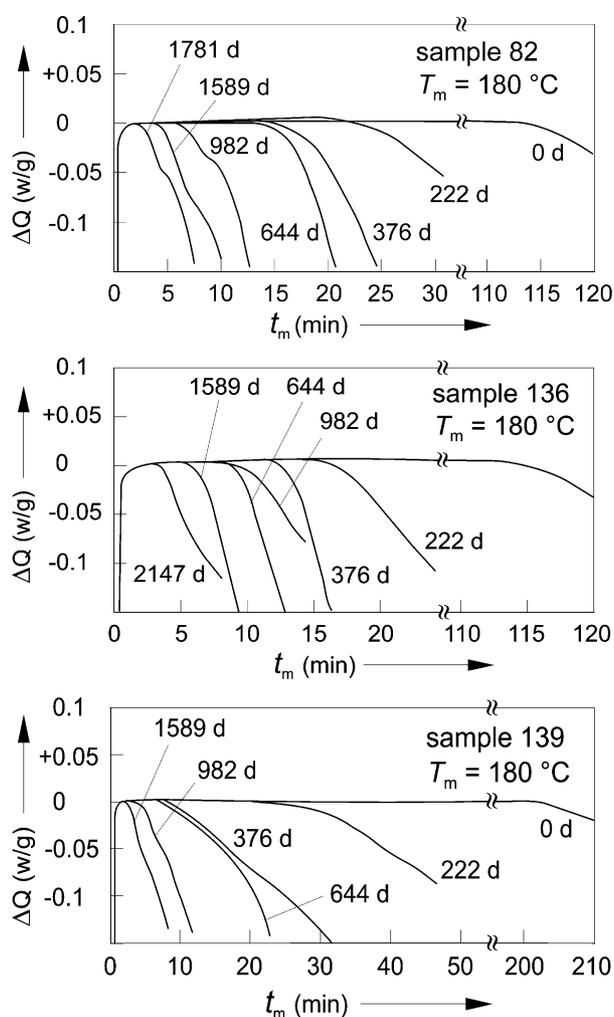


Fig. 2. Examples of OIT curves measured at $T_m = 180$ °C with Cupans on specimens from samples 82, 136, 139 after immersion in hot water. The immersion times are indicated.

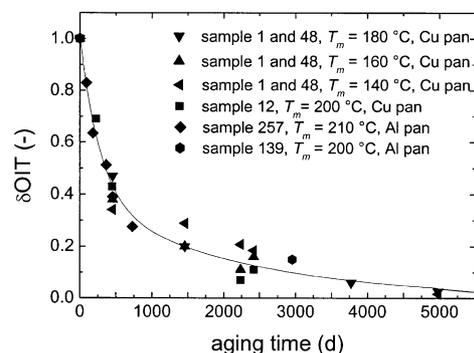


Fig. 3. Change in the relative OIT value δ OIT during aging in air at 80 °C of various samples. Sample 257 was tested in forced air circulation, all other samples in air circulating by gravity convection.

Table 3

Change of melt flow rate, melt flow rate ratio and density of the HDPE GM samples during air oven aging (samples 1 and 12) and water immersion (samples 82, 123, 136 and 146) at 80 °C

Sample	Parameter	Aging or immersion time (days)				
		0	982	2147	2419	4978
1	190/5 (g/10 min)	1.0	–	–	0.8	0.5
	190/21.6 (g/10 min)	18	–	–	16	13
	ratio (–)	18	–	–	20	27
	density (g/cm ³)	0.950	–	–	0.949	0.951
12	190/5 (g/10 min)	1.6	–	–	1.5	1.2
	190/21.6 (g/10 min)	15	–	–	14	12
	ratio (–)	9	–	–	9	10
	density (g/cm ³)	0.943	–	–	0.943	0.946
82	190/5 (g/10 min)	1.4	0.9	1.5	–	–
	190/21.6 (g/10 min)	27	25	37	–	–
	ratio (–)	20	28	25	–	–
	density (g/cm ³)	0.947	–	0.954	–	–
123	190/5 (g/10 min)	0.5	0.5	–	–	–
	190/21.6 (g/10 min)	13	13	–	–	–
	ratio (–)	26	26	–	–	–
	density (g/cm ³)	0.950	0.950	–	–	–
136	190/5 (g/10 min)	1.6	–	1.6	–	–
	190/21.6 (g/10 min)	14	–	15	–	–
	ratio (–)	9	–	9	–	–
	density (g/cm ³)	0.943	–	0.950	–	–
146	190/5 (g/10 min)	0.83	–	0.7	–	–
	190/21.6 (g/10 min)	19	–	18	–	–
	ratio (–)	23	–	26	–	–
	density (g/cm ³)	0.951	–	0.952	–	–

