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Manuscript title: Antioxidant-stabilizer depletion of 4 HDPE geomembranes with high HP-OIT in MSW leachate

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Abstract

The antioxidant-stabilizer depletion of four 1.5-mm HDPE geomembranes from the same manufacturer each with a different resin and additive package is examined in air and a synthetic municipal solid waste leachate at a range of temperatures (40-95°C) for 7.5 years. Two were formulated for high-temperatures and used polyethylene of raised temperature resistance (PE-RT) resins while two used more conventional HDPE geomembrane formulations. The depletion of protective antioxidants and stabilizers was monitored using standard and high-pressure oxidative induction time (OIT) tests and the notably different depletion times for both OIT tests implied they were detecting different groups of AO-S. Although both PE-RT GMBs showed significantly slower AO-S depletion at 85°C in air compared to the conventional PE GMBs, only one PE-RT GMB maintained this status in 85°C leachate, highlighting the limitation of air aging tests (and importance of fluid immersion tests). The importance of running immersion tests long enough to reveal the residual HP-OIT value is stressed. The roles of stabilizer mobility and solubility in polyethylene and their suspected involvement in residual HP-OIT behavior is also illustrated.

Keywords: Geosynthetics, High temperature HDPE geomembranes, PE-RT, antioxidant depletion, HP-OIT, long-term performance, accelerated aging, UN SDG 6: clean water and sanitation, UN SDG 12: responsible consumption and production

Introduction

A geomembrane (GMB) is said to have reached the end of its service life when it no longer provides adequate hydraulic and diffusive resistance; usually, when it develops excessive holes and/or cracks (Rowe 2005, 2011, 2012, 2018, 2020, Abdelaal et al. 2014, Ewais et al. 2014a; Jafari et al. 2014; Rowe and Yu 2019; Rowe et al. 2019). For a GMB that initially has no holes after installation (from good construction QA/QC), the service life will depend on the GMBs ‘resistance’ to ageing (resin and additives), thickness, operating temperature, along with the chemistry of the contained fluid, and magnitude of the in-service induced tensile strains (i.e., the ‘demand’; Rowe, 2020). Conceptually, a GMBs resistance to ageing (in the absence of tensile stress/strain) is commonly described by a 3-stage model: Stage I – the period when antioxidants and stabilizers (AO-S), which are added to protect the polymer, deplete to a residual value leaving it vulnerable to oxidation; Stage II – a lag period between the time when the AO-S have depleted and the time when a notable change in mechanical properties is first detected, and finally; Stage III – the period wherein the mechanical properties continue to degrade until some defined point. The length of Stage I (AO-S depletion) is very important in assessing how long a GMB can perform its intended design function because it controls the length of time that the polymer is protected from oxidative degradation. AO-S typically deplete by two sequential processes: (1) diffusion and/or exudation through the bulk polymer to the GMB surface followed by; (2) depletion on or in close proximity to the surface by either: (a) oxidant consumption (their intended function) or de-activation/neutralization; (b) volatilization, or; (c) extraction via dissolution or hydrolysis in liquid (Scheirs et al. in Rowe and Jeferris, 2022). As Scheirs (2009) noted, physical loss via extraction in fluids is especially critical since loss by oxidative consumption is comparatively much slower . Thus, for the many GMBs in contact with liquid for most of their service life, AO-S extraction is usually the dominant loss mechanism and since these mobile AO-S are the ‘first line’ of defense against ageing (Montes et al. 2012), the time required for them to deplete to a critical level is of major interest.

Muller et al. (2016) classified AO-S into two groups: sacrificial (e.g., phenol and phosphite) and regenerative (e.g., certain oligomeric hindered amine stabilizers, abv. ‘HAS’) noting that geosynthetic AO-S packages generally fall into one of three categories: (P1) predominately sacrificial; (P2) predominately regenerative; or (P3) comparable amounts of both. Hindered phenol and phosphites are irreversibly consumed during auto-oxidation and hence are ‘sacrificial’ in that they ward off polymer oxidation while many HAS types are only activated during oxidative chain scission and function to retard (slow down) polymer degradation and their nitroxyl active species regenerate to some extent until they are exhausted (Zweifel et al., 2009). High molecular weight (HMW) HAS are examples of this class of ‘regenerative’ stabilizer (Muller et al. 2016).

Muller et al. (2016) reported that oven aged geosynthetics comprising a predominately sacrificial, P1, package experienced no change in mechanical properties until the AO depleted, after which point a relatively sudden ‘catastrophic’ loss in properties was observed. Predominately regenerative, P2, packages exhibited loss in mechanical properties right from the beginning however it proceeded gradually (not suddenly). P3 AO-S packages with comparable amounts of both P1 and P2 experienced an initial AO depletion period with no degradation followed by degradation which proceeded gradually.

Although a wide variety of AO-S additives exist, the details of a GMB’s additive package is almost always proprietary to the manufacturer. However, aging studies (e.g., Hsuan and Koerner, 1998; Hsuan et al. 2008; Abdelaal et al. 2019; Abdelaal and Rowe, 2019; Morsy and Rowe 2020) examining both AO-S depletion and the degradation of physical properties show that most HDPE GMBs use a P1 or P3 package (i.e., either predominately phenolic/phosphite with little to no HAS, or with comparable amounts of phenolic/phosphite and HAS).

Predicting the length of Stage I (AO-S depletion) requires accelerated aging in the laboratory. For new GMBs, this usually involves aging coupons of the GMB sheet in forced air ovens (e.g., to demonstrate the GMB meets the 90-day aging requirements of GRI-GM13) or, in more sophisticated studies, immersing the coupons in a fluid simulating the end-use exposure (e.g., leachate). AO-S depletion is assessed using two standard laboratory tests: (a) the standard oxidative induction time test (Std-OIT; ASTM 2007), and/or (b) the high-pressure oxidative induction time test (HP-OIT; ASTM 2006). Since both tests detect different groups of AO-S, typically both tests are needed in order to characterize a GMB’s additive package and its depletion over time.

Accelerated aging has become particularly important given the trend of ever-increasing AO-S concentration in GMBs that can result in extremely high initial OIT values. High initial OIT values do not necessarily imply better performance than a lower initial OIT value because once the additives become supersaturated as the polymer cools from production temperature (to room temperature) the excess additives can readily bloom to the surface where they can (i) be easily and quickly leached if immersed in liquids, or (ii) cause issues with welding during field installation (Scheirs et al. in Rowe and Jeferris, 2022).

Increasingly, GMBs are being used in applications such as bio heap leaching, solar brine ponds, hot industrial effluents, and elevated temperature landfills (Jafari et al. 2014; Benson, 2017). Many of these applications exceed 60°C and, in some cases, temperatures exceeding 80°C have been reported (Scheirs, 2009; Leblanc et al. 2011). At these high temperatures, PE GMBs may experience: (1) accelerated creep and/or material softening (reducing its strength), and; (2) rapid depletion of the protective AO-S (via leaching) leaving the GMB vulnerable to thermo-oxidative degradation. Manufacturers are seeking to formulate GMBs tailored to address those two high temperature issues.

One approach being adopted is to combine a PolyEthylene of Raised Temperature resistance (PE-RT) resin with a masterbatch containing a blend of additional additives specifically selected for retention at high temperatures (i.e., low leaching). Two such GMBs will be examined in this paper. Such AO-S tailoring by GMB manufacturers for a targeted application is not uncommon. For example, methylated (N-methyl) HAS (e.g., Chimassorb 119) exhibits excellent resistance to acid and are the preferred HAS for HDPE GMBs used in aggressive acidic environments such as acidic heap leach pads and tailings dams (Scheirs et al. in Rowe and Jefferis, 2022).

While a variety of PE-RT studies exist in the plastic pipe literature, GMBs are produced differently and often use different AO-S to those in pipes and there is a paucity of data on PE-RT GMBs. For instance, numerous plastic pipe studies (e.g., Damen et al. 2001; Montes et al. 2012; Redhead et al. 2012; Mikdam et al. 2017) have examined PE and/or PE-RT resins either un-stabilized or stabilized with phenolic and phosphite antioxidants but no hindered amine (light) stabilizers (HALS or HAS). Mills and Beaumier (2017) examined the AO-S retention of two PE-RT GMBs and a conventional HDPE GMB in forced air ovens at 70, 90 and 110°C for 1 year, reporting that both PE-RT GMBs had slower depleting AO (judged by Std-OIT). However, they didn’t consider fluid immersion. In follow-up studies, Rangel et al. (2017) and Mills et al. (2019) tested those same GMBs in chlorinated water and brine, respectively, and both studies reported that one of the PE-RT GMBs had much slower AO-S depletion (compared to the control HDPE) while the other PE-RT GMB was only marginally slower than the control. However, they didn’t run the experiments long enough to see any major changes in HP-OIT relying instead on Std-OIT to assess the AO-S performance (despite the possibility HAS were involved). Furthermore, it was difficult to tell what effect the factors of aging medium (e.g., air or liquid), time, temperature, or the PE-RT resins themselves had on the AO-S depletion rate.

Given the foregoing discussion, the overarching objective of this paper is to provide new insight regarding the relative performance of two conventional HDPE and top PE-RT GMBs using a P3 type AO-S package containing HAS. More specifically, the objectives of this paper are to: (a) report on the AO-S depletion of different ‘high temperature’ GMBs compared to conventional HDPE GMBs; (b) examine whether the PE-RT resins played a beneficial role in AO-S depletion or if depletion was more a function of the AO-S package; (c) discuss the relative ranking of the AO-S depletion rate of four GMBs aged at 85°C in air (e.g., as per GRI-GM13) compared with that when immersed in leachate and; (d) examine whether the AO-S depletion ranking of the four GMBs at 85°C was maintained at a lower temperature (e.g., 40°C) and hence demonstrate the extent the role played by different components of the AO-S package can be a function of temperature.

