Application of a four-parameter exponential decay model for modelling antioxidant depletion in HDPE geomembranes

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ABSTRACT: The antioxidants in some high density polyethylene geomembranes deplete at different rates. Under these circumstances, a 4-parameter exponential decay function may be needed to fit the depletion data instead of the traditional 2-parameter exponential model. In this study, two different methods of establishing the length of the antioxidant depletion stage using Arrhenius modeling are investigated for the 4-parameter model. Method A relies on developing a relation between exponential parameters and temperatures while Method B is based on the time temperature superposition technique. For the conditions examined, Method A was easier to implement than Method B. The application of Method A is then illustrated for data sets with different activation energies of the two depilation rates without any approximation in the computations.

Keywords: Geomembranes, degradation, antioxidants, OIT depletion

1 INTRODUCTION

High density polyethylene (HDPE) geomembranes (GMBs) liners are used in many different geoenvironmental applications including municipal solid waste landfills, water reservoirs, and heap leach pads amongst many. This is due to their high chemical and mechanical resistance (Haxo 1990; Scheirs 2009). However, all GMBs (including those with alternative polymers and bituminous GMBs) will eventually fail due to degradation and it is important to be able to estimate the time to failure under appropriate exposure conditions. To date, modern HDPE is the only GMB for which a significant amount of research into long-term performance in geoenvironmental applications has been published in the archival literature and the results presented herein, and elsewhere, for HDPE should be viewed in the context of the lack of equivalent information for other polymers/materials; indeed HDPE manufacturers are to be congratulated for supporting research into the long-term performance of their products which can be used to aid designers and it is a great shame that the same information is not available for other materials.

The first of three stages of the time to nominal failure involves depletion of antioxidants/stabilizers in the GMB (Hsuan and Koerner 1998). In general, oxidative degradation of HDPE GMBs starts sometime after the different antioxidants/stabilizers used to protect the GMB have depleted to low/inactive levels. The rate of depletion of antioxidants in the GMB generally depends on the incubation medium, temperature, and the nature of the antioxidants. For instance, in reduced municipal solid waste (MSW) leachate having surfactants (Maisonneuve et al. 1997; Kjeldsen et al. 2002; Borghi et al. 2003; Rowe et al. 2008), the outward diffusion of antioxidants aided by the role of the surfactant as a wetting agent which tends to have a dominant effect on the rate of antioxidant depletion. In water, there is generally slower diffusion of antioxidants than in MSW leachate and other depletion mechanism such as hydrolysis and chemical consumption may play the dominant role with respect to depletion.

Quantification of the time to antioxidant depletion is required as the first step in defining the time to nominal failure of HDPE GMBs. The length of the antioxidant depletion stage is usually assessed by examining the change in the oxidative induction time (OIT) based on a first order exponential decay function (2-parameter model; e.g. Hsuan and Koerner 1998; Rowe and Sangam 2002; Sangam and Rowe 2002; Gulec et al. 2004; Rowe et al. 2008; 2009; 2010; 2013) given by:

$$OIT_t = OIT_o \times e^{-st} \tag{1}$$

where OIT_t (min) = the OIT remaining at any time t, OIT_o (min) = the initial OIT, s (month^{-1}) = the anti-oxidant depletion rate, and t (month) = the ageing time.

Rowe and Rimal (2009) showed that even with a simple antioxidant package, the 2-parameter model does not capture the very early time OIT depletion data correctly but does fit most of the data. This work demonstrated that there was a fundamental (theoretical) issue associated with using the first order equation (Eq. 1) as an approximation to the diffusion of antioxidants. However, over and above this fundamental issue which is only significant at small times relative to the overall depletion time, the 2-parameter model may also fail to capture the depletion for other practical reasons such as the presence of different antioxidants and/or mechanisms which may result quite different depletion rates at different times. To deal with these more complicated situations, a few investigators have used two exponential functions to model antioxidant depletion data (e.g., Smith et al. 1992; Müller and Jacob 2003; Wong 2011; Abdelaal 2013; Ewais 2014). For GMBs stabilized with hindered phenol and phosphite antioxidants incubated in water, Müller and Jacob (2003) showed that antioxidant depletion can be captured by superimposing two exponential functions (referred to herein as 4-parameter model) that can be described as:

$$\frac{OIT_t}{OIT_o} = a \times e^{-s_1 t} + b \times e^{-s_2 t} \qquad (2)$$

where s_1 (month^{-1}) = the first antioxidant depletion rate, s_2 (month^{-1}) = the second antioxidant depletion rate, a and b are the exponential fit parameters where $a+b=1$.