Table 4

Crystallinity (%) of HDPE GMs studied at various immersion times

Immersion time (days)	Sample				
	82	123	136	139	146
0	52	52	51	48	54
222	54	55	52	49	57
376	56	54	52	50	57
644	58	55	51	51	57
982	55	55	53	51	58
1589	58	56	51	51	57
2147	56	57	53	57	59

can easily be seen in a logarithmic plot of the data. The aging period to date of sample 257 is only 730 days. Within this period the change in the relative OIT value due to aging in forced air circulation follows closely the course of the data from aging samples in air circulated by gravity convection.

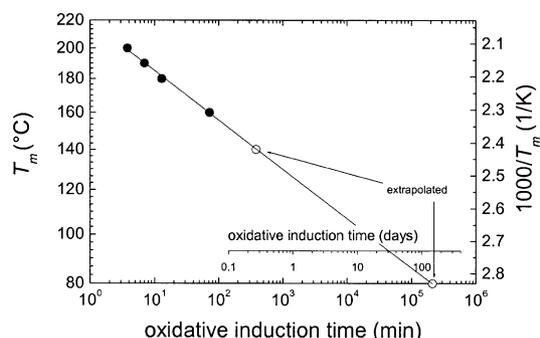


Fig. 4. Arrhenius plot of the reciprocal absolute OIT testing temperatures ($1/T_m$) versus the logarithm of the corresponding initial OIT values of sample 48.

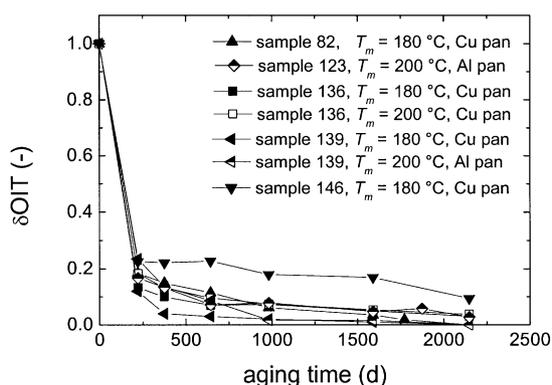


Fig. 5. Change in the relative OIT value ΔOIT during immersion in water at 80 °C of various samples. The OIT testing condition are indicated.

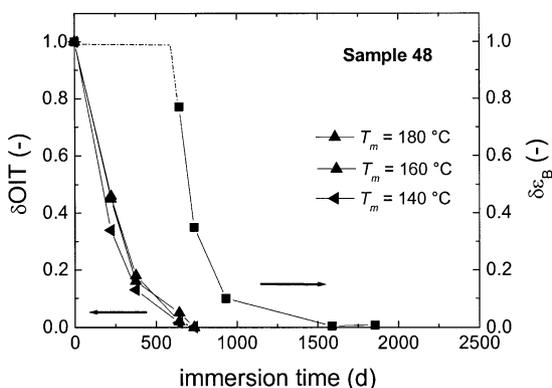


Fig. 6. Change in the relative OIT value ΔOIT and relative elongation at yield $\Delta \epsilon_B$ during immersion in water at 80 °C of sample 48. The OIT testing temperatures are indicated. Cu-pans were used.

4.2. Immersion in hot water

The behavior of the GM samples immersed in water is different from those exposed to air-oven aging. The effect of a two step exponential decline is drastically enhanced in the immersion data. At the beginning of the immersion the relative OIT values of all samples decrease sharply (Fig. 5). The corresponding reduction in the absolute OIT values might be obtained by comparing the OIT values plotted in Figs. 6–11 with the initial values from Table 2. Depending on the amount of the initial OIT value, the decrease is enormous (e.g. sample 139). However, for all but one sample (namely 48) the curve of the OIT versus immersion time levels off at the latest after 200 days and the further decline in oxidation stability is only small.

