Geotextiles and Geomembranes xxx (2014) 1–15

Contents lists available at ScienceDirect

Geotextiles and Geomembranes

journal homepage: www.elsevier.com/locate/geotexmem

Antioxidant depletion from five geomembranes of same resin but of different thicknesses immersed in leachate☆

R. Kerry Rowe*, A.M.R. Ewais [1]

GeoEngineering Centre at Queen's-RMC, Queen's University, Ellis Hall, Kingston, Ontario K7L 3N6, Canada

ARTICLE INFO

Article history:
Received 26 January 2014
Received in revised form
2 July 2014
Accepted 27 July 2014
Available online xxx

Keywords:
Geosynthetics
High density polyethylene
Stabilizers
HALS
Oxidative induction time
Arrhenius modeling

ABSTRACT

The effect of thickness on the antioxidants depletion time for five high density polyethylene geomembranes (with nominal thicknesses of 0.5, 1.0, 1.5, 2.0, and 2.4 mm) immersed in synthetic leachate at six different temperatures (25, 40, 55, 70, 85 and 95 °C) is investigated. The geomembranes were manufactured from the same geomembrane resin (i.e., polymer resin, antioxidant/stabilizer package, and carbon-black batch). Four (1.0, 1.5, 2.0, and 2.4 mm) of the five geomembranes were manufactured during the same production run by changing the pulling speed of the geomembrane from the extrusion die. The depletion of antioxidants/stabilizers inferred from both standard (Std-) and high pressure (HP-) oxidative induction times (OIT)s show that increasing geomembrane thickness resulted in longer depletion times for temperatures above 40 °C but little to negligible difference in projected depletion times below 40 °C for this antioxidant package. The increase in depletion times was not proportional to the square of the geomembrane thickness as theoretically predicted if depletion was diffusion controlled and the diffusion coefficient was the same for each GMB. Thus, the depletion of antioxidants is not fully governed by diffusion and/or the GMB's diffusion coefficients are different. Regardless of the GMB thickness, the time for Std-OIT depletion was shorter than the time to residual HP-OIT above 70 °C but was longer at or below 55 °C. For example, for 2.4 mm GMB, the inferred time for Std-OIT depletion was 0.2–0.3 (at 85 °C), 2–3.5 (at 55 °C) and 9.5 (at 40 °C) times that for the HP-OIT to deplete to residual. The projected Std-OIT depletion times for 1.0 and 2.4 mm GMBs were: 2.7 and 4 years, respectively, at 60 °C; 23 and 26 years, respectively, at 40 °C; and about 330 years at 20 °C.

1. Introduction

Since the contaminating life span of municipal solid waste landfills can be more than a century, the long-term performance of high density polyethylene (HDPE) geomembranes (GMB) used as part of the liner system in many of these landfills is of major interest (Rowe et al., 2004). In a landfill, the GMB is exposed to leachate and the liner temperature can range between 0 and 30 °C for landfills in which there are no biological or chemical reactions taking place (with the temperature depending on local ambient conditions), 30–40 °C for normal municipal solid waste landfills with organic waste but no stimulation of biological activity, 40–65 °C in some ash monofills and some municipal solid waste landfills (especially those with aggressive leachate recirculation), and 65–90 °C in rare cases (Rowe, 2012; Stark et al., 2012). Elevated temperatures would accelerate GMB degradation, resulting in the loss of GMB mechanical properties with time. If subject to tensile stress, eventually, the GMB will rupture and will no longer be able to prevent contaminants and gases from escaping (Abdelaal et al., 2014; Ewais et al., 2014b). The service-life of an HDPE GMB is generally defined as the time during which the GMB will act as an effective hydraulic and diffusive barrier to contaminant migration (Rowe et al., 2004).