The objective of this paper is to examine two different methods for establishing the length of the antioxidant depletion stage (Stage I) using Arrhenius modeling when the 4-parameter model is used for fitting the OIT data.

2 EXPERIMENTAL INVESTIGATION

2.1 *Material and incubation media*

A commercially available HDPE GMB is examined. The GMB contained 1620 ppm hindered phenols (Irganox 1010) and 735 ppm phosphites (Irgafos 168) as antioxidants and 2.6% carbon back. There were no hindered amine light stabilizers (HALS).

The GMB samples were cut into 20 x 10 cm coupons and incubated in synthetic leachate and reverse osmosis (RO) water in four-liter glass jars at different temperatures. The synthetic leachate was prepared by mixing RO water with trace metals, surfactant, and reducing agents as described by Rowe et al. (2010).

2.2 *Index testing*

Due to the absence of HALS in this specific GMB, depletion of antioxidants was monitored using only standard oxidative induction time test (Std-OIT; ASTM D 3895) that can capture the antioxidants stabilizing the GMB tested. To measure the Std-OIT, GMB specimens were heated in a differential scanning calorimeter to 200°C under 35 kPa oxygen pressure. The initial Std-OIT of the examined GMB was 115 ± 1.0 min.

3 RESULTS AND DISCUSSION

For this GMB in simulated MSW leachate (Figure 1a) there is only a slight difference between the very early and later time depletion rates at all the temperatures. This small difference is to be expected when diffusion dominates (Rowe and Rimal 2009). The dominance of diffusion in this case is attributed to the role of surfactant in the leachate masking the effects of other depletion mechanisms. Although a 2-parameter (1st order) exponential function is considered reasonable for obtaining depletion rates for this data, in this study the implications of using rates obtained from a 4-parameter model are examined. In contrast, for the same GMB immersed in water (Figure 1b) there was a noticeable change in depletion rates at different temperatures. With the absence of surfactant, the outward diffusion of antioxidants was slower and the effects of leaching and hydrolysis on antioxidant depletion made the approximation of the data by a 2-parameter model inappropriate. Thus, the 4-parameter exponential model was required in this case to provide a reasonable fit for the Std-OIT depletion data.
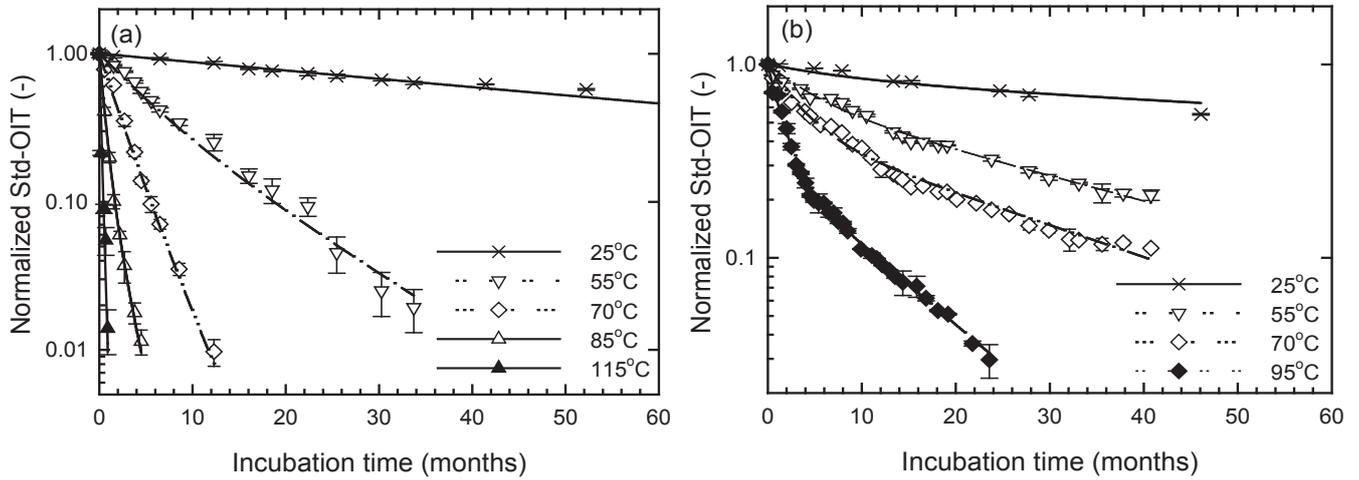
Figure 1. Variation of normalized Std-OIT with time in: (a) MSW leachate; (b) RO water. Modified from Abdelaal and Rowe (2014).

