EFECT OF HDPE GEOMEMBRANE THICKNESS ON THE DEPLETION OF ANTIOXIDANTS

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ABSTRACT: This study describes an accelerated ageing test to evaluate the effect of thickness on the depletion of antioxidant from high density polyethylene (HDPE) geomembranes. Three HDPE geomembranes having nominal thicknesses of 1.5, 2.0, and 2.5mm were examined in the testing program. The geomembranes were immersed in a synthetic leachate at four temperatures: 22, 55, 70, and 85°C. The depletion of antioxidant was monitored in terms of the oxidative induction time (OIT). It was observed that antioxidants depleted at a faster rate from 1.5mm geomembrane than from the 2.0 and 2.5mm geomembranes. Antioxidant depletion time was predicted using Arrhenius modeling and was found to be longer for thicker geomembranes, which suggests that a thicker geomembrane may be expected to have a longer service life (other things being equal).

RÉSUMÉ
Cette étude décrit un test de vieillissement accéléré qui a pour but d’évaluer l’effet de l’épaisseur sur l’épuisement des antioxydants dans des géomembranes polyéthylène haute densité (PEHD). Trois géomembranes de PEHD de 1,5, 2,0, et 2,5 mm d’épaisseurs nominales ont été examinées dans le programme d’essai. Les géomembranes ont été immergées dans un lixiviat synthétique à quatre températures : 22, 55, 70, et 85°C. L’épuisement des antioxydants a été mesuré en terme de temps d’induction d’oxydation (OIT). Il a été observé que les antioxydants ont réduit à un taux plus rapide dans la géomembrane de 1,5 mm que dans les géomembranes de 2,0 et de 2,5 mm. Le temps d’épuisement des antioxydants a été prédit en utilisant le modèle d’Arrhenius et s’est avéré plus long pour les géomembranes plus épaisses, ce qui suggère qu’une géomembrane plus épaisse ait une durée de vie plus longue (les autres paramètres étant égaux).

1 INTRODUCTION

The use of high density polyethylene (HDPE) geomembrane in landfill liners and final cover systems is increasing and is considered to be the state-of-the-art technology in many countries. The overall objective of using HDPE geomembrane is to limit the migration of toxic contaminants to the ground water. Several factors need to be addressed when selecting geomembranes as landfill liners including leachate interaction, geomembrane thickness, imposed stresses from overlying waste, resistance to friction, seamability, and governing regulations etc. (Peggs and Thiel 1998). Among these factors, the thickness of the geomembrane is usually given more emphasis in different regulations in different countries. In Canada, the Ontario Regulation 232/98 (MOE 1998) specifies a 1.5mm thick geomembrane for primary landfill liner and a 2.0mm thick geomembrane for any secondary landfill liner. In the USA, the minimum thickness is 0.75mm whereas, in Belgium the minimum thickness is 2.5mm (Areias et al. 1998). However to this point there has been very little data examining the effect of geomembrane thickness.

It is generally assumed that geomembranes will experience some degree of ageing or degradation during their service life and the question of durability is of major interest to the stakeholders. Oxidative degradation is the primary concern regarding the long-term durability of HDPE geomembranes (Hawkins 1984). Antioxidants are added to the HDPE resin to control oxidation reactions in the polymer both during manufacture of the geomembrane and during its service life (Grassie and Scott 1995). Antioxidants act by converting free radicals and hydroperoxides, generated during oxidation, into stable molecules (Grassie and Scott 1995). However, the amount of antioxidants present in the geomembrane decreases with the increase of ageing time (Gedde et al. 1994; Hsuan and Koerner 1998; and Sangam and Rowe 2002). Therefore, it is important to evaluate the depletion of antioxidants to assess the service life of geomembranes. Generally laboratory accelerated ageing tests are used to assess the depletion of antioxidants and the long term performance of HDPE geomembranes.