Figs. 6–11 show the change of the OIT value itself and the corresponding change in the relative elongation at break $\Delta \epsilon_B$ as a function of the immersion time in 80 °C de-ionized water for samples 48, 82, 123, 136, 139 and 146, respectively. Sample 136 was manufactured from the identical resin as sample 12 which was studied in the

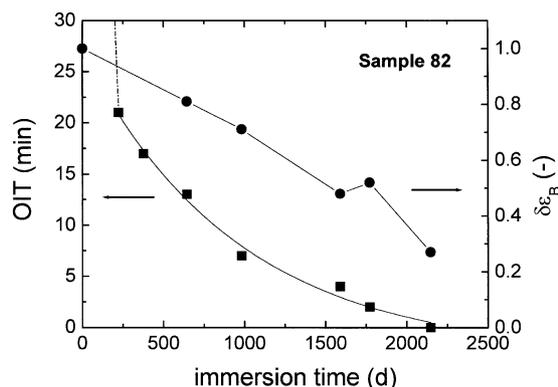


Fig. 7. Change in relative OIT value ΔOIT ($T_m = 180$ °C, Cu-pans) and relative elongation at yield $\Delta \epsilon_B$ during immersion in water at 80 °C of sample 82.

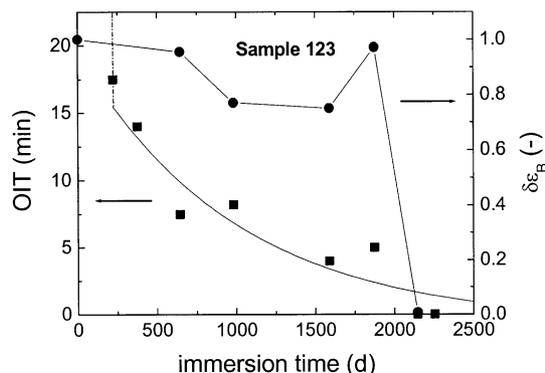


Fig. 8. Results of the immersion test on sample 123, see caption Fig. 7.

air oven aging. Elongation at yield is the tensile test parameter most sensitive to oxidative degradation.

Sample 48 (Fig. 6) is obviously made of a poorly stabilized resin when compared with the other resins tested. The initial OIT value is extremely low (Table 1). For the GMs made of this resin the rapid decrease in OIT value continues. After about 2 years of immersion in water no OIT value was measurable. Even at $T_m = 140\text{ }^\circ\text{C}$ the OIT value was practically zero. The intrinsic oxidation stability of this resin appears to be very low. From the point in time (580 days) when the OIT value reached very

low values, the oxidative degradation process started. A drastic reduction in the elongation and stress at break was observed within months. Yet, at that time there was no change in yield stress and strain and therefore the field performance of the GM would not have changed. However, the oxidation process has continued and at present (6 years of immersion) the elongation at break is now well below the yield point and as low as about 6%, i.e. the samples became very brittle. The decrease of ϵ_B was accompanied by a reduction in the melt flow rate indicating cross linking as the main early degradation effect. The identical oxidative behavior as shown in Fig. 6 was observed in pipe pressure tests at $80\text{ }^\circ\text{C}$ with pipes made of this resin, see Fig. 13 [3]. According to the authors, the stress rupture at 2 MPa was due to oxidation and not due to stress cracking. Indeed, the failure time of the pipes at $80\text{ }^\circ\text{C}$ agrees perfectly with the immersion time at which the drastic change of elongation at break of the immersed GM starts (see Fig. 6).

For sample 139 (Fig. 10) the decline in OIT value evolves much more slowly after the initial strong reduction. The

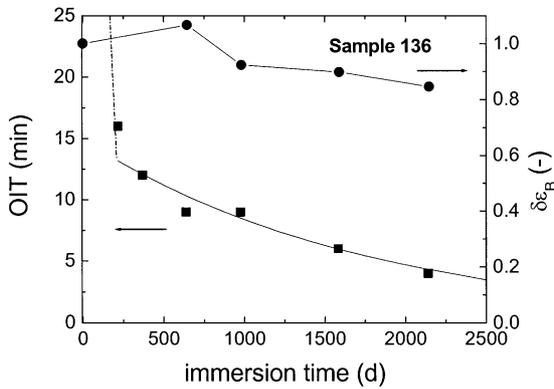


Fig. 9. Results of the immersion test on sample 136, see caption Fig. 7.