The depletion rates, s_1 and s_2 (as per Eq. 2) inferred from fitting the 4-parameters model to the data (Figure 1) are plotted versus the inverse of the incubation temperature in an Arrhenius plot in Figure 2. The Arrhenius equation (Hsuan and Koerner 1998) for each depletion rate can be written as:

$$s = Ae^{-(E_a/(RT))} \tag{3}$$

and, taking the natural logarithm of both sides, Eq. 3 can be rewritten as:

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

where s (month^{-1}) = antioxidant depletion rate, T (K) = temperature, E_a (J.mol^{-1}) = activation energy, A, (month^{-1}) = a constant called collision factor, R = 8.314 (J.mol^{-1}.K^{-1}) is the universal gas constant.

For leachate incubation (Figure 2a), the activation energies (slopes of the Arrhenius regression lines) were 61.6 and 61 kJ/mol for the first and the second depletion rates of the 4-parameter model, respectively. The clear change in the depletion rate in water (Figure 2b) resulted in the activation energies of the first and the second depletion rates of the 4-parameter being quite different at 23.7 and 34.4 kJ/mol, respectively. These Arrhenius plots can be used to extrapolate/interpolate the depletion rates s_1 and s_2 at a field specific temperature of interest.

With the 2-parameter model (Eq. 1), substitution of an interpolated/extrapolated depletion rate, s, from the Arrhenius plot allows the direct evaluation of the depletion time to a residual OIT value and hence the length of Stage I. For the 4-paramter model, even after obtaining the depletion rates s_1 and s_2 from the Arrhenius plot, Eq. 2 still has the exponential parameters a and b that need to be evaluated to calculate the length of Stage I for the temperature of interest. Thus, in the next sub-section, two methods are used to evaluate these two exponential parameters so that the predications of Stage I can be made using the 4-parameter model.
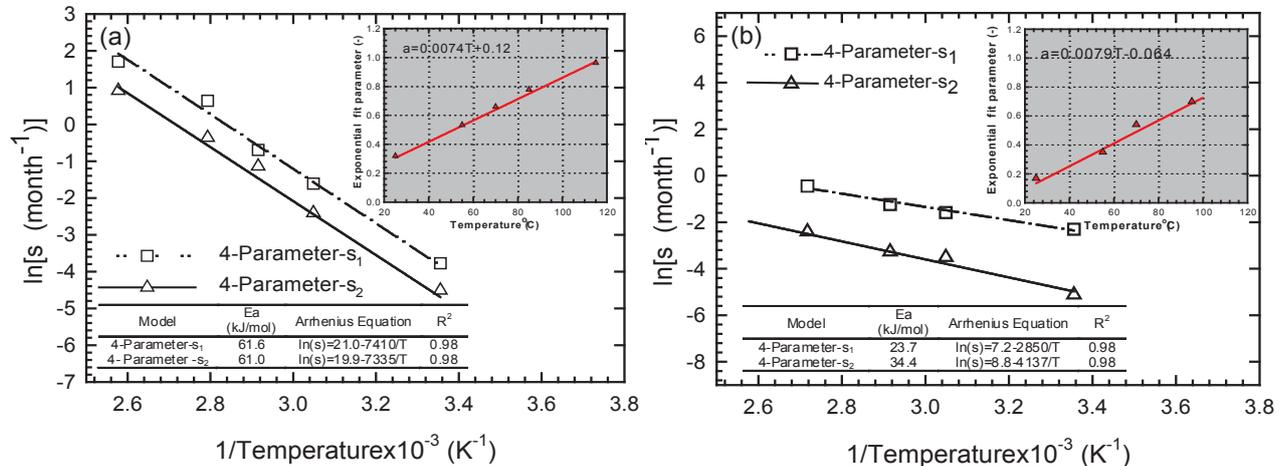