A number of ageing studies have involved the immersion of geomembranes in simulated landfill leachate, acid mine drainage, water, air, and in a simulated landfill composite
liner (e.g., Hsuan and Koerner 1998; Sangam & Rowe 2002; Müller and Jacob 2003; Gulec et al. 2004; Rowe and Rimal 2007 etc.). Samples were periodically tested for different geomembrane properties for example, OIT, melt flow index, crystallinity, tensile strength etc. Lopes et al. (1998) conducted accelerated ageing tests at 60°C using 1.0 and 2.0mm geomembranes by immersing them in real landfill leachate. Their results showed a greater reduction in tensile strength and stiffness for the thinner (1mm) geomembrane than for the thicker (2mm) geomembrane. However, they did not explicitly examine the effect of geomembrane thickness on the depletion of antioxidants in their study.

There is a paucity of research in the literature relating to the effect of thickness on the depletion of antioxidants under similar experimental conditions. Thus the objective of this study is to investigate the effect of thickness on the depletion of antioxidant from HDPE geomembranes.

2 EXPERIMENTAL

2.1 Materials

Three commercially available HDPE geomembranes having nominal thicknesses of 1.5, 2.0, and 2.5mm were used in this study. The geomembranes were manufactured by Solmax International, Varennes, Quebec. The initial OIT (ASTM D3895) of the geomembranes were 135, 150, and 136 min for 1.5, 2.0, and 2.5mm respectively.

2.2 Exposure Conditions

Samples of the geomembranes were cut into 190mm by 100mm coupons which were then placed in 4 litre glass containers. 5mm diameter glass rods were used to separate the coupons from each other and to ensure that each side of every geomembrane sheet was in contact with leachate. The containers were filled with synthetic leachate and were kept in different temperature controlled ovens at 22, 55, 70, and 85°C. The synthetic leachate was produced by mixing trace metals, surfactant, and reducing agents in distilled water (Tables 1 and 2) and was replaced every two weeks. This leachate was shown to be the most conservative and appropriate for evaluating the potential degradation of HDPE geomembranes (Rowe et al. 2007).

2.3 Oxidative Induction Time (OIT) Test

The oxidative induction time (OIT) is a good index of assessing the amount of antioxidant present in the geomembrane (Tisinger 1989; Dudzik and Tisinger 1990; Surman et al. 1995; Hsuan and Koerner 1995 and 1998; Maisonneuve et al. 1997; Sangam and Rowe 2002; Gulec et al. 2004; and Rimal et al. 2004; Rowe and Rimal 2007). The standard OIT tests were carried out according to ASTM D3895 using a TA Instruments Q-100 series differential scanning calorimeter (DSC). In this test, a 6-10 mg specimen was heated from room temperature to 200°C (@20°C/min) under nitrogen atmosphere with a gas flow rate of 50mL/min. The purge gas flow was changed from nitrogen to oxygen at isothermal condition and 35kPa pressure after reaching a temperature of 200°C, and the resulting change in the enthalpy was recorded. The duration between the start of oxygen flow and the onset of exothermal peak was reported as the OIT in minutes.

Table 1. Composition of synthetic leachate

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>Concentration, mL/L (except where noted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trace Metal Solution</td>
<td>1</td>
</tr>
<tr>
<td>Surfactant, Igepal® CA720</td>
<td>5</td>
</tr>
<tr>
<td>E₅ (adjusted by adding 3% w/v Na₂S•9H₂O) (mV)</td>
<td>~ -120</td>
</tr>
</tbody>
</table>

See Table 2

Table 2. Composition of trace metal solution (modified from Hrapovic 2001)