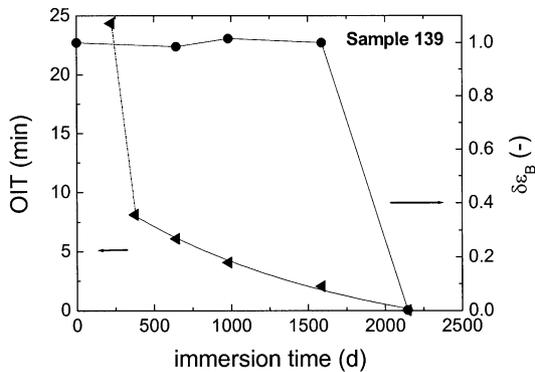


Fig. 10. Results of the immersion test on sample 139, see caption Fig. 7.

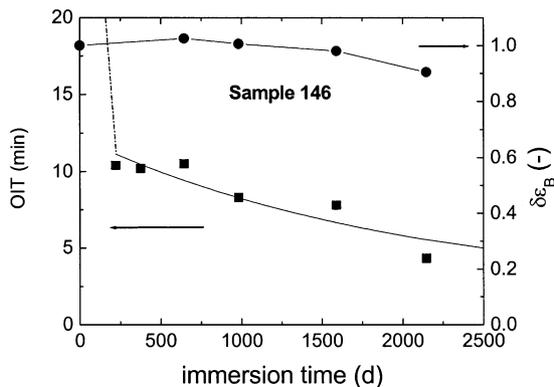


Fig. 11. Results of the immersion test on sample 146, see caption Fig. 7.

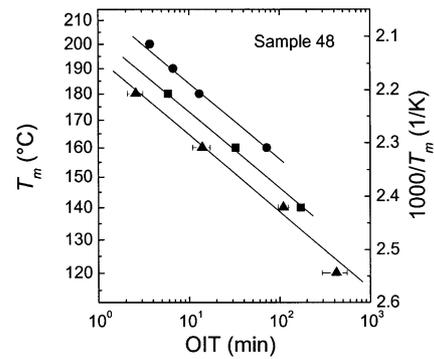


Fig. 12. Arrhenius plot of the reciprocal absolute OIT testing temperature ($1/T_m$) versus the logarithm of the corresponding OIT values for sample 48: initial sample (circles), samples air-oven aged at $80\text{ }^\circ\text{C}$ for 4 years (triangles) and samples immersed in water for 222 days (squares).

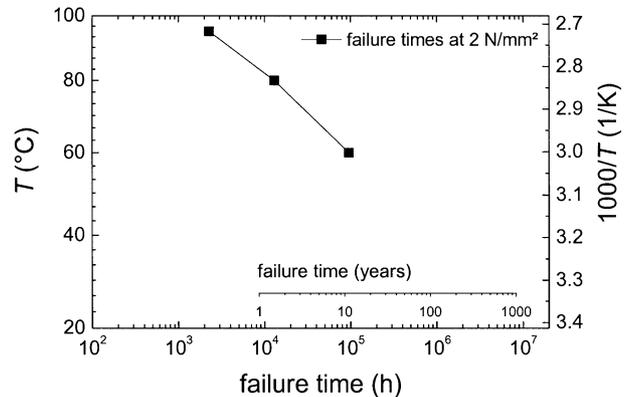


Fig. 13. Reciprocal absolute pipe testing temperatures ($1/T$) versus the logarithm of the mean failure times of the pipe specimens at hoop stress of 2 MPa. The data of the pipe pressure tests were taken from [3].

remaining OIT value after 982 days was 5 min at $T_m = 180\text{ }^\circ\text{C}$ with Cu-pan. However, after 2147 days (i.e. about 6 years) the OIT value has dropped below the detection limit both at $T_m = 180\text{ }^\circ\text{C}$ and $T_m = 200\text{ }^\circ\text{C}$ and with Cu pans as well as with Al-pans. Similar to the behavior of sample 48, the elongation at break of sample 139, which is fairly constant as long as there is a measurable OIT value, has been reduced to values below the elongation at yield by oxidative degradation within several months (see Fig. 1 for the stress–strain curves). The behavior of the mechanical properties and the course of the OIT curve of sample 123 (Fig. 8) are similar to sample 139. After 2147 days of immersion and a considerable decline in OIT value, the material has suddenly become brittle.