Figure 2. Arrhenius plot for incubation in: (a) MSW leachate; (b) RO water. Modified from Abdelaal and Rowe (2014).

3.1 *Method A*

The sum of the two parameters *a* and *b* in Eq. 2 is unity and hence there is only one independent time dependant variable (e.g., *a*). As shown by Abdelaal and Rowe (2014) this variable can be linearly correlated to the temperature (see insert plots in Figure 2). Hence, for the target temperature, parameter *a* can be interpolated/extrapolated and the depletion time can be obtained. This method can be easily used whether there was a clear change in the depletion rate or not and the 4-parameter model equation can be solved for the time to deplete to any residual OIT value.

The parameter *b* (*b* = 1 - *a*), which represent the intercept of the second rate, s_2, with y-axis, decreases with increasing temperature (*a* is given in the insert to Figure 1b).

3.2 *Method B*

The second method referred to herein as Method B relies on the time temperature superposition technique to shift experimental data at a given temperature (*T*) to the target temperature (T_{target}). Hence, different experimentally obtained curves can be shifted one at a time to the target temperature to superpose a single curve called the master curve. The master curve represents the predicted behaviour of the investigated property at the target temperature. Several investigators have used tTS technique to predict different polymer properties. For HDPE GMBs, Sabir and Brachman (2012) used tTS to extrapolate HDPE GMB tensile strains at different temperatures while Soong et al. (1994) used tTS for stress relaxation predictions. Wong (2011) implemented tTS to predict antioxidant depletion at different temperatures. In this case the incubation time for every OIT value can be shifted by a time-shift factor to the master curve at T_{target}.

For a 2-parameter model, the time-shift factor for a temperature *T* is the ratio between the actual incubation time, *t'*, at temperature *T* and master curve time, t_T, at temperature T_{target}:

$$\text{Shift factor} = \frac{t'}{t_T} = \frac{(OIT_o - OIT_t)s_T}{(OIT_o - OIT_t)s'} = \frac{s_T}{s'} \tag{5}$$

where *t'* and t_T (month) = the incubation times corresponding to OIT_t at temperature *T* and T_{target}, respectively, s_T and *s'* (month^{-1}) = the depletion rates at temperatures *T* and T_{target}, respectively. Hence the shift factor can be written as:

$$\text{Shift factor} = \frac{s_T}{s'} = \frac{Ae^{-\left(\frac{E_a}{R} \times \frac{1}{T_{target}}\right)}}{Ae^{-\left(\frac{E_a}{R} \times \frac{1}{T}\right)}} = e^{\left[\frac{E_a}{R}\left(\frac{1}{T_{target}} - \frac{1}{T}\right)\right]} \tag{6}$$

Thus from Eqs. 5 and 6, the transformed time at the master curve is given by:

$$t' = t \times e^{\left[\frac{E_a}{R}\left(\frac{1}{T_{target}} - \frac{1}{T}\right)\right]} \tag{7}$$

Based on Eq. 7, every data point at any given temperature (*t*, OIT_t)$_T$ can be transformed to (*t'*, OIT_t) at T_{target} on the master curve. For instance, if T_{target} = 30°C, an experimentally obtained data point at 85°C with (*t* = 1 month, OIT_t = 20 min.) would be shifted to the master curve to be (*t'*= 1 month x shift factor, OIT_t =20 min.). The value of the shift factors for temperatures > T_{target} are greater than 1 while temperatures below T_{target} they are less than 1. The data points at the target temperature can be fitted using an exponential function to obtain the master curve and hence the depletion time can be calculated at the target temperature.

