EVALUATION OF PHOTO DEGRADATION OF GEOMEMBRANE

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ABSTRACT

In some geotechnical applications a geomembrane may be exposed for varying periods where UV (ultraviolet) radiation and elevated temperature cause degradation of geomembrane in a free radical oxidation mechanism. In this paper, the effect of UV (ultraviolet) exposure on HDPE (high density polyethylene) and f-PP (flexible polypropylene) geomembranes is evaluated. The results of density, carbon black content (CBC) tensile properties, Melt Flow Index (MFI) and Oxidation Induction Time (OIT) (both Standard-OIT and High Pressure-OIT) are discussed. An increase in density implies increase in brittleness and a slight decrease in CBC implies the effectiveness of carbon black to prevent photo-oxidation. Although tensile properties of the exposed samples remained unchanged, the depletion of antioxidants was found higher for f-PP than for HDPE. There was no significant difference between the MFI value of the virgin and exposed HDPE GM samples but a decrease in MFI was found in f-PP GM that signifies that cross-linking has occurred.

Keywords: Photo-degradation, geomembrane, oxidative induction test

INTRODUCTION

There are many geotechnical applications where the geomembranes (GM) may be exposed for varying periods. Ultraviolet (UV) radiation and elevated temperatures are very harmful to all geosynthetics (Lodi et al 2008). The weathering factors affect durability are: solar radiation, temperature (elevated, depressed, and cycles and fluctuations), water (solid, liquid, and vapor), and normal air constituents (oxygen and ozone) (Rollin 2004). The radiation of the sun, particularly the ultraviolet (UV) portion is mainly responsible for limiting the lifetime of materials exposed to the environment. Exposed GM to sunlight can oxidize and crack over time. This degradation is the result of the combined effects of thermal and UV radiation that can generate damaging free radicals. These free radicals quickly react with oxygen leading to unstable intermediates called hydroperoxides that can in turn cause oxidative degradation of polymers (Suits et al. 2003). Antioxidants, stabilizers and carbon black present in the GM formulation can all scavenge or neutralize free radicals thus delaying onset of the oxidation degradation. While carbon black is permanent filler residing in the polymer, antioxidants and stabilizers can be depleted by leaching or consumption and thus they have a limited lifetime (Scheirs 2009).

Solar radiation is generally divided into various regions or bands on the basis of wavelengths, for example: infrared region (780-1400 nm), visible region (400-780 nm), and UV region (290- 400 nm). When solar radiation strikes the exposed polymer surface, photons with energy similar, or higher than the chemical bond strength of the polymer cause a series of reactions that can lead to polymer chain scission and eventual degradation of polymer properties. For instance, the chemical bond strengths of *C-C* and *C-H* bonds are 420 and 340 kJ/mol, respectively. On the other hand, the energies of 300 and 400 nm photons (in the UV range) are 390 and 300 kJ/mol, respectively. Thus, the UV radiation has adequate energy to break chemical bonds of polymers, with the shorter wavelengths being more severe. The most effective spectral region of irradiation to cause the photo-oxidation of PE and PP is in the range 330-360nm and 335-360nm respectively which fall within the UV region (<400 nm) (Hu 1997, Zhang et al. 1996).

Degradation of polyethylene (PE) or polypropylene (PP) is controlled by photo-oxidation through a series of free radical reactions in Sunlight or UV radiation:

$$RH + O2 + h\upsilon \longrightarrow R\cdot + ROO\cdot + RO\cdot + OH\cdot \qquad (1)$$

where *RH* is the polymer chain, hυ is the photon energy with h and υ representing Planck's constant and wavelength, respectively, and *R·*, *ROO·*, *RO·* and OH· are the free radical species with *R* representing the polymer chain. The oxidation

reaction beaks down the polymer chain and capitulates carbonyl compound. It has been found that a lower energy is needed to generate free radicals in polyolefins than to break a bond which may indicate the vulnerability of polyolefins to UV degradation than other types of polymers. Therefore, an appropriate UV stabilization is usually required in polyolefin products (Suits et al. 2003).