The behavior of the mechanical properties of sample 82 is quite unique (Fig. 7). The decline in OIT of this sample is accompanied by a continuous decline of its mechanical strength and of the melt flow rate over several years. However, the elongation at break is still far above the yield point (see Fig. 1 for the stress–strain curves). The MFR (190/5) and MFR (190/21.6) decreased from 1.4 and 27 g/10min (initial values) to 0.9 and 25 g/10min (at 982 days) and then increased to 1.5 and 37 g/10min (at 2147 days) (Table 3). After about 6 years testing time the OIT value has dropped below the detection limit both at $T_m = 180\text{ }^\circ\text{C}$ and $T_m = 200\text{ }^\circ\text{C}$ when measured either with Cu-pans or with Al-pans. The behavior of sample 82 gives rise to the question of morphological changes during aging. Table 4 shows the crystallinity of the samples at the different immersion times, which was determined by the heat of melting assuming 292 J/g for fully crystallized HDPE. In the first year of immersion in some of the samples a small recrystallization occurred which creates a so called memory peak in the melting curve. The position of this small peak is characteristic for the immersion temperature. Afterwards crystallinity remained constant within the measurement errors.

The OIT value at $T_m = 180\text{ }^\circ\text{C}$ of samples 136 (Fig. 9) and 146 (Fig. 11) at 982 days was 9 min (136) and 8 min (146). After 2147 days the OIT value is still 3 min ($T_m = 180\text{ }^\circ\text{C}$, Cu pans) and 8 min ($T_m = 180\text{ }^\circ\text{C}$, Al-pans) for sample 136 and 4.5 min ($T_m = 180\text{ }^\circ\text{C}$, Cu-pans) and 15 min ($T_m = 180\text{ }^\circ\text{C}$, Al-pans) for sample 146, respectively. For these samples no change was observed in tensile properties (Figs. 9 and 11), melt flow rate or density (Table 3) during the entire 6-year time period of immersion. Obviously we have to assume that a considerable amount of stabilizer is still available even after this very long period of time.

Table 5 assembles the data of the elongation at break, tensile strength and the stress at yield, if the yield point was reached, and of the OIT values at $T_m = 180\text{ }^\circ\text{C}$ for all the GM samples after 2147 days of immersion in hot water. These data show that the mechanical properties

Table 5
OIT values and mechanical properties of HDPE GM determined after 5.9 years of immersion in $80\text{ }^\circ\text{C}$ water for samples 82, 123, 136, 139, 146 and after 5.1 years for sample 48

Sample	Properties after 2147 days (5.9 years) of immersion in hot water			
	ϵ_B (%)	σ_B/σ_Y (N/mm ²)	OIT value $T_m = 180\text{ }^\circ\text{C}$ Cu-pans	OIT value $T_m = 180\text{ }^\circ\text{C}$ Al-pans
48	6	22	0	0
82	500	13/21	0	0
123	5	12/–	0	0
136	1650	29/19	3	8
139	3	16/–	0	0
146	1400	25/22	4.5	15

of HDPE GMs are not substantially deteriorated as long as a significant OIT value is measurable. When the OIT-value reaches zero or very low values as compared with the initial OIT, the oxidative deterioration evolves quite rapidly.