Calculating the shift factor based on 4-parameter model depletion is more complicated and cannot be simplified to the form presented in Eq. 7 because the OIT of each data point generally has a contribution from each of the two exponential functions with different activation energies; hence every data point has two different shift factors. In the next section, a means of using Method B for data fitted using the 4-parameter model is discussed for cases with similar and different depletion rates s_1 and s_2 (i.e., leachate and water incubation) and the predictions from this approach are compared with those obtained from Method A.

3.2.1 *Incubation in leachate*

In leachate incubation, the activation energies of both the first and second rates of depletion are almost the same. Hence, Eq. 7 can be used, in an approximate manner, in conjunction with the average activation energy of the two rates to shift all the data at the five temperatures obtained experimentally (25→115°C) to

different target temperatures. Figure 3a shows the experimental data shifted to 55°C using Eq. 7 and their best fit (i.e., master curve; labeled as best fit Method B). Despite some scattering of the shifted data around the experimentally obtained data at 55°C, the master curve of all the shifted data (i.e., best fit Method B) almost coincides with the best fit to the experimentally obtained data. Based on Figure 2a, at 55°C the exponential parameters are predicted to be $a = 0.54$ and $b = 0.46$, giving a regression line obtained from Method A that coincided with the master curve obtained from Method B (Figure 3a; labeled as best fit Method A). Compared to the experimentally obtained data, this shows that both methods well predict the depletion of antioxidants at 55°C. At 50°C (Figure 3b), the predicted master curve obtained from Method B also coincides with the best fit regression line obtained from Method A (based on Figure 2a).
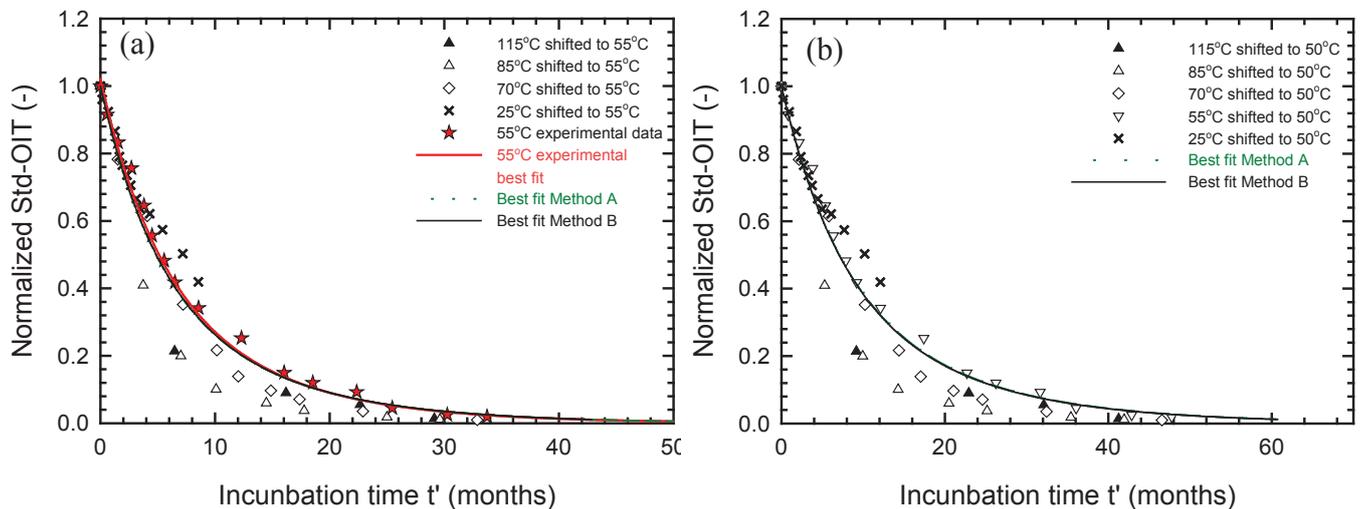

Figure 3. Variation of normalized Std-OIT with transformed incubation time showing the master curve data at: (a) 55°C; (b) 50°C for samples incubated in leachate.