Materials and Methods

Geomembranes Examined

Four smooth black 1.5-mm HDPE GMBs from the same manufacturer were examined (Table 1). Each GMB had a different resin and additive package (e.g., antioxidants, stabilizers, and carbon black); two different conventional medium-density PE resins (GMB1 and 2) and two different medium-density PE-RT resins (GMB3 and 4). All resins fell within the MDPE range but the addition of 2-3% carbon black increased their density into the high-density polyethylene (HDPE) GMB classification (> 0.941 g/cm^3 ASTM 2012). GMB1 and GMB2 were manufactured using the blown film process while GMB3 and GMB4 were made with the flat die process.

Although GMB1 and GMB2 used different resins, their physio-mechanical properties were relatively similar (Table 1) in contrast to their additive packages, which were notably different (see Std-OIT, HP-OIT, and carbon black content in Table 1). In contrast, GMB3 and GMB4 had distinctly different physio-mechanical properties as well as dissimilar stabilizer packages. In addition to GMB2 having a higher carbon black content (2.7%), it also used a finer particle size compared to the others. The exact composition of each GMB (AO-S, types and amounts added) is proprietary to the GMB manufacturer and cannot be reported herein. It is noted that a US Patent for a high temperature geomembrane (Prachoomdang et al.2016) indicates the presence of HALS.

Exposure Conditions

Samples from each GMB were cut into 190×100 mm coupons and placed in 4 L glass jars filled with synthetic MSW leachate. The jars were then placed in forced air ovens at 95, 85, 75, 65, and 40°C. The coupons were separated by 5-mm glass rods in the jars to ensure leachate contact from both sides. Although Scheirs (2009) recommended that the maximum temperature for ageing GMBs should be approximately 50°C below the melting point, T_m, or about 75-85°C (HDPE T_m ~126-130°C), 95°C was included to represent an extreme case sometimes encountered in practice. The synthetic leachate examined in this study was a simplified version of the full version examined by Abdelaal and Rowe (2015) which simulated leachate from the Keele Valley landfill in Ontario, Canada. It was a mixture of RO water, organic/inorganic salts, trace metals, surfactant and was reduced (target Eh =-120 mV) to minimize available dissolved oxygen thereby simulating anaerobic leachate found in MSW landfills (Rowe et al., 2008). The concentration of surfactant (5 ml/L IGEPAL® CA630) provided a conservative (i.e., aggressive) simulation of the levels typically found from disposal of detergents in the waste stream (Borghi et al. 2003; Rowe et al., 2008); Complete details of this leachate can be found in Rowe et al. (2010a). The leachate was replaced at regular intervals based on the findings of Rowe et al. (2008) who examined the effect of leachate renewal durations on OIT depletion. GMB samples were also aged in force air ovens at 85°C in accordance with GRI-GM13 (2021) and ASTM (D5721) to examine the effect of exposure medium (i.e., leachate vs air) on AO-S depletion.

OIT testing

OIT is a relative measure of a GMB specimen's resistance to thermo-oxidative decomposition at a specified temperature and oxygen atmosphere and is measured as the time after introduction of oxygen to onset of an exothermic oxidation (as per ASTM 2006; 2007a). Differential scanning calorimetry (DSC) was used to monitor the depletion of AO-stabilizers in the GMBs by tracking the changes in Std-OIT and HP-OIT periodically during the 7.5-year incubation period. Std-OIT (200°C, 35 kPa oxygen; ASTM 2007) was used to detect the presence of hindered phenols and phosphites while HP-OIT (150°C, 3500 kPa oxygen; ASTM 2006) was used to detect the presence of hindered phenols along with any HAS and/or thiosynergists that may be present. Hindered phenols (primary AOs: effective temperature range; 0-300°C) are detected by both OIT tests while HAS and thiosynergists are only effective up to about 150°C and hence the lower temperature of HP-OIT is needed to detect them (Scheirs 2009).

HP-OIT thermogram interpretation

Although each GMB had a different HP-OIT thermogram signature, they all exhibited an initial first peak (or shoulder) followed by a second (final) peak representing full exhaustion of the AO-S and complete oxidation of the polymer (e.g., GMB4; Figure 1a). This behavior can be attributed to the ability of HP-OIT to 'distinguish' different groups of AO-S present in the GMB (Scheirs, 2009). ASTM 2006 is flexible in the OIT interpretation of HP DSC thermograms, leaving the decision to individual judgement (provided that it is made clear in the report how the tangent lines were drawn; e.g., Figure 1a). For the GMBs examined, the differences between the first and second slope interpretation of HP-OIT was not trivial. For instance, unaged GMB4 had HP-OIT$_1$ ~ 600 min and HP-OIT$_2$ ~ 1400 min, with a more than two-fold difference in the interpretation of HP-OIT.
Both interpretations of the depletion of HP-OIT for GMB4 immersed in leachate at 85°C for 26 months (Figure 1b) indicate very similar depletion for both methods with both methods reaching a residual value around 12-14 months with the main difference being that the second peak method had notably higher initial and residual values (Figure 1b). The 2nd peak high residual value is likely due to HMW HAS since these molecules are known to be relatively immobile and resistant to extraction, even in hot fluids (Scheirs, 2009) and are thought to be primarily responsible for high residual HP-OIT values (Ewais et al. 2014b). Past GMB studies have shown that high residual HP-OIT values resulting from immobile HMW HAS do not prevent the onset of mechanical degradation (e.g., Ewais et al. 2014b), however, provided they are not de-activated before Stage III, some HMW HAS may function to slow down (but not stop) the rate of mechanical degradation (Muller et al. 2016). This conclusion was reached based on the observation that nitroxyl radicals and hydroxylamine ethers, considered to be the most important stabilizing species of HAS, are only formed during polymer chain cleavage (Muller et al. 2016). There is also some evidence that immobile HMW HAS may act as

physical filler barriers when strong oxidizers are present (e.g., chlorinated water) and slow down the ingress of oxidants into the polymer structure (Morsy et al., 2021). The role played by HP-OIT is discussed in more detail later in the paper). On the other hand, the ‘sacrificial’ free-radical scavengers (phenolic AOs) function mainly in Stage I as a first line of defense by hindering the formation of hydroperoxides and preventing the onset of oxidative degradation, so long as there is still some AO remaining.

Based on the forgoing, the likely explanation for the unaged HP-OIT thermogram of GMB4 (Figure 1a), was the first HP-OIT_1 ~ 600 min mainly represented the depletion of ‘sacrificial’ primary AOs (e.g., hindered phenols) until they were fully consumed. Next, in their absence, the polymer started oxidizing (as inferred by exotherm #1: ~ 600 min) and the bi-products of this chain cleavage activated another additive group (likely HMW HAS) which then decelerated auto-oxidation for a period of time until they were exhausted at HP-OIT_2 ~ 1400 min. The question as to whether the mobile AO-S contributing to HP-OIT were also detected by Std-OIT will be addressed in the following sections. Lastly, since the final HP-OIT peak represents all the AO-S detected by this test, the HP-OIT values reported in the remainder of this study for all GMBs are based on the final exothermic peak (e.g., GMB4 =1400 min).

Results and Discussion

Antioxidants depletion

Initial impressions at 85°C

Since the GMBs all have different initial values, for the purposes of comparison, the results are presented (e.g. Figure 2) in terms of the normalized OIT (i.e., the OIT value at any time, t, relative to the initial value; OIT/OIT_o). Samples were air aged at 85°C as per ASTM (2018). Commonly used de facto industry standard, GRI-GM13 (2021), requires that a new GMB should, *inter alia*, have either: (I) Std-$OIT_o \geq 100$ min with 55% retained after 90 days air aging at 85°C or; (II) HP-$OIT_o \geq 400$ min with 80% retained after 90 days air aging at 85°C. GMB3 and GMB4 passed both options (Figures 2a and b) and while GMB1 and GMB2 did not meet the Std-OIT option, they did meet the HP-OIT option and thus all four GMBs met the ageing requirements of GRI-GM13 (2021). However, these requirements raise the question as to whether the relative AO-S depletion of these GMBs aged in air (i.e., ranking of slowest to fastest depleting) provides any insights into the likely performance in leachate.

In air at 85°C, the Std-OIT of GMB1 and GMB2 had depleted to ~25% of the initial value (Std-OIT /Std-$OIT_o \simeq 0.25$) in the 90 days of testing required by GRI GM 13 (Figure 2a; air) whereas GMB3 and GMB4 only depleted to ~80% in that time and took nearly 10 months of air aging to reach Std-OIT/Std-$OIT_o \simeq 0.25$ (Figure 2a). On this basis alone, the AO-S packages of GMB3 and GMB4 appeared better at high temperatures (85°C) than those in GMB1 and GMB2. In contrast, in leachate at the same temperature (Figure 2a; leachate), only GMB4 depleted slowly while the depletion for GMBs 1, 2 and 3 were similar. Thus, the apparently good Std-OIT retention of GMB3 in air was lost in leachate. Possible explanations for the notably slower (better) depletion of AO-S in GMB4 in leachate compared to other GMBs include (i) it contained AOs with lower leachability such as Irganox 1330 (Scheirs, 2009), and/or, (ii), the resin had a lower diffusivity (more tortuous structure). This issue will be explored later.

In air at 85°C, the depletion of HP-OIT was much slower than Std-OIT which made it more difficult to establish clear trends between the four GMBs (Figure 2b; air). However, taking the average of available air-aged data for each GMB (i.e., at 3, 6 and 10 months) gave HP-OIT/HP-OIT$_o$ of 0.81, 0.85, 0.89 and 0.97 for GMBs 1, 2, 3 and 4, respectively, revealing a pattern not unlike the Std-OIT air results in that GMB3 and GMB4 were the best. The fact that GMB4 had the highest HP-OIT$_o$ (1410 min) and that this had hardly depleted at all after 10 months (HP-OIT/HP-OIT$_o$=0.97) suggests there was something quite different about this GMB’s formulation compared to the others.