4.3. Oxidation process at high temperature in oxygen atmosphere

In the DSC apparatus the specimens are oxidized in pure oxygen flow at high temperatures to measure the OIT value. Since sample 48 is most sensitive to oxidation, its behavior in the OIT test could be examined more closely. Fig. 12 shows an Arrhenius plot of the reciprocal absolute OIT testing temperature ($1/T_m$) versus the logarithm of the corresponding OIT values of GM sample 48 after air-oven aging for 4 years and after immersion in water for 222 days. Note that OIT measurements were performed even at $T_m = 120\text{ }^\circ\text{C}$ below the melting point of the HDPE resin (onset of melting peak: $118\text{ }^\circ\text{C}$, peak maximum: $128\text{ }^\circ\text{C}$). In this case the variation is quite large: minimum: 305 min, maximum: 580 min over five measurements. At each stage of aging, the data follow an Arrhenius line with the same slope as the data from the initial sample. However, the lines are shifted parallel to each other to lower OIT values according to the severity of aging. The high temperature oxidation of the samples in an oxygen atmosphere is therefore characterized by a well defined activation energy of 140 kJ/mol which is completely independent of the aging conditions the samples have gone through. Only the intercept with the y -axis decreases with aging time. This finding can be immediately explained by assuming a continuous reduction of the antioxidant concentration during aging [Eqs. (2) and (3)], while the intrinsic properties of the polymer remain intact. Extrapolating the line in Fig. 4 further, an oxidative induction time of 148 days would be obtained at $80\text{ }^\circ\text{C}$ for sample 48 when exposed to a flow of pure oxygen. On the other hand the oven aging data show that the induction time in air at $80\text{ }^\circ\text{C}$ is > 5000 days.

5. Discussion

According to the simple model introduced in Section 2, the service time t_L is the sum of the induction time t_1 of the autoxidation of the unstabilized polymer and the antioxidant depletion time t_2 . For our discussion it is crucial that the change in OIT value gives at least a rough estimate for the depletion time t_2 . This assumption was established for the antioxidant package commonly used in HDPE GMs [10–12] and it explains the oxidation behavior in the OIT measurement itself as described in Section 4.3. In the following we will show that a consistent explanation of all our experimental results is possible within this interpretation scheme.

Common to the aging behavior of all GM samples studied is that as long as there is a significant OIT value measurable at temperatures above the melting point, the mechanical properties remain intact. This includes even the mechanical behavior of sample 82 since elongation at break in tensile testing remains still well above the yield point. When the OIT value has dropped to zero or to very low values the oxidative degradation starts and the materials become brittle within several months. Brittleness means that bending the GM specimen by hand one can easily break it without yielding in the fracture surface. However, the HDPE material remains essentially intact and can sustain high pressure. There is no indication of complete deterioration as is sometimes observed when aging PP materials.

Significant is the difference in the behavior between aging in air and immersion in hot water. During aging in air the OIT-value slowly decreases in an exponential-like, steady fashion. After 13.6 years the melt flow rate indicates that finally oxidative degradation with cross linking effects might have started but there is still enough oxidative resistance to prevent any change in the mechanical properties. During aging in water a steep decrease in the OIT value occurs before it levels off. For most samples it approaches then to very low values within a few years and oxidation of the polymer itself starts. However, closer inspection of the decline of the OIT value during oven aging clearly shows that also these data follow a two-step exponential decline with aging time. Fig. 3 shows that the data are nicely fitted by a superposition of two exponential declines, numbered 1 and 2 and each described by Eq. (5), with a short-term antioxidant depletion time constant of $\tau_{\text{eff},1} = 280$ days and a long-term one of about $\tau_{\text{eff},2} = 2200$ days. The corresponding depletion rates are $k_{\text{eff},1} = 0.11 \text{ month}^{-1}$ and $k_{\text{eff},2} = 0.014 \text{ month}^{-1}$. The offset $B = B_1 + B_2$ is zero and the amplitudes are $A_1 = 0.6$ and $A_2 = 0.4$. The superposition of two different depletion rates is obvious for the immersion in water. Here the first antioxidant depletion time is so short (< 100 days) that the long-term behavior is essentially described by the second component alone. In Figs. 7–11 the

curves are plotted which were obtained by fitting the long-term antioxidant depletion data with Eq. (5). Reasonably accurate fits are obtained with antioxidant depletion times in the range 1000–2000 days. As expected the constant B is either zero or negative with a value of minus a few minutes.

Two mechanisms might contribute to the depletion. The first one is migration of stabilizer from the bulk HDPE material, which is a combined process of stabilizer diffusion to the surface driven by a concentration gradient followed by evaporation or leaching and accompanied possibly by chemical degradation of the stabilizer (i.e. hydrolyses of phosphites). The second one is the consumption of stabilizer by inhibiting the oxidative reaction chain. We may therefore write:

$$k_{\text{eff}} = k_{\text{migration}} + k_{\text{consumption}} \quad (6)$$

If the stabilizer depletion is dominated by antioxidant consumption, it should be controlled by the oxygen supply and therefore strongly depend on the aging conditions, i.e. nearly stationary air or forced air circulation or immersion in water. Even if the oxygen supply is high enough that equilibrium is established, antioxidant consumption for aging in air could not be slower than for immersion in water, as we expect the equilibrium concentration of oxygen in the GM to be at least similar for both aging conditions. Therefore the consumption should proceed more rapidly in air than in water. On the contrary, both the short- and the long-term depletion rates are higher for immersion in water than aging in air. Furthermore, there is no difference in the change in OIT value between aging in nearly stationary air and aging in forced air circulation. All these findings support the view that the stabilizer depletion observed in our experiments, where oxygen partial pressure is not higher than in normal air and fresh air supply is to some extent limited, is essentially determined by migration processes and not by consumption.

On the other hand, the oxidative induction time of the high-temperature oxidation process in a pure oxygen atmosphere, i.e. in the DSC-apparatus, should be due to consumption of antioxidants in the oxidative reaction chain, because of a high rate of free radical initiation and a large oxygen supply. This assumption is confirmed by the much shorter OIT values obtained in DSC measurements with Cu pans than with Al pans: transition metals like copper enhance radical production by catalytic effects and therefore the antioxidant consumption rate [13]. However, the activation energy of the antioxidant migration process is lower (see later) than the activation energy of the high temperature oxidation process (see Section 4.3). By decreasing the temperature, the rate of oxidative consumption will decrease much faster than the depletion rate due to migration processes.

Therefore at low temperatures and at low oxygen supply one should indeed fulfill the condition:

$$k_{\text{consumption}} < k_{\text{migration}} \quad (7)$$

and therefore

$$k_{\text{eff}} \approx k_{\text{migration}}$$

From pipe pressure tests it is well known that antioxidant migration should proceed faster for immersion in water than in air, as is observed in our experiments. Smith et al. attributed this to the influence of the carbon black [9]. Antioxidants are adsorbed at the carbon black surface. The migration process is thereby retarded considerably. During immersion in water some moisture is also present in the HDPE bulk material and this is preferentially adsorbed at the carbon black aggregates. The adsorption of water thereby supersedes that of the antioxidants and therefore decreases the retardation coefficient and increases the apparent diffusion coefficient of the latter. In addition it was suggested that the antioxidant form loosely bonded clusters within dry PE bulk material which may disperse slowly in contact with diffusing water, thus enhancing the antioxidant diffusion coefficient [14].

Since the phosphite stabilizer substantially determines the amount of the initial OIT of a HDPE GM product and since this stabilizer forms the largest part of the antioxidant package, we assume that depletion especially of the phosphite component is seen in the first short-term depletion process. All of this stabilizer seems to get lost in the first year of immersion in hot water. Within this context it is plausible to assume that not only leaching but also hydrolytic deterioration of the phosphite stabilizer, possibly even within the bulk material, is seen in the steep decrease of the OIT value during immersions in hot water. The long-term antioxidant depletion time would then be determined by the migration of the remaining phenolic stabilizer. Therefore, a high initial OIT does not necessarily correlate with good long-term oxidation stability.

Since GMs are part of liner systems we should assume as a worst case that most of the time they are under conditions with high moisture or even under a permanent water head. Therefore, we consider the failure time for immersion in hot water or the corresponding long-term antioxidant depletion rate as a starting point to extrapolate a lower limit of the relevant service lifetime for most geotechnical applications at normal temperature. For all our samples except the purely stabilized material 1 and 48, oxidative degradation starts only after 5 years of immersion in water at 80 °C and much later for aging in air at that temperature. We can take this time interval of 5 years as a lower boundary of the antioxidant depletion time t_2 at $T=80$ °C or alternatively we can take the corresponding long-term antioxidant

depletion rates 0.015–0.03 month⁻¹ at 80 °C as lower boundary for an estimate of the depletion rate at ambient conditions.