The predictions of the antioxidant depletion times at different temperature for leachate incubation (Table 1) from the two methods agree well at temperatures at the middle of the tested temperature range while for higher and lower temperatures there were small deviations. For example, predicted times to antioxidant depletion based on Methods A/B were 55/50, 4.9/4.9, and 0.2/0.3 years at 20, 50, and 90°C, respectively. The small deviation in the predictions is attributed to the use of the average activation energy for the two depletion rates in Method B as compared to the actual values for each depletion rate in Method A.

Table 1. Antioxidant depletion stage predictions for leachate incubation

Temperature (°C)	Antioxidant depletion stage prediction (years)*	
	Method A	Method B
20	55	50
30	24	22
50	4.9	4.9
90	0.2	0.3

*Residual OIT = 1.5 min.

3.2.2 Incubation in water

For water incubation, Method B cannot be simplified the same way as in leachate since the activation energies of both depletion rates are significantly different. However, the 4-parameter model can be divided into three regions in order to simplify the data shifting. Region 1 from the start of incubation (i.e., $t = 0$) until the two exponential functions intersect contains data points having contribution from both terms of Eq. 2, with the larger contribution coming from the first term. Region 2 starts from point of intersection of the two exponential functions until the contribution of the first term approaches zero with an increasing contribution of the second term. Region 3 only has a contribution of the second term of the 4-parameter model. When there is a low residual OIT, as in the case studied herein (OIT_r=1.5 min.), the end of antioxidant depletion stage occurs in Region 3. Thus, the tTS technique needs only to be implemented for the second term of the 4-parameter model to obtain this time using the activation energy of the second rate in Eq. 7.

In order to assess the start of Region 3 for the OIT curves obtained experimentally, the times at which the first term tends to zero is calculated. Since the first term reaches zero at t→∞, the cutoff value of *OIT*

= 1.5 min. (i.e., similar to OIT_r; $OIT_o/OIT_t = 0.013$) was used to calculate the time at which the first term of Eq. 2 approaches zero and hence the start of Region 3. Based on this assumption, Region 3 was calculated to start after 6.2, 13, 16, and 25.4 months at 95, 70, 55, and 25°C, respectively. Hence, data points at each temperature beyond these times are shifted using shift factors calculated from Eq. 7 using the activation energy of the second depletion rate (i.e., 34.4 kJ/mol).

Figure 4a shows the shifted antioxidant depletion data at T_{target} = 70°C and compared to the experimentally obtained data. There is an agreement between the master curve (Method B), best fit from Method A and the experimental data. However, at other temperatures (e.g. 55°C; Figure 4b), there is a difference between the best fits obtained from both methods and the experimental data unlike leachate incubation. This could be because in leachate, full antioxidant depletion was achieved for four temperatures while in water, full depletion was achieved at only one temperature and hence there is less data to define the parameters in the 4-parameter model and the resulting in the deviation of the predicted depletion rates from the experimentally obtained rates for water incubation. In addition, the short incubation at room temperature with only a few data points in Region 3 resulted in less contribution of the room temperature data to the master curve of Method B and an early estimates of the exponential parameters a and b in Method A and hence resulted in the deviation of predicted best fit from both methods from the experimentally obtained best fits. Thus, longer incubation in water is needed for refinement of the depletion rates and the exponential parameters, especially at 25°C.
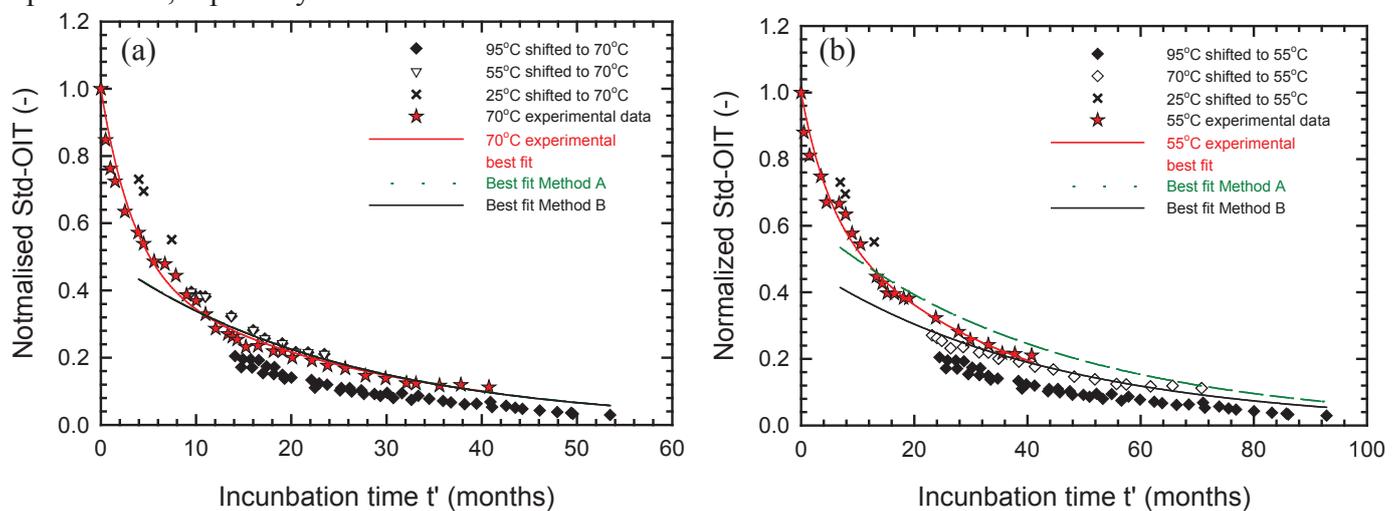