In leachate at 85°C, the HP-OIT depleted far more significantly in 90 days than in air and a notably different ranking (i.e., impression) of the relative GMB performance compared to that for Std-OIT. At 85°C, the HP-OIT of GMB3 depleted the fastest to the lowest value of normalized HP-OIT at 90 days and reached the lowest normalized residual in about 5 months. GMB1 had the highest normalized HP-OIT at 90 days and appeared to have reached the highest normalized residual at about 7 months. Although GMB4 had the second-highest normalized HP-OIT at 90 days, it took by far the longest time to reach residual (~ 14 months compared to next best ~7 months; Figure 2b; i.e., it was the slowest depleting). Normalized HP-OIT at 90 days for GMB2 was only slightly lower than GMB4 but it reached residual much earlier at about 7 months. The HP-OIT depletion time (t_{HP}) was defined as the time at which HP-OIT reached residual and no longer decreased with time. The ranking of these GMBs in terms of t_{HP} (from longest to shortest) was GMB4 (~ 14 mo.), GMB1 and GMB2 (both ~ 7 mo.) and lastly GMB3 (~ 5 mo.; Figure 2b).

In addition to AO-S depletion being slower in air than in leachate, air aging was not able to identify the relevance of the AO-S package to its use in applications such as a landfill bottom liner exposed to leachate. For instance, the overall impression of GMB3 aged in air (considering both Std- and HP-OIT depletion) ranked it 2nd best however, in leachate at the same temperature, it appeared the worst in-terms of AO-S depletion, suggesting one or more of its additives was particularly prone to extraction in this leachate (e.g., via dissolution and/or hydrolysis). Thus, 90-day aging in air at 85°C provided little useful information for selecting a preferred GMB for use as a landfill bottom liner or for quality control. This example provides further evidence to support the recommendation by Rowe (2020) that 90 days of aging in liquid (ideally one simulating the likely exposure) would provide a much better indication of relative performance amongst different candidate GMBs and for quality control, being more sensitive to the components in the antioxidant package.

The remainder of this paper focuses on the AO-S depletion in leachate for a range of temperatures to explore the effect of temperature on the relative performance of different AO-S packages in the four geomembranes.

Std-OIT

The Std-OIT depletion results for the four GMBs immersed in leachate at five temperatures (e.g., Figure 3) were fitted using a two-parameter exponential decay function (Hsuan and Koerner, 1998; Rowe et al. 2008; Abdelaal et al. 2019), viz:

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

where: OIT_t (minutes) = OIT at time t; OIT_o (minutes) = initial OIT; and s (month^{-1}) = antioxidant depletion rate.

For all examined GMBs, the Std-OIT depleted to very low residual values (~3 min; or ~1.5% of Std-OIT$_o$) at all incubation temperatures except 40°C which was still depleting after 7.5 years. GMB1 consistently had the fastest Std-OIT depletion rates (Table 2) and shortest times to depletion (t_{Std}; Table 3) at all observed temperatures. Although GMB2 was similar to GMB1 at the two highest temperatures of 95 and 85°C, its depletion time started to become longer at 75°C and by 65°C it was 1.5-fold longer than GMB1 (Table 3). This divergence between the Std-OIT depletion times of GMB1 and GMB2 increased further with decreasing temperature and by 40°C the observed rate of GMB2 (0.006 month^{-1}) was half that of GMB1 (0.012 month^{-1}). GMB3 exhibited depletion rates that were between those of GMB1 and GMB2 but were closer to GMB2. GMB4 had much slower Std-OIT depletion than the other GMBs at the three highest temperatures examined (95, 85 and 75°C) but started to approach the other GMBs somewhere between 65°C and 40°C (Table 2). For instance, GMB4's depletion rates at 75, 65 and 40°C were 3.6, 2.3 and 1.5-fold, respectively, lower than those of GMB1. Thus, the initial impressions in 85°C leachate showing GMB4 had the best AO-S retention of the group diminished with decreasing temperature. In other words, the relative behavior or 'ranking' of the examined GMBs changed with temperature. Such change in relative depletion or 'ranking' of candidate GMBs with a change in temperature (when two GMBs may look quite similar or different at one temperature) is related to the activation energy of depletion (E_a; discussed in section 3.2) and highlights the importance of using multiple immersion temperatures when different GMBs are being evaluated.

HP-OIT

Unlike Std-OIT which depleted to very low residual values in leachate, the HP-OIT (Figure 4) depleted to much higher residual values that varied by GMB and, in some cases, with incubation temperature (e.g., GMB1 95°C). Thus, the depletion was fitted using a three-parameter exponential decay function:

$$OIT^{*}_{t} = OIT^{*}_{o} \times e^{-st} \qquad (2)$$

where, $OIT^{*}_{t} = (OIT_{t} - OIT_{r})$ is the amount of HP-OIT above the residual value at time, t; $OIT_{o}{}^{*} = (OIT_{o} - OIT_{r})$ is the total amount of HP-OIT that depleted; OIT_r (minute) is the residual HP-OIT; and s (month^{-1}) is the depletion rate. Residual HP-OIT (HP-OIT_r) was considered to be reached when the HP-OIT no longer decreased with time (Rowe et al. 2010a).

Previous studies that examined GMBs stabilized with HAS have reported high HP-OIT_r values in a variety of incubation fluids (e.g., high/low pH leachates, Abdelaal and Rowe, 2017; chlorinated water, Morsy et al. 2021). Ewais et al. (2014b) examined HDPE GMBs stabilized with and without HAS in MSW leachate and found that those with HAS had higher initial HP-OIT_o (> 400 min) but also notably higher residual HP-OIT_r compared to those without HAS.. Ewais et al. (2014b) attributed these high and persistent residual values to immobilizing effects such that some stabilizers continued to be detected by the HP-OIT test (in the melted state) even though they did not prevent the eventual onset of GMB degradation (in the solid state). These immobilizing effects (causing high HP-OIT_r) can be attributed to high molecular weight (HMW) HAS since these stabilizers have an intentionally bulky design for enhanced resistance to extraction (Muller et al. 2016). However, it could also be attributed to: (a) adsorption of AO-S into the carbon black rendering them ineffective (Pena et al. 2001), and/or; (b) microprecipitation (entrapment) of insoluble stabilizer located in the GMB core while the insoluble stabilizer near the surface blooms (Christmann et al. 2021). Although past studies have shown that these high HP-OIT_r values do not prevent the onset of mechanical degradation (e.g., Morsy et al. 2021; Abdelaal et al. 2019; Ewais et al. 2014b), these findings do not exclude the possibility that HP-OIT_r may play a role in Stage II and/or Stage III.

The HP-OIT reached a notable (i.e., much higher than for Std-OIT) residual value for all GMBs at all incubation temperatures examined except at 40°C where it was still depleting after 90-months (Figure 4). Where residual HP-OIT was reached (i.e., $T \geq 65°C$), the time to HP-OIT depletion (t_{HP}) was between 1.7 to 4-fold longer than that of Std-OIT (Table 3) indicating that both tests were detecting different groups of antioxidant-stabilizers for the examined GMBs such that the tests could not be used interchangeably. This information combined with the high initial and high residual HP-OIT values suggests that HAS and/or thiosynergists (effective $T \leq 150°C$) were present in the GMBs examined (Ewais et al. 2014b; Thomas and Ancelet, 1993). Even if HAS are not added by the GMB manufacturer, some GMB grade PE resins (e.g., Marlex K306 and K307) already come formulated with HAS; for instance Marlex K307 resin has an HP-OIT > 800 min (Scheirs, 2009) and many of the de-formulated HDPE GMBs reported by Scheirs (2009) had total HAS loading (measured in ppm) that was comparable to that of the hindered phenols.

In addition to the observed t_{HP} being longer t_{Std}, the relative ranking amongst the four GMBs in terms of t_{HP} was slightly different than that of t_{Std} (Table 3). For instance, although both OIT tests generally ranked GMB4 better than GMB1 and 2, they differed in their assessment of GMB3; In terms of Std-OIT GMB3 was similar to GMB1 and 2 however in terms of HP-OIT GMB3 had the fastest depletion at all observed temperatures (i.e., highest depletion rates and shortest t_{HP}; Tables 2 and 3). Furthermore, although GMB4 had the slowest depletion of both Std-OIT and HP-OIT at the three highest incubation temperatures (75, 85 and 95°C), it approached GMBs 1 and 2 at 65°C (for HP-OIT) and 40°C (for Std-OIT; Table 2). Thus, the AO-S depletion ‘ranking’ of these GMBs in leachate depended on: (a) the metric used (Std- or HP-OIT) and; (b) the immersion temperature.

At 95°C, some of the observed depletion rates and times to depletion for both OIT tests were suspicious since some were nearly equal to (or appeared slower) than at 85°C (Tables 2 and 3). This implies a change in behavior occurred at 95°C for some of these GMBs. Several past GMB studies have reported issues at GMB temperatures greater than 85°C. For instance, Rowe and Ewais (2014) examined the OIT depletion of different HDPE GMBs incubated in leachate at temperatures ranging from 25-95°C and found that the OIT depletion rates at 95°C departed from an otherwise linear time-temperature (Arrhenius relationship) at $T \leq 85$°C. They examined the change in polymer morphology using DSC melt scans and found a significantly greater difference in lamella structure at 95°C (compared to that for $T \leq 85$°C) in as little as 0.5 months (and prior to AO-S depletion) and they attributed the OIT departure at 95°C to an increase in lamella thickness associated with annealing. Abdelaal et al. (2015) examined the effect of elevated temperatures (85-115°C) on HDPE GMBs aged in air and reported a change in morphological structure at 95°C in as little as 0.9 months of incubation that was not seen at 85°C even after 28 months of testing.

To examine if this had occurred in this study, DSC melt scans (i.e., crystallinity tests; ASTM 2018b) were performed on GMB4 samples aged in leachate for 1.2 months at 75, 85 and 95°C. Specimens were held at 0°C for 5 min and then ramped from 0 to 200°C at a rate of 10oC/min and the resulting scans recorded. There was negligible change in the thermogram from unaged to 75°C however there was a change at 85°C and substantially more change at 95°C (Figure 5). In addition to a statistically significant (at the 95% confidence level) increase in crystallinity from 54% for the unaged, 75 and 85°C specimens to 57% at 95°C, there was also an increase in lamella thickness, a decrease in melting in the 85-95°C scan range and an increase in melting in the 95 to 118°C range suggesting a change in the crystal structure due to annealing. The change is considered responsible for the departure of the

OIT depletion rates at 95°C from the otherwise linear time-temperature (Arrhenius relationship) in Figure 6 at $T \leq 85°C$.