Knowing the failure time at 80 °C, we need the activation energy of the depletion process to perform the lifetime estimate. For the poorest stabilized HDPE resin of our study, sample 48, Koch et. al. extrapolated an activation energy of 100 kJ/mol from extensive pipe burst pressure test data generated at 60, 80 and 95 °C and at low pressures (Fig. 13) [3]. G. Hsuang presented oven aging data for antioxidant depletion of a commercially available HDPE GM, extrapolating 200 years and activation energies of about 60 kJ/mol [2]. From high temperature OIT measurements they obtained an antioxidant depletion rate at 85 °C of about 0.14 month⁻¹ for aging conditions which were a mixture of air below the geomembrane and immersion in water above the geomembrane and which lasted for about 2 years. This depletion rate agrees nicely with the depletion rates, that we observed for the short-term depletion process within the first two years. However, our data clearly show that the long-term oxidation stability is determined by a long-term depletion process with a rate which is about half an order of magnitude lower: 0.015–0.03 month⁻¹. Therefore we expect that also service lifetimes and activation energies are much higher than estimated by Hsuan and Koerner from 2 years of testing [2]. The activation energy of the diffusion process of organic molecules with high molecular weight in HDPE bulk material is typically in the range of 100 kJ/mol, for example, the activation energy of Irganox 1010, a phenolic stabilizer typically used for geosynthetics, was determined to be 115 kJ/mol in LDPE [15], 100 kJ/mol in PP homopolymer and 113 kJ/mol in a PP–PE copolymer [16]. Smith et al. found an activation energy of the overall migration process of a combined phosphite and phenolic antioxidant package of 80 kJ/mol for aging in air and 100 kJ/mol for immersion in water [9].

With Eq. (3) the van't Hoff rule for the temperature dependence of the antioxidant depletion time $t_2(T)$ can be written as:

$$t_2(T) = t_2(T') \cdot e^{\frac{E}{R} \left[\frac{1}{T'} - \frac{1}{T} \right]} \quad (8)$$

Taking $t_2(T')=5$ years at $T'=80$ °C and a very low value of the activation energy of 60 kJ/mol (or $E/R=7200$ K), we expect the lower limit of the service time with respect to oxidative degradation under ambient conditions ($T=20$ °C) to be at least 300 years. However, we obtain more than 1000 years with 100 kJ/mol (or $E/R=12,000$ K). The time until the functional engineering properties of a HDPE GM are significantly affected by oxidation is therefore so long that oxidative degradation is not relevant for design consideration even of landfill liner systems. The durability of HDPE GM could in this respect be classified as permanent.

Test procedures and specifications have been established to assess the oxidation stability of HDPE GMs. Obviously, high initial OIT-values need not correlate with long-term oxidation stability. It was therefore suggested to combine OIT measurements with oven aging procedures which accelerates stabilizer migration. The GR-13 Standard requires an initial OIT value at $T_m = 200$ °C of 100 min or a high pressure OIT value of 400 min at $T_m = 150$ °C and $p_{O_2} = 38$ bar. The reduction in OIT value must be less than 45% following 90 days oven aging at 85 °C. BAM certification requirements [5] for GM specify initial OIT values at $T_m = 200$ °C of > 20 min and > 10 min after 0.5 years of air-oven aging at 80 °C. Continuing the aging for 1 year, the relative change in OIT value between 0.5 years and 1 year must be less than 30%. In the light of our data, a combination of requirements for the initial value and the change during aging seems a reasonable approach even if the testing conditions for accelerating antioxidant depletion are still quite weak.

Oven aging not too close to the melting temperature requires long testing time to monitor change in the materials properties. It was therefore suggested to test with high oxygen pressure [17–19]. However, the extrapolation of our high temperature OIT values, see Section 4.3, agrees with findings [18] that the change from air to flowing pure oxygen atmosphere at ambient pressure by itself causes a dramatic decrease in failure time. Therefore, the results of high pressure tests have to be interpreted with caution. Increasing oxygen partial pressure and supply one can easily get from the antioxidant migration into the antioxidant consumption regime. Oven aging at high oxygen pressure obviously measures essentially antioxidant consumption rate (under the specific test conditions) and completely neglects antioxidant depletion effects, since testing periods are usually only a few weeks:

$$k_{\text{consumption}} \gg k_{\text{migration}} \quad (9)$$

and therefore

$$k_{\text{eff}} \approx k_{\text{consumption}}$$

However, the consumption regime is not relevant for typical geotechnical field conditions where the migration regime always prevails. Although the change in OIT value clearly monitors antioxidant depletion, it is not meaningful to use absolute OIT values themselves, even when measured at elevated oxygen pressure below the melting point, to extrapolate service life times or to assess the oxidation stability of HDPE GMs.

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