Generally, region UV can be subdivided in three bands of wave lengths: UV-A (315-400 nm), UV-B (290-315 nm) and UV-C (below of 290 nm). Band of UV-B is mainly the responsible one for the photochemistry changes in polymers (Scheirs 2009). The single most significant component of simulated weather is the nature of the radiation source. The type and intensity of radiation to which the materials are exposed are the dominant factors in accelerating degradation (ASTM G154). Fluorescent UVB lamps have the spectral distribution of radiation peaking near the 313-nm mercury line. They emit significant amounts of radiation below 300 nm, the nominal cut on wavelength of global solar radiation, which may result in aging processes not occurring outdoors. In this study UVB-313 lamps (Fig.1) were used that emit UV below the normal sunlight cut-on that can lead to rapid polymer degradation.
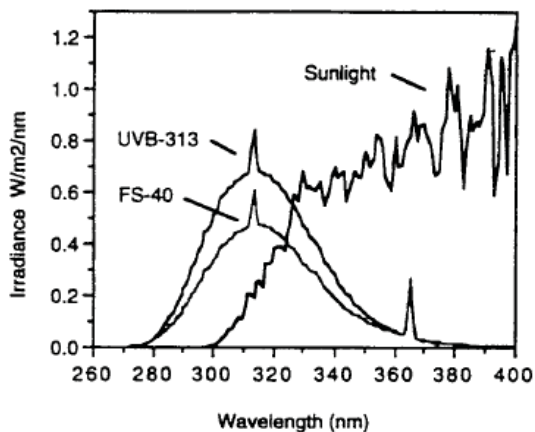

Fig 1 Spectral power distributions of UVB lamps and sunlight (ASTM G154).

This paper presents the effect of UV degradation and condensation in HDPE (high density polyethylene) (both smooth and textured surfaced) and f-PP (flexible polypropylene) GM that were exposed to laboratory accelerated UV exposure. The results of density, carbon black content (CBC) tensile properties, Melt Flow Index (MFI) and Oxidation Induction Time (OIT) (both Standard-OIT and High Pressure-OIT) are discussed.

MATERIAL AND EXPOSURE CONDITION

Three types of GM were used for photo-degradation experiments: commercially available f-PP GM (1.14mm) and HDPE GM: black smooth (2.0 mm) and black textured (2.0 mm). f-PP GM was supplied by Firestone specialty products and HDPE geomembrane was supplied by Goldenpow Co., Ltd. Using UVB-313 lamps three types of specimens were exposed for photo degradation at a customized cycle of 4 hrs UV (IR = 1.23 Wm-2) at 80º C and 4 hrs condensation at 60º C for 4320 hrs (upto 6 months). Q-UV weatherometer was used in this regard (Fig. 2). The following tests were carried out after exposure.

Fig 2 Interior of the Q-UV weatherometer.

TESTING METHOD TO EVALUATE DEGRADATION

Density: The density or specific gravity of a GM is dependent on the base material from which itin is made. There are distinct differences, however, even in the same generic polymer. For example, polyethylene comes in very low density, low density, linear low density, medium density, and high density varieties. The range for all geomembrane polymers falls within the general limits of 0.85 to 0.96 g/cm3. A relevant ASTM test method is D792. This test method is based on the fundamental Archimedean principle of specific gravity as the weight of the object in air divided by its weight in water. A more accurate method is ASTM D1505, "Density Determination by the Density Column." Here a long glass column containing liquid varying from high density at the bottom to low density at the top is used. For example, isopropanol with water is used for densities less than 1.0. Upon setup, spheres of known densities are immersed in the column to generate a calibration curve. Small pieces of the polymer test specimens are then dropped into the column. Their equilibrium level within the column is used with the calibration curve to find the specimen's density. Accuracy is very good, within 0.002g/cm3, when proper care is taken.