Figure 4. Variation of normalized Std-OIT with transformed incubation time showing the master curve data at: (a) 70°C; (b) 55°C for samples incubated in water.

In general the predictions in water showed a greater difference between the two methods at different temperature than leachate incubation. Predictions for water based on Method A/B were 67/58, 47/37, and 3.4/3.8 years at 20, 30, and 90°C (Table 2). The difference in the predictions from the two methods is mainly due to the difference in the assumption of the variation of the exponential parameter b between the two methods. In order to simplify the shift factor (Eq.7) for Method B, it is assumed that the initial OIT for the second term of the 4-parameter model (i.e., b) is a constant value for all temperatures whereas Method A considers the variation of b with the incubation temperature. The two methods only agree in predictions at similar values of b (e.g. 70°C; Figure 4a). The experimental data suggests that, at least for the GMB examined in the current study, b varies with the temperature. Thus, Method A was more suitable for the predictions of the examined GMB in water than Method B. Nevertheless, Method B gave good approximations with the average deviation from the Method A predictions being about 10% for the temperatures examined.

Table 2. Antioxidant depletion stage predictions for water incubation

Temperature (°C)	Antioxidant depletion stage prediction (years)*	
	Method A	Method B
20	67	58
30	41	37
50	17	16
90	3.4	3.8

*Residual OIT = 1.5 min.

4 CONCLUSIONS

A 4-parameter exponential function was used to fit the antioxidant depletion data for a HDPE GMB incubated in leachate and water. The predictions of antioxidant depletion were compared using two different methods based on Arrhenius modeling. Method A, relies on developing a correlation between the exponential parameters (*a* and *b*) with the incubation temperatures and extrapolate their values at the target temperature. Method B is based on time-temperature superposition technique whereby the antioxidant depletion data is shifted to a target temperature using a shift factor which is a function of the activation energy obtained from the Arrhenius plot. Based on the data presented herein, the following conclusions were reached:

1. For leachate incubation, since there was no significant change in the depletion rates and the depletion of antioxidants was achieved at most of the temperatures examined, Methods A and B gave very close predictions at different temperatures. For this case, the conventional 2-parameter model would also have worked well.

2. For water incubation, there was a difference between the predictions of the antioxidants depletion times between the two methods attributed to the assumption of constant parameter *b* at different temperatures in Method B versus a liner variation of parameter *b* with temperature for Method A. However, the average difference in predictions between the two methods was 10% at different temperatures.

3. For the conditions examined, the implementation of Method A was easier than Method B and Method A better reflected the observed depletion of antioxidants. In addition, Method A was used for both data in leachate and water without any approximation in the computations.

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