Antioxidant depletion predictions

Arrhenius modelling was used to predict the depletion rates of Std-OIT and HP-OIT at different temperatures using the experimentally derived rates, viz:

$$s = A \times e^{-\left[E_a/(RT)\right]} \qquad (3)$$

where, s = antioxidant depletion rate (month^{-1}); A (month^{-1}) is a constant; E_a (J・mol^{-1}) = activation energy for depletion; R = 8.314 (J・mol^{-1}) = universal gas constant; and T (K) = absolute temperature.

Arrhenius plots of the observed Std-OIT rates (Figure 6a) were used to predict the rates and hence the time to depletion (t_{Std}) at a range of temperatures (Table 4). Since the observed rates at 95°C (open symbols; Figure 6a) generally did not fit well with the observed rates ≤ 85°C (closed symbols), likely due to annealing as previously discussed, they were excluded from the regression analyses that considered the rates at the other four observed temperatures (40, 65, 75 and 85°C)..

GMB1 had the shortest predicted t_{Std} at all predicted temperatures (5 to 85°C; Table 4); GMB2 and GMB3 had similar predictions at the full range of temperatures and were nearly twice those of GMB1 at $T \leq 40°C$ with GMB2 having the longest predicted depletion times for $T < 40°C$. Lastly, GMB4 had the longest t_{Std} predictions at the higher temperatures ($T \geq 40°C$) that were about two-fold longer than the other GMBs at 85, 75, 65°C) but by 40°C approached GMB2 and GMB3 (Table 4; Std-OIT).

Similar to Std-OIT, Arrhenius plots of the observed HP-OIT depletion rates were used to predict the rates at different temperatures (Figure 6b). The resulting HP-OIT depletion activation energies, Ea (kJ/mol) calculated from the Arrhenius plot slope were similar for GMBs 1, 2 and 3 but notably lower for GMB4 (Figure 6b) suggesting that some component of GMB4 was quite different to the other GMBs.

Unlike Std-OIT (which depleted to very low residual values), prediction of the HP-OIT depletion time (t_{HP}) is more complex in that it requires knowledge of both the depletion rate and the likely residual value (HP-OIT$_r$) to substitute into Eq. (2). Although the observed HP-OIT depletion rates, s for each GMB varied predictably with temperature (fitting a linear Arrhenius model; Figure 6b), this was not case for the observed HP-OIT$_r$ which, in most cases, appeared independent of temperature (Figure 4) while in other cases was less clear (Figure 4a). Based on 1-way ANOVA testing of the available residual data for each GMB (at the 95% confidence level; Table 5), the difference between 95°C and the other temperatures was significant for GMB1 and GMB2. For GMB3, the difference between 95 and 85°C was not statistically significant and likewise difference between 75 and 65°C was not significant, however the difference between the pairs 95 /85° and 75/65°C was significant.

For GMB4, there was no significant difference (at the 95% confidence level) in the HP-OIT$_r$ at all temperatures where residual was reached (i.e., 65, 75, 85, 95°C). Since 95°C was the dominant outlier from an otherwise relatively temperature-independent behavior, it was excluded and the HP-OIT$_r$ used for predictions was taken as the average of residual data 65, 75, and 85°C for each GMB. Although a similar case of temperature independent HP-OIT$_r$ behavior for a HAS stabilized GMB exists (Abdelaal et al. 2019), most other studies have reported a trend of increasing HP-OIT$_r$ with decreasing temperature. This issue will be discussed in the next section. The predicted t_{HP} at various temperatures of interest based on the Arrhenius relationship (Figure 6b) and HP-OIT$_r$ (Table 5) are given in Table 4.

The time to depletion of the mobile AO-S detected by the HP-OIT test, t_{HP}, was greater than the time to depletion of the AO-S detected by the Std-OIT test, t_{Std}, at high temperatures and vice versa at low temperatures (Table 4). Thus, there was a crossover temperature where the predicted t_{Std} became greater than t_{HP} for each GMB. This crossover occurred at ~ 35-40°C for GMB1, ~ 45-50°C for GMB2; ~ 55-60°C for GMB3; and ~ 50°C for GMB4 (Table 4). Past studies have also reported similar transitions in the OIT predictions of HDPE GMBs (e.g., Abdelaal et al., 2019; Rowe and Ewais, 2014). This behavior could be related to the higher activation energy (E_a) of Std-OIT depletion relative to HP-OIT (Figure 6) which makes it harder for the AO-S detected by Std-OIT to deplete at lower incubation temperatures where there is less thermal energy available (higher E_a reactions need more heat). One hypothesis is that it is related to the phosphite stabilizers which, owing to their high effective temperature range (150–300°C; Scheirs 2009), have reduced activity at end-use temperatures despite their high activity in the Std-OIT test at 200°C. Although the function of phosphite stabilizers is generally limited to the temperatures of GMB melt processing (Scheirs, 2009; Schwetlick et al. 1991), they can remain in the GMB in significant levels post-manufacturing. For instance, Abdelaal and Rowe (2015) reported two HDPE GMBs that only consumed ~ 40% of their phosphite stabilizer (Irgafos 168) during manufacture, 60% remained prior to testing. Thus, one hypothesis is that at lower temperatures where loss by extraction is very slow (e.g., 30°C), these remaining phosphites are conserved more easily than other AO-S which are more active at lower temperatures (e.g., hindered phenols and HAS). A counter argument to this hypothesis is that phosphites, being susceptible to hydrolysis (Muller et al. 2016), readily decompose into phenol and hydrogen phosphite groups and thus are unlikely to remain inert at lower temperatures; however, this will depend on: (a) the type of phosphite stabilizer, and; (b) the temperature. While non-hindered aryl phosphites are susceptible to hydrolysis at ambient temperatures, hindered aryl phosphites (e.g., Irgafos 168) exhibit a much more temperature-mediated hydrolysis with it being slowed or even retarded at lower temperatures (Schwetlick and Habicher 1996; Schwetlick et al. 1991). Scheirs (2009) attributed the rapid Std-OIT depletion of hot water immersed GMBs to hydrolysis of phosphite stabilizers. The fact that hydrolysis of hindered aryl phosphites (e.g., Irgafos 168) is highly temperature dependent could explain the shift in OIT predictions at lower temperatures and since these types of phosphites are commonly used in GMBs, the forgoing is something that requires more attention by GMB researchers.

At the higher temperatures examined (e.g., 85°C)—where physical loss by extraction dominates over consumption (Scheirs, 2009)—the faster Std-OIT depletion relative to HP-OIT could be explained by: (a) the aforementioned affinity of hindered aryl phosphites to undergo hydrolysis preferentially at higher temperatures (whose depletion would be detected by Std-OIT) and/or; (b) possible presence of mobile but slow moving HAS which would be detected preferentially by HP-OIT and/or; (c) possible volatility of some antioxidants in the OIT tests which would occur preferentially for Std-OIT because of the higher test temperature (Scheirs, 2009; Pospisil et al., 2003).

The predictions in Table 4 are for the GMBs immersed in simulated MSW leachate. Experience has shown that they are likely to be longer for less aggressive solutions with less surfactant. Also, several studies have demonstrated the time to depletion in a composite liner can be substantially longer than immersed in leachate by a factor of 3.4 or greater (e.g., Rowe and Rimal, 2008; Rowe et al. 2010b)

Discussion of residual HP-OIT

Although the differences in observed residual HP-OIT$_r$ at most temperatures for each GMB were not statistically significant, similar to the case reported by Abdelaal et al. (2019), other GMBs have shown a trend of increasing HP-OIT$_r$ with decreasing temperature (e.g., Ewais and Rowe, 2014; Rowe and Ewais 2014; Abdelaal and Rowe, 2017). This casts some doubt in the assumption (necessary for predictions) that HP-OIT$_r$ in the present study did not change at ≤ 65°C. However, two inter-related properties: (1) polymer free-volume, and; (2) stabilizer solubility (both temperature dependent properties) may offer insights into why HP-OIT$_r$ appeared temperature-dependent in some GMB studies and not so in others.

Free volume (sometimes referred to as sorption centers) is defined as the volume of polymer not occupied by the polymer chains themselves (Valiya et al. 2020) and is related to the distribution of openings between the chains in the amorphous zone called free volume 'holes' (Zweifel et al., 2009). Changes in free volume occur immediately with a change in temperature and are manifest macroscopically as the polymer's coefficient of thermal expansion (Dlubek et al., 1998). Based on the findings of Dlubek et al. (1998), this thermal expansion /contraction occurs predominately in the amorphous zone of semi-crystalline polymers. Slower changes in free volume can also occur with physical aging and the associated change in morphology (e.g., increase in crystallinity) or due to swelling. Pospisil et al. (2003) noted that free volume in the amorphous zone controls transport properties such as diffusion/mobility of oxygen and stabilizers and that non-linearities in the solid state (e.g., complex HP-OIT$_r$ residual behavior) may be attributed to changes in free volume with temperature and hence stabilizer solubility and/or mobility.

In the GMB literature, evidence of a link between polymer free volume (i.e., morphology) and HP-OIT$_r$ can be found in Rowe and Ewais (2014) who examined four GMBs of different thickness (1.0, 1.5, 2.0 and 2.4 mm) but from the same resin, additive package, and production line (the only difference was pulling rate to produce different thickness). Although all thicknesses had near identical initial Std-OIT$_o$ and HP-OIT$_o$, the residual HP-OIT$_r$ value (after ageing in synthetic leachate) appeared to vary by thickness being higher in the thicker samples. Since the depletion rate multiplied by the square of thickness ($s \times H^2$) was different for each thickness, they noted that the depletion of AO-S detected HP-OIT was either: (a) not totally controlled by diffusion and/or; (b) that the diffusion coefficient of each supposedly identical GMB material was different due to different morphologies (free volume structure) associated with the different pulling speeds and rates at which the GMBs cooled. They reported that this was more pronounced for HP-OIT than Std-OIT (likely because the HAS molecules were more size-limiting than the AO molecules detected by Std-OIT).