Carbon Black Contents: Carbon black is added into a HDPE and f-PP GM formulation mainly for UV light blocking agent stabilization. Carbon black absorbs the harmful UV radiation and dissipates the energy into heat, thus prolonging the outdoor life of the GM. The loading range of carbon black in GM is typically 2 to 3% for HDPE and 2 to 4% for f-PP by weight. Up to the level of capacity, the higher the loading of carbon black, the greater is the degree of ultraviolet light stability. However, the addition of carbon black above the capacity level (which is around 3%) will not further improve ultraviolet resistance. Thermal gravimetric analyzer (TGA) is used for this study.

Tensile Test: The mechanical performance of the incubated GM samples was evaluated using a tensile test (INSTRON 3343), since stress and strain are the essential design parameters for the material. ASTM D6693-04 was used to conduct the test. Four tensile properties were monitored in the investigation: yield stress, yield strain, break stress and break strain. Three replicate tests were performed and average values are reported. It should be recognized that break strain and break stress have a greater sensitivity to molecular changes than yield strain and yield stress. Also, modulus is a contentious parameter in tensile property of a polymer (Hsuan and Koerner 1998). This is because strain value at the beginning of the tensile test is very difficult to measure and greatly depending on the type of extensometer used. Hence, it is not reported.

Melt Flow Index (MFI) test: The MFI test, ASTM D1238, is a qualitative method to assess the molecular weight of the polymer. The MFI test measures the amount of molten polymer at 190ºC for polyethylene and 230ºC for polypropylene extruded through an orifice with a defined diameter under a load of 2.16 kg in 10 minutes. The result is expressed in units of g/10 min. A high melt index value indicates a low molecular weight, and vice versa. Hence, the melt index value will decrease for cross-linking reactions and increase to chain scission reactions (Hsuan and Koerner 1998). In this study, 3 grams of material were taken from each of the exposed and intact GM. The material was cut in small pieces approximately 2 to 3 mm cubes in size. The amount of molten polymer extruded in 6 min was determined. The result was then converted to g/10 min. Three replicates were tested for each specimen and the results were averaged.

Standard Oxidative Induction Time (Std-OIT) test: The Std-OIT test was performed according to ASTM D3895. The test uses a different scanning calorimeter (DSC) with a specimen testing cell that can sustain a 35 kPa gauge pressure. A 5mg test specimen was taken from the UV exposed samples.

The specimen was cut from the surface to surface across the thickness of the GM near the center portion of the sample. Therefore, the resulting OIT values represent the average amount of antioxidant across the thickness of the test specimens (Hsuan and Koerner 1998). The specimen was heated from room temperature to 200° C at a heating rate of 20° C/min under a nitrogen atmosphere. The gas flow rate was maintained at 50mL/min. When 200° C was reached, the cell was maintained in an isothermal condition for 5 min. The gas was then changed from nitrogen to oxygen. The pressure and flow rate of oxygen were 35 kPa gauge pressure and 50mL/min, respectively. The test was terminated after an exothermal peak, hence oxidation of the GM was detected. Fig. 3 shows an example thermal curve with its identified OIT value.
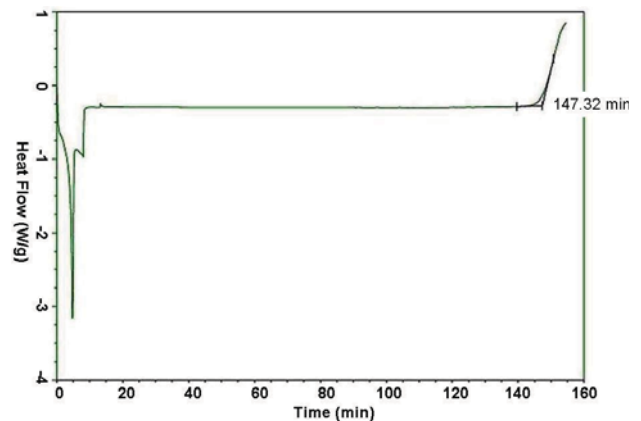