Modern stabilized HDPE GMBs normally comprise 96–97% (by weight) medium density polyethylene resin, 2–3% carbon-black and around 0.5% antioxidants and stabilizers (e.g., hindered amine (light) stabilizers, HALS or HAS; Hsuan et al., 2008; Scheirs 2009). The carbon-black, antioxidants and stabilizers are used to enhance the long-term performance of the GMB by protecting the polymer from degradation due to photo-oxidation and/or thermal oxidation. However, the antioxidants/stabilizers will deplete and the time to depletion is a major component of the service-life of a GMB.

☆ Dr. R.J. Bathurst acted as Editor for the review of this paper.

* Corresponding author. Tel.: +1 613 533 3113; fax: +1 613 533 2128.
E-mail addresses: kerry@civil.queensu.ca, rowe.gng@queensu.ca (R.K. Rowe), amr.ewais@ce.queensu.ca (A.M.R. Ewais).
[1] Tel.: +1 613 533 6000x77142; fax: +1 613 533 2128.

http://dx.doi.org/10.1016/j.geotexmem.2014.08.001
0266-1144/

The depletion of antioxidants/stabilizers in an HDPE GMB may be due to: (a) chemical reactions involving free radicals, oxygen and hydroperoxides and/or hydrolysis, and/or (b) physical loss associated with diffusion and volatilization (Luston, 1986; Haxo and Nelson, 1984; Koerner et al., 1990; Hsuan and Koerner, 1998; Müller and Jacob, 2003). One would expect that mechanisms dominated by diffusion such as physical loss of antioxidants out of the GMB or diffusion of oxygen into the GMB to react with antioxidants would be affected by GMB thickness. Antioxidant depletion would also be affected by exposure conditions (Rowe et al., 2008, 2009), type of antioxidants (Pauquet et al., 1993), and carbon-black characteristics (Wong and Hsuan, 2012).

Carbon-black can play an important role in antioxidants depletion or deactivation. Wong and Hsuan (2012) showed that increasing the surface area of the carbon-black would result in increasing the depletion of the antioxidants (Irganox 1010 and Irgafos 168) detected by the standard oxidative induction test (Std-OIT, ASTM D3895) due to the presence of carbon–oxygen functional groups on the carbon black surface (Kovacs and Wolkober, 1976). Peña et al. (2001a–f) studied the interaction of different types of antioxidants and stabilizers with different types of carbon-black and found that in addition to the specific surface area of the carbon-black, the interaction between antioxidants/stabilizers and carbon-black is also affected by the chemical nature of carbon-black surface and the chemistry and molecular structure of the antioxidants/stabilizers. These interactions may result in deactivation of some antioxidants/stabilizers present in GMBs such that they are still detected by the test but are not effective in protecting the GMB from chemical degradation (Ewais et al., 2014a).

Even for one manufacturer, the values of the initial properties of a geomembrane that meet a generic specification (such as GRI-GM13, 2011) may change from time to time (although their nominal thicknesses are identical) because of: (a) a change in the specific polyethylene resin being used (e.g., due to a change in resin supplier), (b) a change in the carbon-black batches, and/or (c) a change in antioxidant/stabilizer package. With respect to the latter, the manufacturers of the polyethylene resin generally add the main antioxidants used in protecting the GMB to the polyethylene resin; however, the GMB's manufacturer may add additional antioxidants/stabilizers to the original resin for a specific product or application and the specific antioxidants/stabilizers and/or their concentration may be varied from time to time. Thus, the antioxidant depletion time and service-life of HDPE GMBs of the same thickness (even from the same manufacturer) may vary depending on the interactions between the components of the final GMB and the environment in which they are used (Ewais et al., 2014a).