During melt processing, AO-stabilizers may be added at concentrations higher than their room temperature solubility resulting in super-saturation in the polymer after cooling to room temperature (Scheirs et al. in Rowe and Jeferris, 2022). Numerous researchers (e.g., Gedde et al. 1994; Mar’in 1998; Christmann et al. 2021) have noted that stabilizer supersaturation results in two phenomena: (1) microprecipitation from the phase change forming insoluble ‘ineffective’ stabilizer nodules within the polymer, and; (2) blooming (surface loss through exudation). Excessive supersaturation can lead to polymer swelling (e.g., Mar’in, 1998) and issues with GMB weldability (Scheirs 2009; Scheirs et al. in Rowe and Jefferis, 2022), thus not only does adding too much AO-S do little in the way of enhancing performance (and cause misleadingly high initial OIT$_o$ values) but it can cause undesirable changes in the base polymer (swelling) and GMB surface. This may be why Malik et al. (1992), who examined the diffusion and solubility of different HAS types in polyethylene, concluded that solubility was more important than diffusion for HAS effectiveness.

Christmann et al. (2021) studied the blooming and solubility of Tinuvin 770® (low molecular weight HAS) in LLDPE films at room temperature and at 52°C and found that bloomed stabilizer at room temperature experienced re-solubilization back into the polymer at 52°C (due to increased solubility). Although this is unlikely to occur for GMBs since bloomed stabilizer would simply be washed away in the leachate, it does highlight the role of temperature in stabilizer solubility. Furthermore, although blooming is considered to be the dominant end-result for the *insoluble* stabilizer in thin films (e.g., Christmann et al. 2021), GMBs (typ. 1.0 to 2.5-mm thick) are much thicker than films and there is evidence to suggest blooming loss in GMBs might be limited to the insoluble stabilizer near the GMB surface with the rest being trapped in the GMB core. For example, Rowe and Ewais (2014) measured the HP-OIT$_r$ in the outer and middle 1/3rd of a 2.4-mm thick GMB aged in 70°C leachate for 57 months (it had been at HP-OIT$_r$ for nearly 45 months at the time of sampling) and found ~ 20% higher HP-OIT$_r$ in the in the central 1/3rd compared to the outer 1/3rd which they attributed to more trapped stabilizer there. In the context of the forgoing discussion this could suggest that: (a) only the insoluble fraction near the surface bloomed and washed away but was trapped elsewhere in the GMB (if one accepts that stabilizer insolubility affects residual HP-OIT behavior) and/or, possibly related; (b) the polymer morphology varied across the GMB thickness having a more open free-volume structure near the surface and hence permitting some of the HMW AO-S to be released there. If the total insoluble fraction across the entire GMB thickness could bloom then one might expect to see residual HP-OIT$_r$ values gradually decrease with time in leachate however they remain constant. Notwithstanding this, Muller et al. (2016) statement that ‘it is still unclear in many details how the loss of the AO proceeds from such a supersaturated state’ remains true in 2023.

The aforementioned complexity and non-linearity in solubility (which is only exacerbated when a mixture of different stabilizers are used together; e.g., Mar’in, 1998) might explain why some HAS stabilized GMBs exhibit a more temperature-dependent HP-OIT$_r$ behavior (e.g., Rowe and Abdelaal, 2016) than others (e.g., Abdelaal et al., 2019 and the present study). This can be attributed, at least in part, to the size-limiting nature of different HAS types which cover a wide range of molecular weights and structures (e.g., Malik et al., 1992). For example, if the free volume holes approach but are incrementally larger than a given stabilizer size, then an incremental decrease in temperature would cause an incremental contraction of free-volume enough to potentially render the once mobile stabilizer, immobile (i.e., trapped), especially in the core, resulting in higher HP-OIT$_r$. On the other hand, if the stabilizer size was much larger (or smaller) than the free holes, then an incremental change in temperature, possibly even a large change in temperature, might not affect the mobility or solubility of that particular species; This might explain GMB cases where HP-OIT$_r$ appears constant over a range of temperatures.

Lastly, there are mechanisms other than solubility that could be playing an important role in HP-OIT$_r$. For example, the absorption of AO-S to carbon black (immobilizing them) or that some immobile HAS parent molecules can change size from attack of peroxy radicals and generate mobile fragments, some of which remain efficacious (Muller et al., 2016). In summary, it appears that HP-OIT$_r$ could depend on the combination of the nature and size of stabilizers used (with some combinations being far more effective than others), their solubility, the polymer free-volume (i.e., morphology) as well as the fluid chemistry (e.g., high/low pH; Abdelaal and Rowe, 2017); More research is needed to fully explain HP-OIT$_r$.

Effect of resin density on depletion

The four GMBs examined (which each used a different resin and additive package), appeared to show some correlation between resin density and HP-OIT depletion rate in this leachate at ≥ 75°C (Figure 7a; leachate). Although Scheirs (2009) noted that lower density resins (e.g., LLDPEs) have a greater 'AO-S migration potential' relative to HDPE GMBs, presumably due to the larger free volume of lower density resins, there is evidence that the characteristics of the additive package can play an even larger role in the AO-S depletion rate than the resin. For example, studying 12 different PE GMBs in a chlorinated water at 85°C (covering a range of MDPE used in HDPE GMBs as well as into the LLDPE range), Morsy et al. (2021) reported an overall poor correlation between resin density and the AO-S depletion rate for both Std- and HP-OIT (e.g., triangles shown on Figures 7a and b). Despite their lower resin density, two of the slowest depleting GMBs reported by Morsy et al. (2021) were LLDPEs which was attributed to the nature of the additive packages playing a more dominant role than the resin. This raises the question as to whether the apparent trend observed between resin density and HP-OIT depletion rate in the present study, most notably at 85°C (Figure 7a; leachate) was merely a coincidence. The difference in immersion fluid (this leachate vs chlorinated water) and how they interacted differently with the GMBs may offer some insight into this question.

Since GMB1, GMB2 and GMB3 from the present study were three of the 12 GMBs examined by Morsy et al. (2021) at 85°C, a direct comparison between their depletion rates in leachate and chlorinated water was possible. In addition to the Std-OIT and HP-OIT depletion rates, $s_{Std\text{-}OIT}$ and $s_{HP\text{-}OIT}$, of GMBs 1, 2 and 3 being slower in chlorinated water than leachate (likely due to the surfactant in this leachate), the apparent relationship between resin density and $s_{HP\text{-}OIT}$ in leachate at 85°C for these three GMBs (Figure 7a; 85°C leachate; steep slope) was diminished in chlorinated water at the same temperature (Figure 7a; the three corresponding triangles for GMBs 1, 2 and 3; shallow slope). Since the overall depletion rate is typically governed by two sequential, rate limiting steps [(Step #1) diffusion through bulk polymer to GMB surface followed by; (Step #2) interactions at the surface (e.g., dissolution, hydrolysis, free radical consumption etc.), one hypothesis is that since the leachate facilitated faster surface extraction of the mobile HP-OIT relative to the chlorinated water, the resin density [and by analog, resin diffusivity] was allowed to play a larger role in resisting depletion since surface extraction (Step #2) occurred so fast in leachate and hence may no longer have been the rate limiting step at 85°C. Sangam and Rowe (2002) found that surfactants in leachate increased the diffusion flux of AO-S inside the GMB by increasing the surface wettability and hence increasing the rate of extraction. On the other hand, extraction of mobile HP-OIT in chlorinated water (which contained no surfactant) was slower than in leachate and hence the diffusive flux through bulk polymer was slower which could explain why the resin density appeared to matter less in chlorinated water (Figure 7a).

Because resin density may affect both the diffusion rate and the mobility of the AO-S as does the chemical composition and molecular size of the AO-S, it is difficult to clearly distinguish the effect of the two factors. For Std-OIT at 85°C there was little effect of resin density on depletion rate between GMB3, GMB2 and GMB1 but a notable decrease in $s_{Std\text{-}OIT}$ for the denser PE-RT resin GMB4 (Fig. 7b). However, in chlorinated water at 85°C and leachate at temperatures < 85°C there was no apparent relationship between density and $s_{Std\text{-}OIT}$. Thus, although there was an apparent relationship between resin density and $s_{HP\text{-}OIT}$ in this leachate at 85 and 75°C, its effect was not very apparent at less than 75°C (e.g., 65°C $s_{HP\text{-}OIT}$ were near identical for GMBs 1, 2 and 4) and hardly at all for $s_{Std\text{-}OIT}$ at any temperature.

Although it is acknowledged that resin density does play a role in AO-S depletion, the findings taken with Morsy et al. (2021) are evidence that the AO-S. This agrees with the understanding that AO-S depletion is more related to the specific details of the additive package (e.g., carbon black and AO-S) and its interaction with the contained fluid can play an even larger role than it is with the resin. For example, Irganox 1330 and 1010 are both phenolic AOs used in HDPE GMBs, however the former has better resistance to hydrolysis and leaching (Scheirs et al. in Rowe and Jefferis, 2022). Lastly, although only two PE-RT resins were examined (GMB3 and 4), there was no compelling evidence that PE-RT itself slowed the AO-S depletion rate (e.g., Figure 7a; GMB3 and 4); rather, as mentioned, the depletion rate appeared more influenced by the different AO-S packages used.