Fig. 3 Thermal curve from Std-OIT test of HDPE geomembrane

High Pressure Oxidative Induction Time (HP-OIT) test: The HP-OIT test was also performed using a differential scanning calorimeter (DSC) with a different cell that can sustain 5,500 kPa. This type of cell is called a higher pressure cell and consequently the test is called high pressure OIT (ASTM D 6693).The HP-OIT test procedure was performed according to D5885, with a minor modification. A 5 mg test specimen was cut from surface to surface across the thickness of the UV exposed sample near the center portion of the sample. The specimen was heated from room temperature to 150° C (for HDPE) and 170º C (for f-PP) at a heating rate of 20° C/min under a nitrogen atmosphere. The pressure of the cell in this stage was maintained at 35 kPa gauge pressure. The gas flow rate was not monitored. When 150° C temperature was reached, the cell was maintained in an isothermal condition for 5 min. The gas was then changed from nitrogen to oxygen. The oxygen pressure in the cell was increased to 3,400 kPa within 1 min. The test was terminated after an exothermal peak was detected. The response thermal curve is similar to that shown in Figure 3 for the Std-OIT test.

The main reason behind developing the HP-OIT test is that the 200° C testing temperature used in the Std-OIT test is unable to evaluate the stabilization effect of hindered amine antioxidants. The maximum effective temperature of hindered amine is below 150° C (Hsuan and Koerner 1998). At 200° C, hindered amine molecules rapidly volatilize from the GM, thus losing their intended effect at in-situ temperatures. As a result, GM with hindered amine antioxidants will exhibit a shorter OIT value than those without. Yet the long-term performance of these GM may be very similar to, or even better than, those without hindered amine antioxidants. In the HP-OIT test, the test temperature is lowered to 150° C for HDPE and 170º C for PP, which is the minimum temperature to ensure complete melting of the HDPE and PP GM specimen respectively. The low testing temperature, however, results in a relatively long test at the standard pressure of 35 kPa making the test somewhat unpractical. Hence, a high pressure is applied. At a higher oxygen pressure, the concentration gradient of oxygen atoms becomes greater. This increases the number of oxygen atoms diffusing into the molten specimen, thereby accelerating the oxidation and reducing the testing time.

RESULTS AND DISCUSSION

Density: HDPE and PP GM is semi-crystalline polymer and its density is related to the degree of crystallinity. Any change in the density is regarded as a modification in the crystallinity. For example, any decrease in density implies a decrease of the crystalline content of the material. The density of the samples under investigation was measured according to ASTM D 1505. Three specimens cut from samples from each exposure conditions were tested and the average values are presented in Table 1. The results are slightly increased, but very similar for all conditions. Based on these results, the density values were changed within the high density range. The high density implies a high degree of crystallinity and a GM that would be more susceptible to stress cracking than a less crystalline GM. The increase indicates that the material brittleness increases.

Table 1 Density of intact and UV exposed geomembrane.

Types	Intact (g/cm^3)	UV exposed (g/cm^3)
HDPE smooth	0.949	0.951
HDPE textured	0.948	0.950
f-PP	0.939	0.944

Carbon Black Content (CBC): Carbon black is

added into HDPE and PP GM formulation for general stabilization purpose.

Tests were performed using Thermal Gravimetric Analyzer (TGA). Three replicates were tested for each sample. CBC results are show in Table 2. The CBC values were slightly decreased after UV exposure. The carbon black was exhausted by UV radiation that the temperature and ageing time influenced to consume the carbon black. The period of UV exposure was not too long to consume all the carbon black in the GM.

Table 2 Carbon black content of intact and UV exposed geomembrane.