The minimum GMB thickness required by regulations/specifications varies from country to country although 1.5 mm is the most common. The requirement for a thicker GMB (e.g., MoE, 1998) is usually linked to an anticipated longer service-life for the thicker GMB (Rowe et al., 2010a). When antioxidant depletion is governed by diffusion, a GMB thickness would increase the time taken by antioxidants to deplete out of the GMB (Rimal and Rowe, 2009) and would be controlled by Fick's second law, viz;

$$\frac{\delta c}{\delta t} = D_g \frac{\delta^2 c}{\delta z^2} \tag{1}$$

where c is the concentration of antioxidants [ML^{-3}], D_g is the diffusion coefficient of the antioxidant out of the GMB [L^2T^{-1}], t is the time [T], and z is distance parallel to the direction of diffusion [L]. Rimal and Rowe (2009) gave an expression for the depletion in the OIT with time for a GMB based on the analytical solution of Eq. (1) (Crank, 1975), viz;

$$\frac{OIT_t}{OIT_o} = \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left\{ -(2n+1)^2\pi^2 \frac{D_g}{H^2} t \right\} \tag{2}$$

where OIT_t is the OIT (min) at the time of interest t, OIT_o (min) is the initial OIT (min) (i.e., at $t = 0$), t is the incubation time (months), n is an integer number, and H is the thickness of the GMB (mm). Several investigators (e.g., Hsuan and Koerner, 1998; Sangam and Rowe, 2002; Müller and Jacob, 2003; Gulec et al., 2004; Rowe et al., 2009,2010a,b) have monitored OIT depletion with time for different GMBs and found, empirically, that OIT depletion data can be approximated by a two parameter exponential decay model, viz;

$$OIT_t = OIT_o \exp\{-st\} \tag{3}$$

where s is the antioxidant depletion rate ($months^{-1}$). Rimal and Rowe (2009) fitted some experimental data with both Eqs. (2) and (3) and they found that Eq. (2) provided a better fit to the OIT data than the exponential model (Eq. (3)); however both equations were satisfactory and in close agreement provided that there was data over sufficient time to capture a significant depletion in OIT. Comparing Eqs. (2) and (3) it may be inferred that s is inversely proportional to square the thickness of the GMB (Eq. (4)), viz;

$$s \alpha \frac{D_g}{H^2} \tag{4}$$

Rowe et al. (2010a) investigated the effect of thickness on the diffusion of antioxidants from three commercial HDPE GMBs of different thickness (1.5, 2.0 and 2.5 mm). They found that the antioxidant depletion rate decreased with increasing thickness; however, the decrease in the antioxidants depletion rate was not inversely proportional to the square of the thickness as would be expected based on Eq. (4). Although the HDPE GMBs investigated by Rowe et al. (2010a) were supplied by the same manufacturer, they were manufactured at different times and their initial properties were different, implying that one or more of the components of the GMB resin (polyethylene resin, antioxidants/stabilizers and carbon-black) was different and this may have affected the antioxidant depletion from the three GMBs. Rowe et al. (2010a) concluded that their findings may not fully explain the effect of thickness and indicated the need to study the effect of thickness for GMBs manufactured from the same resin (all components). Thus, the objective of this study is to investigate the effect of GMB thickness on antioxidant depletion for HDPE GMBs produced sequentially by the same manufacturer from the same GMB resin and production run.

2. Test methods

2.1. Differential scanning calorimetry (DSC) scan

Differential scanning calorimetry (DSC) was used to measure the changes in heat-flow with increasing temperature (ASTM E793) using a TA Instruments, Q-100 series DSC. Specimens were cut through the whole thickness of the GMB and were placed in clean aluminum pans such that the thickness of the specimen perpendicular to the pan is equal to 1.0 mm as recommended in Ewais and Rowe (2014a). The temperature of the chamber was held at 0 °C for 5 min; then heated to 200 °C at a rate of 10 °C per minute and the endothermic heat-flow with the change in temperature was recorded and plotted versus temperature. This plot will be referred to as the DSC scan.

The endothermic heat generated in the DSC scan at a given temperature is due to the melting of the crystal lamellae (of equal

Please cite this article in press as: Rowe, R.K., Ewais, A.M.R., Antioxidant depletion from five geomembranes of same resin but of different thicknesses immersed in leachate, Geotextiles and Geomembranes (2014), http://dx.doi.org/10.1016/j.geotexmem.2014.08.001