Conclusions

The antioxidant depletion time of two high-temperature PE-RT GMBs immersed in synthetic MSW leachate for 7.5 years at various temperatures (40-95°C) was compared with two conventional HDPE GMBs from the same manufacturer. Samples were also aged in forced air ovens to explore the effect of incubation medium on depletion behavior (air vs leachate). All four GMBs used different MDPE resins and different additive packages but fell into the ASTM (2012) high-density HDPE range after addition of carbon black. The depletion of protective antioxidants and stabilizers (AO-S) was monitored using standard and high-pressure oxidative induction time tests (Std-OIT and HP-OIT). Although all four GMBs met the minimum GRI-GM13 requirements for new GMBs, they exhibited very different performances and based on the GMBs tested and conditions examined, the following conclusions were reached.

1. Air aging at 85°C is not a useful indicator of AO-S stability or likely long-term performance for geomembranes used to contain liquids. For example, in this study air aging at 85°C resulted in a misleading impression of both (a) the retention of the AO-S package at elevated temperature, and (b) the relative AO-S performance of the four GMBs for leachate containment. After 90 days at 85°C, PE-RT GMB4 retained 97% HP-OIT and 78% Std-OIT in air but only 75% HP-OIT and 10% Std-OIT in leachate. The traditional HDPE GMB2

retained 85% HP-OIT and 30% Std-OIT in air but only 67% HP-OIT and <1% Std-OIT in leachate. PE-RT GMB3 appeared to have nearly 4-fold slower Std-OIT depletion in air than the traditional HDPE GMB1 but there was negligible difference in leachate.

2. The relative AO-S depletion among different GMBs at a single temperature will not necessarily be the same at a different temperature. For example, GMB4 was 2-3 times slower depleting than GMB2 at 85°C but the depletion rates of both GMBs was similar at around 65°C for Std-OIT and 50°C for HP-OIT.
3. Most of the depletion rates at 95°C deviated from an otherwise well-fitted linear Arrhenius relationship at the other incubation temperatures (85-40°C) due to a change in behavior not representative of temperatures ≤ 85°C. This was attributed to annealing and a change in crystalline structure.
4. Std-OIT and HP-OIT should not be used as alternatives; both were needed to understand the GMB behaviour. The time required for AO-S depletion (Stage 1) was governed by HP OIT at elevated temperatures and by Std-OIT for temperatures less than 35°C (GMB1) - 55°C (GMB3).
5. HP-OIT provides little insight into long-term performance unless the immersion tests are run long enough to reach the residual HP-OIT$_r$ value at a minimum of two immersion temperatures. There is no simple way to estimate HP-OIT$_r$ from initial values.
6. A higher initial OIT does not imply a longer depletion time and better performance. For example, GMB3 had the second highest HP-OIT$_o$ but the shortest HP-OIT depletion time at all temperatures examined.
7. Any role played by the PE-RT resins in decreasing the AO-S depletion rate was masked by the dominant role played by the different AO-S packages. However, the combination of AO-S package and PE-RT resin in GMB4 provided much better relative performance at elevated temperatures (T > 65°C) than the other three GMBs examined.
8. When seeking to evaluate the relative AO-S depletion of several candidate GMBs, it is recommended that, at the very least, two immersion temperatures ≤ 85°C be used (e.g., 85 and 70°C) and three temperatures (85, 70, 55°C) is extremely desirable. Three months testing at 85 and 65°C (or 75°C) provided general insight into the relative performance of the four GMBs in terms of AO-S depletion. If realistic predictions are to be made based on elevated temperatures, at least three temperatures and a minimum 12 months testing is recommended to obtain reasonable quantitative predictions of actual AO-S depletion rates.

It is acknowledged that the work reported in this study is limited to two high-temperature PE-RT GMBs and that different GMBs and AO-S packages can have different performances; considerable care should be taken in generalizing the conclusions provided above. Also, this study only dealt with one important aspect of GMB durability (AO-S depletion). Future work should focus on the physical-mechanical behavior of such GMBs. Lastly, the AO-S depletion predictions in this paper are for GMBs immersed in leachate and should be regarded as conservative (i.e., shorter) than in applications where the GMB is only exposed to leachate on one side (e.g., in composite liners; see Rowe et al. 2020).

Data Availability Statement

Data generated or analyzed during this study are available from the corresponding author upon reasonable request.

Competing Interests

The authors declare there are no competing interests.

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Abbreviations

AO-S	Antioxidants and stabilizers
ASTM	American Society for Testing and Materials
GMB	Geomembrane
HAS	Hindered amine stabilizers.
HP-OIT	High pressure oxidative induction time
HMW	High molecular weight
HDPE	High density polyethylene
PE-RT	Polyethylene of raised temperature resistance
Std-OIT	Standard oxidative induction time

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Table 1. Initial properties of the GMBs examined

Property	GMB1	GMB2	GMB3	GMB4
Designator	yF1	yF2	yF3	yF4
Type based on ASTM D883-11	HDPE	HDPE	HDPE	HDPE
PE-RT base resin[1]	No	No	Yes	Yes
Production date[2]	2013	2013	2013	2014
Nominal thickness (mm) - (ASTM D5199)	1.5	1.5	1.5	1.5
Color	Black	Black	Black	Black
Resin Density[1] (g/cm^3)	0.937	0.936	0.933	0.939
GMB density[1] (g/cm^3)	0.943	0.945	0.943	0.949
Carbon black[1] (%) (ASTM D1603)	2.4	2.7	2.3	2.3
Std-OIT (min) - (ASTM D3895)	179 ± 2	206 ± 2	209 ± 18	254 ± 16
HP-OIT (min) - (ASTM D5885)	1220 ± 60	950 ± 20	1260 ± 90	1410 ± 70
HLMI (g/10 min) - (21.6 kg)	11.8 ± 0.2	10.2 ± 0.2	19.8 ± 0.3	32.4 ± 0.2
LLMI (g/10 min) - (2.16 kg)	0.096 ± 0.001	0.084 ± 0.002	0.74 ± 0.044	0.575 ± 0.071
Melt flow ratio (-)	123	121	27	56

The values in the table represent the mean ± standard deviation

[1] Provided by GMB manufacturer

[2] Testing commenced in 2013 (for GMBs 1, 2 and 3) and 2016 (for GMB4).

The GMB properties may vary with time when stored on a roll at room temperature for a long period. In this paper, the terms unaged and initial value correspond to the GMBs just prior to test commencement.

Table 2. Observed OIT depletion rates (month^{-1}) in leachate

Temperature (°C)	Std-OIT				HP-OIT			
	GMB1	GMB2	GMB3	GMB4	GMB1	GMB2	GMB3	GMB4
40	0.012	0.006	0.008	0.008	0.009	0.011	0.021	0.012
65	0.41	0.26	0.31	0.18	0.07	0.07	0.17	0.07
75	1.31	1.11	0.93	0.36	0.23	0.21	0.45	0.14
85	1.73	1.68	1.74	0.89	0.43	0.48	0.87	0.23
95	2.33	2.32	1.30	0.89	0.66	0.36	0.72	0.34

Table 3. Observed times to depletion in leachate (months)

Temperature (°C)	Std-OIT				HP-OIT			
	GMB1	GMB2	GMB3	GMB4	GMB1	GMB2	GMB3	GMB4
65	12	18	15	24	48	50	28	48
75	3.4	4.1	4.2	13	16	17	8.5	23
85	2.5	2.6	2.5	5.1	7.2	7.5	5.0	14
95	1.9	1.9	3.1	5.5	7.9	10	5.6	11

Table 4. Predicted antioxidants depletion time; rounded to 2 significant digits [years; months in ()] Largest values in bold.

Temperature (°C)	Std-OIT				HP-OIT			
	GMB1	GMB2	GMB3	GMB4	GMB1	GMB2	GMB3	GMB4
5	> 3000	> 3000	> 3000	> 3000	1700	1300	720	520
10	2200	> 3000	> 3000	2400	920	730	400	330
15	1000	2200	1900	1200	510	410	220	210
20	460	950	840	590	290	230	130	130
25	220	420	380	300	160	130	75	87
30	106	190	180	160	95	78	45	57
35	53	91	85	84	57	47	27	39
40	27	44	41	46	34	29	17	26
45	14	22	21	25	21	18	10	18
50	7.0	11	11	14	13	12	7.0	13
55	4.0	5.6	5.5	8.3	8.2	7.5	4.3	8.8
65	1.2	1.6	1.6	2.9	3.3	3.2	1.8	4.4
75	0.4 (4.7)	0.5 (5.5)	0.5 (5.6)	1.1	1.5	1.5	0.8 (10)	2.4
85	0.14 (1.6)	0.15 (1.8)	0.16 (1.9)	0.4 (5)	0.7 (8)	0.7 (8)	0.4 (5)	1.3 (16)

[a] Time to AO depletion (Stage I) defined as time to +2 minutes of residual Std-OIT and +11 minutes of residual HP-OIT. These criteria were based on the observed times to depletion. Note: Uncertainty in predictions increases the further the temperature is from the temperatures at which data was collected and predictions exceeding 3000 years are simply shown as > 3000.

Table 5. Observed residual HP-OIT values by temperature and GMB

	GMB1				GMB2				GMB3				GMB4			
Temperature (°C)	95	85	75	65	95	85	75	65	95	85	75	65	95	85	75	65
mean (min)	476	721	649	746	376	458	471	455	267	283	383	371	642	643	629	676
SD (min)	64	101	118	51	42	37	44	29	48	34	29	30	40	34	55	52
n	11	12	9	5	7	9	8	7	9	8	8	7	8	6	7	6
Outlier[1]	yes	no	no	no	yes	no	no	no	yes	yes	no	no	no	no	no	no
Avg. HP-OIT$_r$[a] (min)	701				462				346				650			
HP-OIT$_o$ (min)	1220				950				1260				1410			
HP-OIT$_r$/HP-OIT$_o$	0.57				0.49				0.27				0.46			
HP-OIT*$_o$	519				488				914				760			

[1] Significance assessed using 1-way analysis of variance (ANOVA) testing at the 95% confidence level

[a] Average of residual values at 85, 75 and 65°C

HP-OIT*$_o$ = HP-OIT$_o$ - HP-OIT$_r$ = ‘available’ or ‘deplete-able’ HP-OIT in this leachate

Figure captions

Figure 1. (a) HP-OIT DSC thermogram evolution with ageing time for GMB4 in 85°C leachate at 0, 2, 7 and 16 months. Virgin specimen showing two interpretations of HP-OIT; 1st peak (shoulder) and 2nd peak (final exotherm) where OIT is taken as the intersection of exotherm tangent with a horizontal baseline extending from the isothermal portion; (b) depletion of both HP-OIT interpretations for GMB4 in 85°C leachate.