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>Concentration, mg/L (except where noted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrous Sulfate, FeSO₄•7H₂O</td>
<td>2000</td>
</tr>
<tr>
<td>Boric Acid, H₃BO₃</td>
<td>50</td>
</tr>
<tr>
<td>Zinc Sulfate Heptahydrate, ZnSO₄•7H₂O</td>
<td>50</td>
</tr>
<tr>
<td>Cupric Sulfate Pentahydrate, CuSO₄•5H₂O</td>
<td>40</td>
</tr>
<tr>
<td>Manganese Sulfate Monohydrate, MnSO₄•H₂O</td>
<td>500</td>
</tr>
<tr>
<td>Ammonium Molybdate Tetrhydrate, (NH₄)₆Mo7O₂₄•4H₂O</td>
<td>50</td>
</tr>
<tr>
<td>Aluminum Sulphate 16-Hydrate, Al₂(SO₄)₃•16H₂O</td>
<td>30</td>
</tr>
<tr>
<td>Cobaltous Sulphate Heptahydrate, CoSO₄•7H₂O</td>
<td>150</td>
</tr>
<tr>
<td>Nickel (II) Sulfate, NiSO₄•6H₂O</td>
<td>500</td>
</tr>
<tr>
<td>Sulfuric Acid, H₂SO₄ (mL/L)</td>
<td>1</td>
</tr>
</tbody>
</table>
3 RESULTS AND DISCUSSIONS

3.1 Depletion of Antioxidants

Antioxidants deplete with time according to a first order reaction (Hsuan and Koerner 1998; Sangam and Rowe 2002; and Gulec et al. 2004):

\[ OIT_t = OIT_0 e^{-st} \]  

or, by taking natural logarithm on both sides

\[ \ln(OIT_t) = -st + \ln(OIT_0) \]  

where \( OIT_t \) and \( OIT_0 \) represent the OIT remained at time \( t \) and unaged OIT respectively, in minutes, \( s \) is the antioxidant depletion rate in month\(^{-1} \), \( t \) is the leaching time in months. The depletion of antioxidants in the leachate is plotted as \( \ln(OIT) \) versus leaching time in Figure 1 for samples immersed at 85\(^\circ\)C. Each data point is the average of at least five replicate specimens and the vertical bars represent standard deviations. It can be seen that the relationship between \( \ln(OIT) \) and time is linear, where the slope of the regression lines represents the antioxidant depletion rate. The values of depletion rate, \( s \) and the coefficient of determination, \( R^2 \) are shown in the figure legend. The depletion rate for 1.5mm geomembrane is 1.2 and 1.5 times faster than 2.0 and 2.5mm geomembranes respectively (Figure 1a). A similar variation in depletion rates was observed for other temperatures examined. For example, at 22\(^\circ\)C, the depletion rate of 1.5mm geomembrane is 1.4 and 1.6 times faster than for the 2.0 and 2.5mm geomembranes (Figure 2).

It should be noted that the depletion of antioxidants ceases to follow the relationship defined by Eq.2 once the antioxidants are nearing depletion and there is a residual OIT value even when all antioxidants are gone. Thus depletion rate of antioxidants can be sensitive to the lower OIT values. For instance, at 85\(^\circ\)C the retained OIT values for 2.0mm geomembrane were 1.92±0.41, 1.41±0.31 and 0.98±0.37min respectively, after 4.5, 5.5 and 6.5 months of ageing duration. A depletion rate of 0.902month\(^{-1} \) (Figure 1a) was calculated by including OIT data up to 5.5months whereas, a 7% lower depletion rate i.e., 0.844month\(^{-1} \) (Figure 1b) was calculated using data points up to and including 6.5months. Therefore, care should be taken in taking low OIT data points when calculating regression lines.

3.2 Prediction of Antioxidant Depletion Time

The prediction of antioxidant depletion rate at a temperature of interest can be evaluated according to the Arrhenius equation (Hsuan and Koerner 1998):

\[ \text{Figure 1. Variation in } \ln(OIT) \text{ with time at 85}^\circ\text{C for 1.5, 2.0, and 2.5mm geomembranes. (a) Considering up to 5.5months of OIT data in drawing regression line for 2.0mm geomembrane. (b) Considering up to 6.5months of OIT data in establishing the regression line for 2.0mm geomembrane.} \]

\[ \text{Figure 2. Variation in } \ln(OIT) \text{ with time at 22}^\circ\text{C for 1.5, 2.0, and 2.5mm geomembranes.} \]
\[ s = Ae^{-\left(\frac{E_a}{RT}\right)} \]  

or taking natural logarithm on both sides

\[ \ln(s) = \ln(A) - \left(\frac{E_a}{R} \right) \left(\frac{1}{T}\right) \]  

where \( s \) is the antioxidant depletion rate (\( \text{month}^{-1} \)), \( E_a \) is the activation energy of the depletion process (\( \text{J/mol} \)), \( R \) is the universal gas constant (8.314 \( \text{J/(mol K)} \)), \( T \) is the absolute temperature (K), and \( A \) is the collision factor which depends on the material and exposure condition.