Types	Intact (%)	UV exposed (%)
HDPE smooth	2.6	2.2
HDPE textured	2.3	2.2
f-PP	7.9	7.0

Tensile Properties: The responses of tensile properties of the UV exposed samples are presented in the Fig. 4. Each of the properties is plotted as a percent retained from its original, intact value against the value after exposure. The four sets of material property data (yield stress, yield strain, break stress, break strain) do not appear to have any significant change over 8-month incubation period.
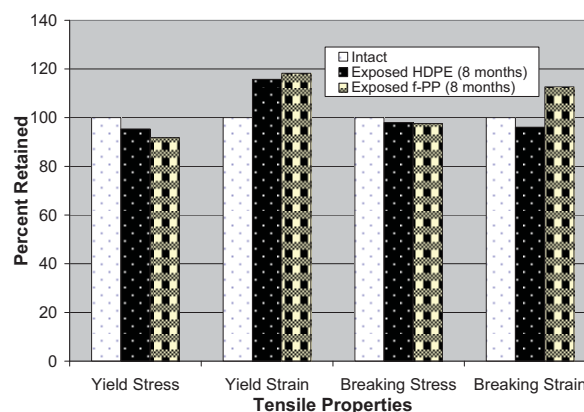

Fig. 4 Tensile properties of geomembrane

Melt Flow Index (MFI) test: Melt flow index values provide information on molar mass related phenomena. MFI is a measure of the ability of the material to flow under pressure and relates to melt viscosity. The MFI has an inverse relationship to melt viscosity under the conditions on test. The viscosity measurement is dependent on the applied force. An increase in the MFI indicates a decrease in the molar mass (due to chain scission reaction), a decrease in the viscosity and hence the material flows more easily. In the same way, a decrease in MFI can signify that cross-linking has occurred. The melt flow index (MFI) test results for the HDPE and f-PP GM were obtained in the laboratory (Fig. 5). It

was noted that there was no significant difference (less than 5% decrease) between the MFI value of the virgin and exposed HDPE (smooth) GM samples. This is consistent with the results for tensile properties of the GM. The MFI results imply that there was no change in molecular weight of the material. In contrast, a significant decrease in MFI which is 25% for exposed f-PP GM samples and 56% for HDPE-textured is clearly the evidence of cross-linking. However, Crosslink after exposure is always an indicative of superficial degradation (Lodi et al. 2008).
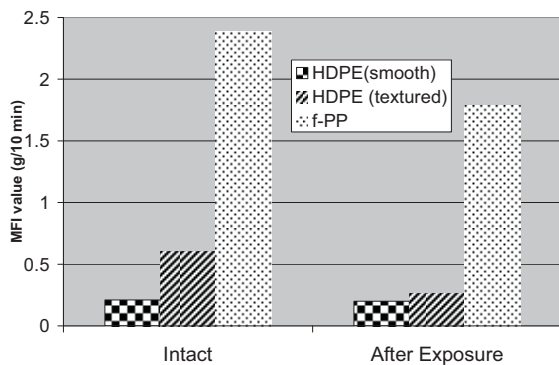

Fig. 5 Melt flow index of geomembrane

Std-OIT and HP-OIT Test Results: The OIT test results on specimens taken from the retrieved UV exposed samples are shown in Fig. 6 for std-OIT and Fig. 7 for HP-OIT. While some scatter is seen, the trend of exponential decrease at all incubation temperature is obvious for HP-OIT for all types of sample and for Std-OIT for f-PP samples. On the contrast, Std-OIT value decreases drastically for HDPE that implies antioxidants in the GM consisted of hindered amines.
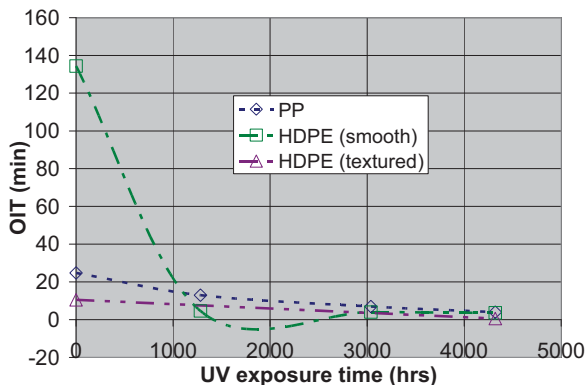