Figure 2. Depletion of normalized: (a) Std-OIT and; (b) HP-OIT for the four GMBs in air and leachate at 85°C. Dashed lines indicate the GRI-GM13 90-day air aging requirements. Error bars represent the range (min and max) of duplicate tests on a specimen. Note: time scale (x-axis) is longer for (b) than (a).

Figure 3. Change in normalized Std-OIT (OIT_t/OIT_o) with time at 40, 65, 75, 85, and 95°C for: (a) GMB3, (b) GMB3 (first 10 months), (c) GMB4, (d) GMB4 (first 10 months). Error bars represent the range of duplicate tests.

Figure 4. Change in the normalized HP-OIT (OIT_t/OIT_o) with time in leachate at 40, 65, 75, 85, and 95°C for: (a) GMB1; (b) GMB2; (c) GMB3; and (d) GMB4. Error bars represent range of two tests.

Figure 5. DSC melt thermograms from samples aged in leachate for 1.2 months at 75, 85 and 95°C for GMB4.

Figure 6. Arrhenius plots of OIT depletion using observed rates from temperatures between 40 and 85°C (solid symbols): (a) Std-OIT and (b) HP-OIT. Observed rates at 95°C (open symbols) were excluded from regression analyses.

Figure 7. AO-S depletion rate plotted against resin density for the examined GMBs in leachate at 65, 75 and 85°C for: (a) HP-OIT and; (b) Std-OIT. Results from Morsy et al. (2021) who examined GMBs 1, 2 and 3 in chlorinated water at 85°C (CW) are reported along with three other 1.5-mm HDPE GMBs from that study (MyE, MyEW and MxC). To distinguish them from other GMBs that shared the same resin density, GMB1 and GMB2 are identified by subscripts 1 and 2. Morsy et al. (2021) did not examine GMB4 hence its behavior in chlorinated water was unavailable.

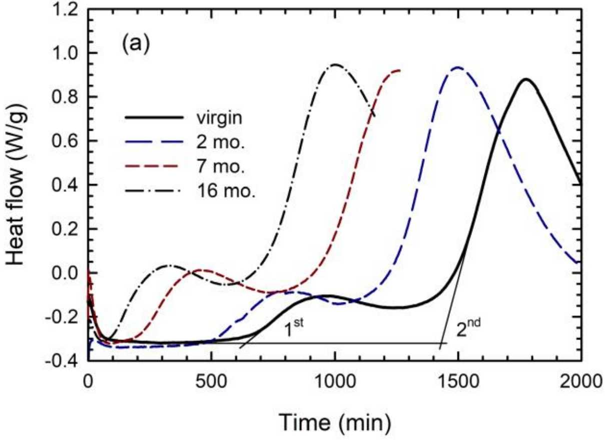


Figure 1a

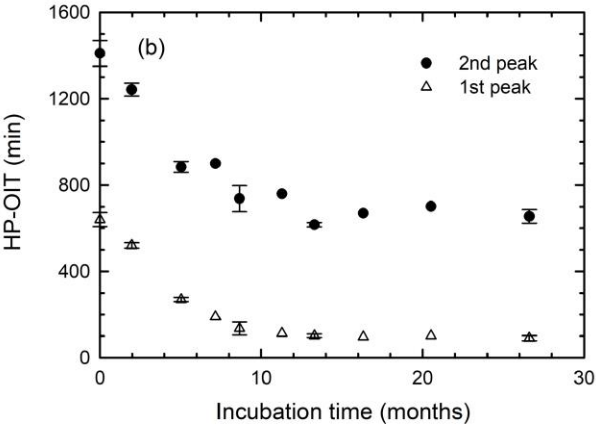


Figure 1b

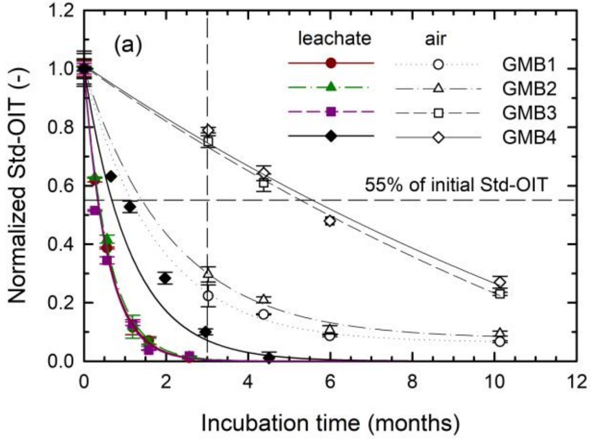
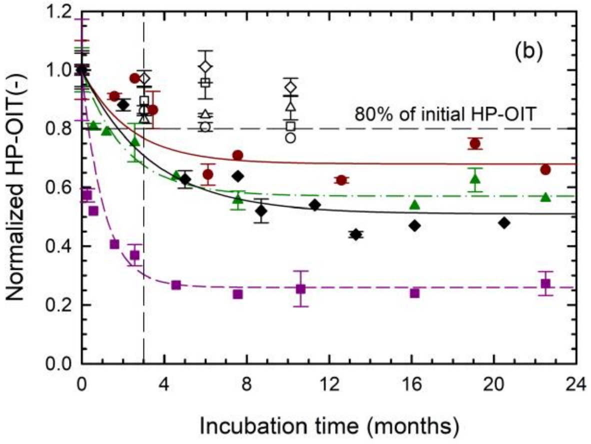


Figure 2a



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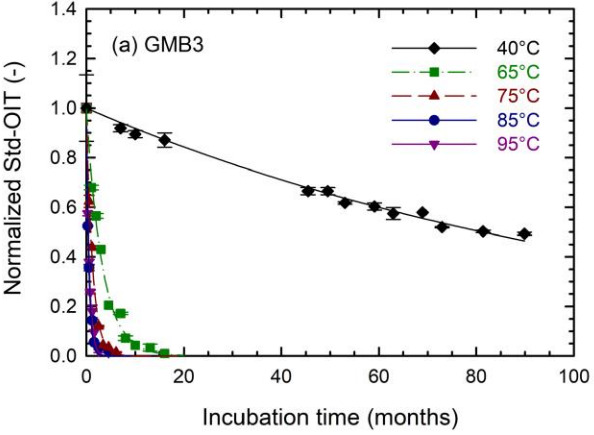
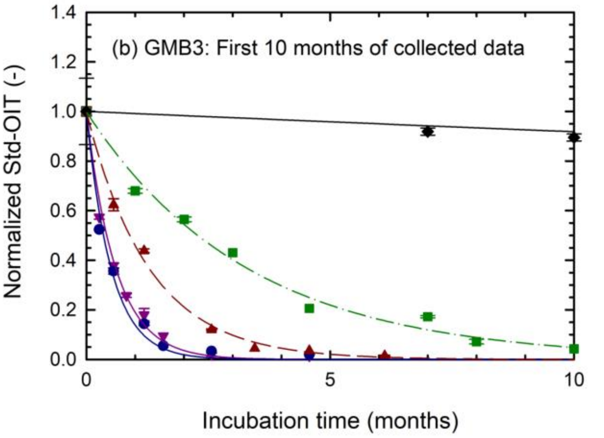


Figure 3a



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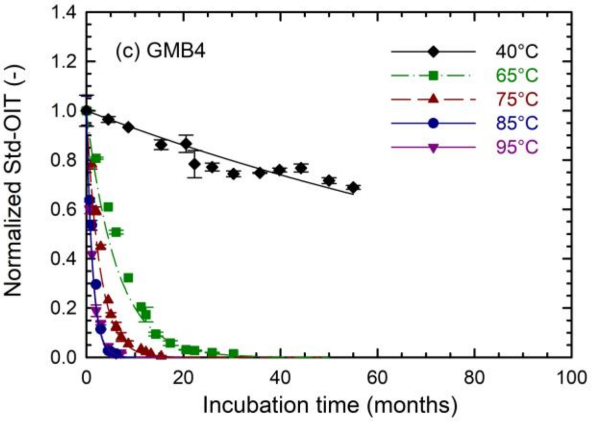