Figure 3 shows the Arrhenius plot obtained using Eq. 4 for the three geomembranes. The parameters of the Arrhenius equation are obtained from linear regression analysis and are shown in Table 3. The activation energy varied between 60.3 and 61 kJ/mol for all three geomembranes suggesting that the antioxidant depletion process was similar in all three geomembranes.

Table 3. Activation energy and Arrhenius equation for 1.5, 2.0, and 2.5mm geomembranes.

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Activation Energy, ( E_a ) (kJ/mol)</th>
<th>Arrhenius Equation ( \ln(s) = 20.443 - \frac{7329}{T} )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>60.9</td>
<td>0.993</td>
<td></td>
</tr>
<tr>
<td>2.0(^a)</td>
<td>61.0</td>
<td>0.991</td>
<td></td>
</tr>
<tr>
<td>2.0(^b)</td>
<td>60.3</td>
<td>0.994</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>60.5</td>
<td>0.993</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Considering up to 5.5 months of OIT data at 85°C in drawing regression line for OIT depletion rate.

\(^b\) Considering up to 6.5 months of OIT data at 85°C in drawing regression line for OIT depletion rate.

Table 4. Predicted antioxidant depletion times at three different temperatures for 1.5, 2.0, and 2.5mm geomembranes.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Antioxidant Depletion Time (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.5mm</td>
</tr>
<tr>
<td>20</td>
<td>47</td>
</tr>
<tr>
<td>40</td>
<td>9.5</td>
</tr>
<tr>
<td>60</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\(^a\) For 2.0mm geomembrane, the values inside the parenthesis represent the depletion time when regression line was drawn considering up to 5.5 months of OIT data at 85°C and the values outside the parenthesis represents the depletion time when regression line was drawn considering up to 6.5 months of OIT data at 85°C.

Table 4 shows the calculated antioxidant depletion time for the geomembranes at three hypothetical landfill temperatures (e.g., 20, 40, and 60°C). It can be seen that the time of antioxidant depletion increases with the increased geomembrane thickness. For example, the predicted depletion times at 20°C were 47, 62, and 71 years respectively, for 1.5, 2.0, and 2.5mm geomembranes.

All three geomembranes were produced by the same supplier but from three different resin lots. However while...
there may be some difference in the resin used in each geomembrane, the primary factor contributing to the longer depletion time for thicker geomembrane is the longer diffusion path for antioxidants in a thick geomembrane compared to a thin geomembrane.

It was previously indicated that there is some uncertainty regarding the depletion rates depending on exactly which data is used towards the time when antioxidant are nearly depleted. However when the two different values obtained for the 2mm geomembrane were used, there was negligible difference in predicted antioxidant depletion time (Table 4) and hence this is a second order effect.

4 CONCLUSIONS

A laboratory accelerated ageing test on the depletion of antioxidant from three HDPE geomembranes (e.g., 1.5, 2.0, and 2.5mm) at four different temperatures has been described. Based on the results presented herein, it can be concluded that geomembrane thickness has a significant impact on the depletion of antioxidants with the thicker geomembrane giving the longest antioxidant depletion time. However, it should be emphasized that the selection of geomembrane should be made based on the intended use of the geomembrane, the expected liner temperature and the required service life. For many applications a 1.5mm geomembrane meeting the specifications of GRI GM-13 may be expected to provide adequate performance. Consideration of a thicker geomembrane may be warranted when seeking a longer service life than can be provided by a traditional 1.5mm geomembrane. Even then care must be given to the specification of the material to ensure that the combination of liner thickness, antioxidant package, and resin (e.g., its stress crack resistance) will provide the service life required for the proposed application.

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