Fig. 6 Std-OIT value vs. UV exposure time at 80º C

The behavior in each test indicates that the OIT reduction occurred continuously and gradually as incubation time increased in both tests for f-PP. OIT values exhibited very similar depletion trends, although the depletion rates of the HP-OIT data

were slower than that of the Std-OIT. A linear correlation was found between these two sets of OIT values for f-PP, as shown in Figure 8. This suggests that either Std-OIT or HP-OIT can be used to evaluate the depletion of antioxidant for this particular f-PP GM formulation.
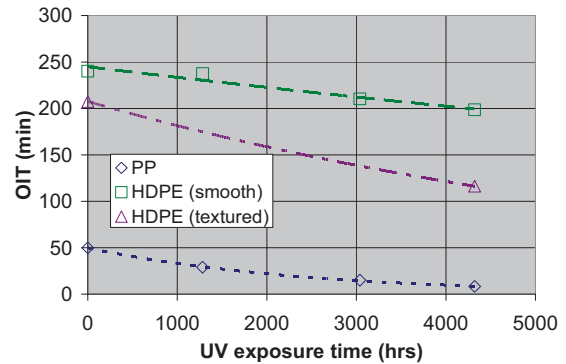

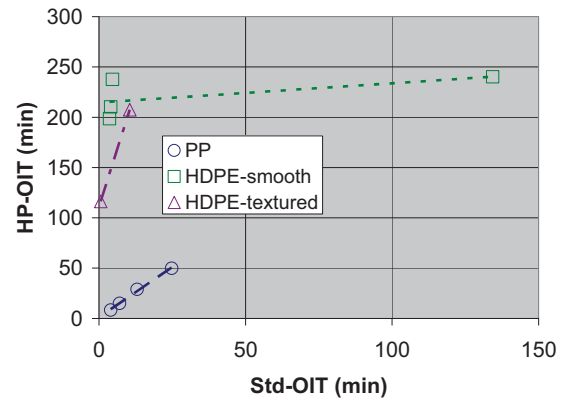Fig. 7 HP-OIT value vs. UV exposure time at 80º C

Fig 8 HP-OIT vs. Std-OIT

On the other hand, no linear correlation was found between these two sets of OIT values for HDPE, as shown in Fig. 8 which may suggest that only HP-OIT should be used to evaluate the depletion of antioxidant for the particular HDPE GM formulation. Furthermore, it implies that there are no hindered amines in the f-PP GM and major antioxidants in this GM probably consisted of phosphites and hindered phenols; but the major antioxidants in the HDPE GM probably consisted of hindered amine. (Hsuan and Guan 1997).

CONCLUSIONS

The changes in chemical and physical properties resulting from accelerated laboratory UV exposure of HDPE and f-PP GM were studied, by exposure to Q-UV weatherometer at 80º C for a period of 6 months. The mechanical properties of the polymer remained unaffected. There was an increase in density that implies increase in brittleness and a slight decrease in CBC implies the effectiveness of

carbon black to prevent photo-oxidation. The molecular weight remained essentially constant as was shown by the MFI measurements for HDPE but a decrease in MFI for f-PP is the evidence of cross-linking. OIT decreased with exposure time for all exposed specimen. The above data indicate that within the experimental conditions used in this work, HDPE GM showed an acceptable performance and was not significantly deteriorated upon exposure to this specific condition used in this work while the particular f-PP GM may not be able to withstand long-term UV exposure.

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