Figure 3c

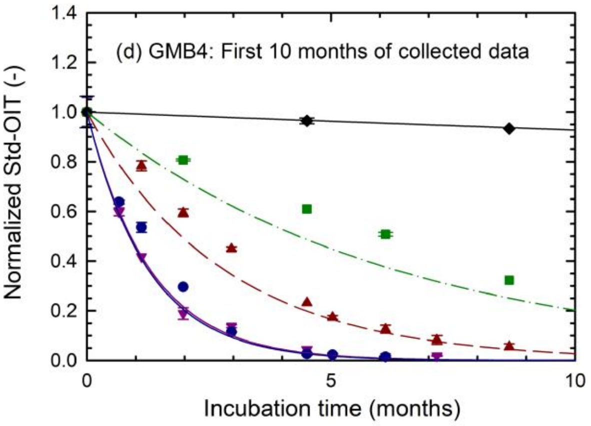


Figure 3d

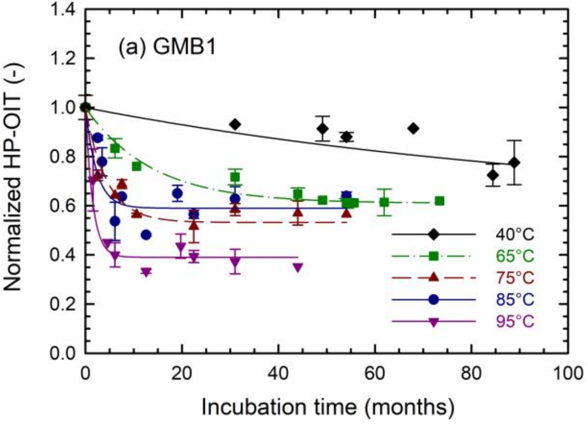


Figure 4a

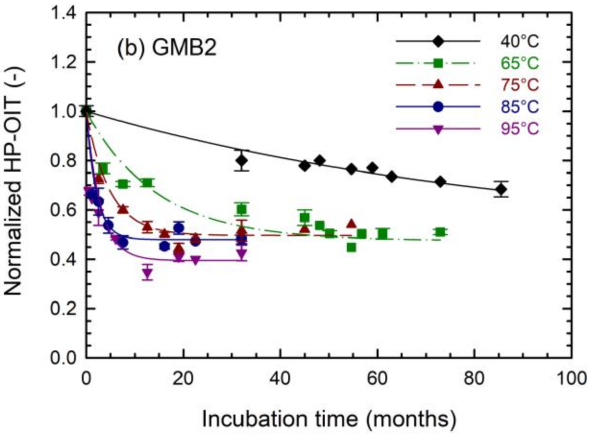


Figure 4b

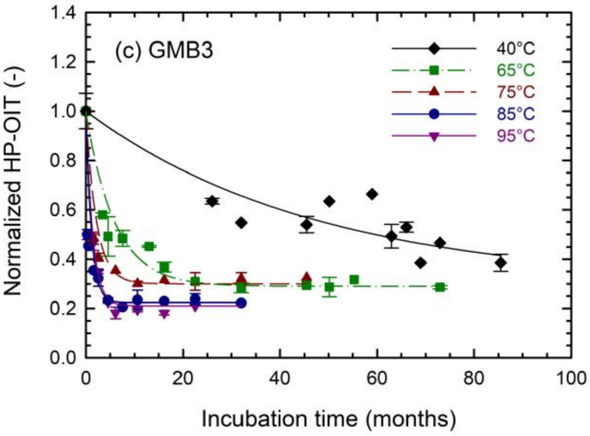


Figure 4c

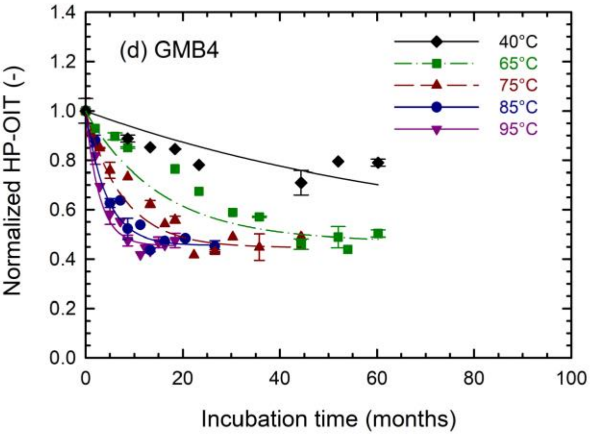


Figure 4d

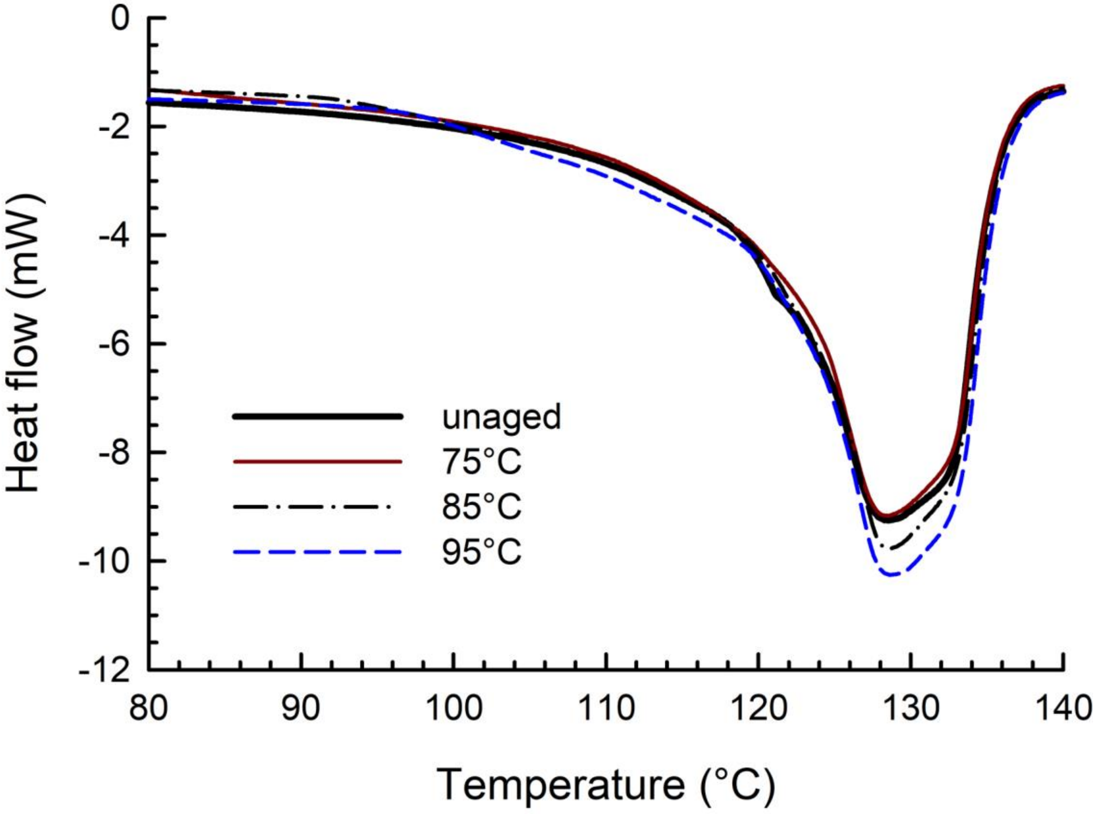
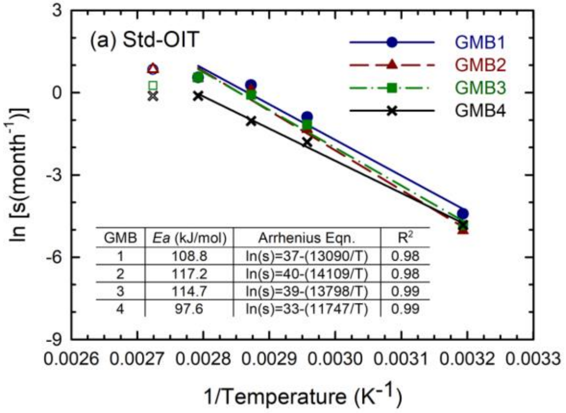
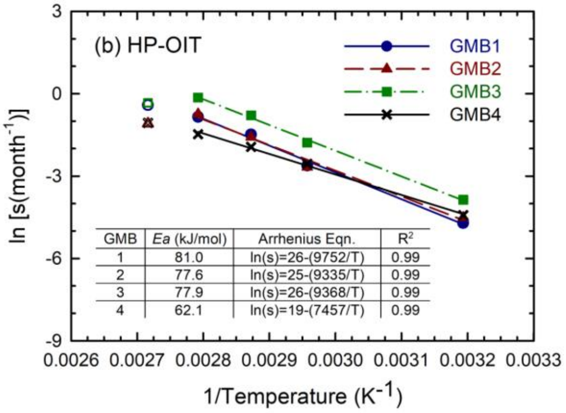

0
-2
-4
-6
-8
-10
-12
Heat flow (mW)
80
90
100
110
120
130
140
Temperature (°C)
unaged
75°C
85°C
95°C

Figure 5



GMB	*Ea* (kJ/mol)	Arrhenius Eqn.	R^2
1	108.8	ln(s)=37-(13090/T)	0.98
2	117.2	ln(s)=40-(14109/T)	0.98
3	114.7	ln(s)=39-(13798/T)	0.99
4	97.6	ln(s)=33-(11747/T)	0.99

Figure 6a



GMB	*Ea* (kJ/mol)	Arrhenius Eqn.	R^2
1	81.0	ln(s)=26-(9752/T)	0.99
2	77.6	ln(s)=25-(9335/T)	0.99
3	77.9	ln(s)=26-(9368/T)	0.99
4	62.1	ln(s)=19-(7457/T)	0.99

Figure 6b

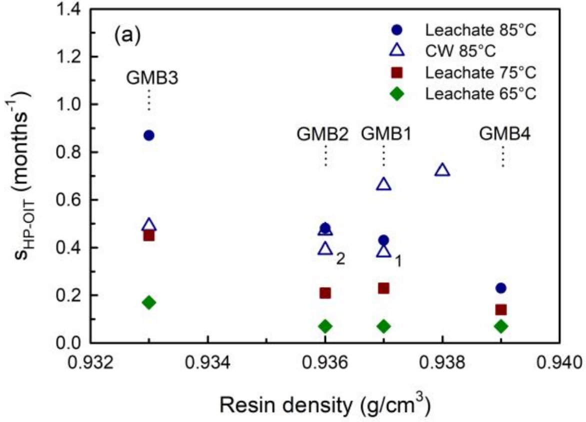


Figure 7a

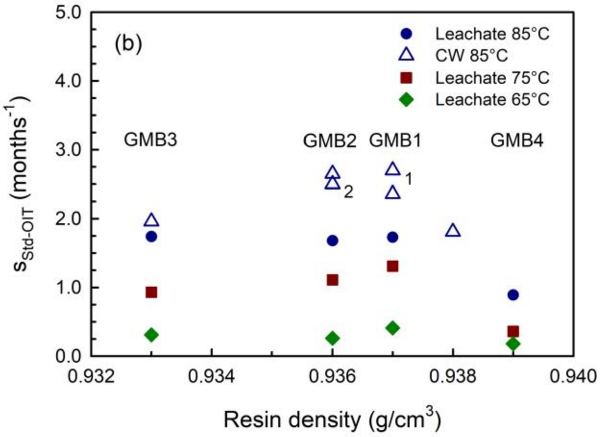


Figure 7b