

자외선 노출조건 하에서 가속시험에 의한 지오폴리머의 분해거동 해석

박영목 · Belas Ahmed Khan* · 전한용**†

영남대학교 건설시스템공학과, *인하대학교 대학원 섬유공학과, **인하대학교 나노시스템공학과
(2012년 5월 30일 접수, 2012년 8월 21일 수정, 2012년 9월 15일 채택)

Analysis of Degradation Behaviors of Geomembrane by Accelerated Test under UV Exposure Conditions

Yeong Mog Park, Belas Ahmed Khan*, and Han Yong Jeon**†

Department of Civil Engineering, Yeungnam University, Gyeongsan 712-749, Korea

*Department of Textile Engineering, Inha University Graduate School, Incheon 402-751, Korea

**Division of Nano-systems Engineering, Inha University, Incheon 402-751, Korea

(Received May 30, 2012; Revised August 21, 2012; Accepted September 15, 2012)

초록: 본 연구에서는 UVB-313(자외선 파장 290-315 nm) 노출 하에 smooth HDPE 지오폴리머와 flexible PP 지오폴리머에 대한 자외선 노출의 영향을 평가하였다. 인장특성, 용융지수, 표준 및 고압 산화유도시간 및 FTIR/ATR 결과들을 고찰하였다. 노출된 지오폴리머 시료의 인장특성은 변하지 않았지만, HDPE 지오폴리머보다 flexible PP 지오폴리머의 경우 산화방지제의 감소가 더 큼을 알 수 있었다. 대표적인 현상온도 20 °C에서의 산화방지제의 수명을 예측하기 위하여 외삽에 의한 Arrhenius 모델을 적용하였다. 자외선 노출 전후의 HDPE 지오폴리머 시료는 용융지수의 큰 차이는 없었지만 flexible PP 지오폴리머는 가교발생으로 인한 용융지수 감소가 발생하였다. FTIR 스펙트럼으로부터 자외선에 노출된 시료의 경우 카르보닐기와 관련된 1750 cm⁻¹ 부근에서 작은 피크가 발견되었으며, 이는 산화가 진행되었음을 예시하고 flexible PP 지오폴리머의 경우 3100~3500 cm⁻¹에서 하이드록시기 또는 하이드로퍼옥사이드기에 의한 새로운 피크를 확인할 수 있었다.

Abstract: In this paper the effect of UV (ultraviolet) exposure on HDPE (high density polyethylene)-smooth and f-PP (flexible polypropylene) geomembranes is evaluated under UVB-313 (ultraviolet wavelength 290-315 nm) exposure. Tensile property, melt flow index (MFI), oxidation induction time (OIT), both standard-OIT and high pressure-OIT and Fourier transform infrared spectroscopy/attenuated total reflectance (FTIR/ATR) results are discussed. Although tensile properties of the exposed geomembrane samples remained unchanged, the depletion of antioxidants was found higher for f-PP than for HDPE geomembrane. Arrhenius model by extrapolation was used on the data to predict the antioxidant lifetime to a typical site temperature of 20 °C. There was no significant difference between the MFI value of the virgin and UV exposed HDPE geomembrane samples but a decrease in MFI was found in f-PP geomembrane that signifies that crosslinking has occurred. From FTIR spectra, the small peak (near 1750 cm⁻¹) observed in the spectrum of UV exposed sample corresponds to a carbonyl (C=O) linkage, which suggests that oxidation has occurred in the polymer structure, and another new band for f-PP between 3100 and 3500 cm⁻¹ is attributed to a hydroxyl bond and/or hydroperoxide bond.

Keywords: UV degradation, geomembrane, melt flow index, oxidative induction time, Arrhenius model by extrapolation.

Introduction

Geomembranes (GM) may be exposed for varying periods in many geotechnical applications where they can degrade when in contact with sunlight. Ultraviolet (UV) radiation and

elevated temperatures are very harmful to all geosynthetics.¹ The radiation of the sun, particularly the ultraviolet (UV) portion is mainly responsible for limiting the lifetime of materials exposed to the environment. Generally, UV radiation is characterized by photochemical degradation and thermal oxidation or a combination of these factors. Moreover, factors such as intensity, temperature, and moisture are the agents that cause aging in polymers.²

†To whom correspondence should be addressed.
E-mail: hyjeon@inha.ac.kr

Therefore, the weathering factors affect durability are as follows: solar radiation, temperature (elevated, depressed, and cycles and fluctuations), water (solid, liquid, and vapor), and normal air constituents (oxygen and ozone).^{3,4} GM exposed 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.^{1,5,6} 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 a permanent filler residing in the polymer, antioxidants and stabilizers can be depleted by leaching or consumption and thus they have a limited lifetime.

Service life of HDPE (high density polyethylene) GM can be divided into three stages where Stage I represents the time for antioxidant depletion, Stage II refers to induction time to the onset of polymer degradation, and Stage III is the polymer degradation involving the decrease in a GM property to an arbitrary level often taken to be 50% of the original value or "half-life".⁹ Hence, the service life of a GM is the sum of the three stages. As stated earlier, a small amount of antioxidant (typically 0.5-1%) is added to the GM to retard oxidation and increase their service life. The long-term performance of GM in landfill is initially controlled by the rate of antioxidant depletion in Stage I. Oxidation of polymer takes place without any measurable decline in mechanical properties in Stage II. In Stage III oxidative degradation of polymer continues and the mechanical properties (e.g. tensile strength at break) change to the end of service life.⁷

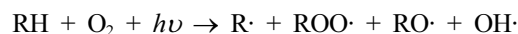
Although the ideal way of assessing the service life of GM would be by examining actual field samples over the service life, it is not feasible because it would take too long to obtain results under field conditions. Consequently, the service life is generally assessed using laboratory-accelerated ageing tests.⁸ This study has focused on Stage I of GM exposed to UV at elevated temperature. Results of this study has shown that Stage I depends on the exposure conditions.

This paper presents the effect of UV degradation and condensation in HDPE and f-PP (flexible polypropylene) GM that were exposed to laboratory accelerated UV exposure. The results of MFI, OIT (both Std-OIT and HP-OIT) and FTIR/ATR are discussed and service life of geomembranes is predicted using Arrhenius equation.

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.⁵ 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.⁵ 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 (polyethylene) and PP (polypropylene) is in the range 330-360 nm and 335-360 nm respectively which fall within the UV region (<400 nm).^{9,10}

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



where RH is the polymer chain, $h\nu$ is the photon energy with h and ν representing Planck's constant and frequency, respectively, and $\text{R}\cdot$, $\text{ROO}\cdot$, $\text{RO}\cdot$ and $\text{OH}\cdot$ are the free radical species with R representing the polymer chain. The oxidation reaction breaks 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.⁵

Generally, region UV can be subdivided in three bands of wavelengths: 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.^{2,11} 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.^{2,11} 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.¹⁴ In this study UVB-313 lamps (Figure 1) were

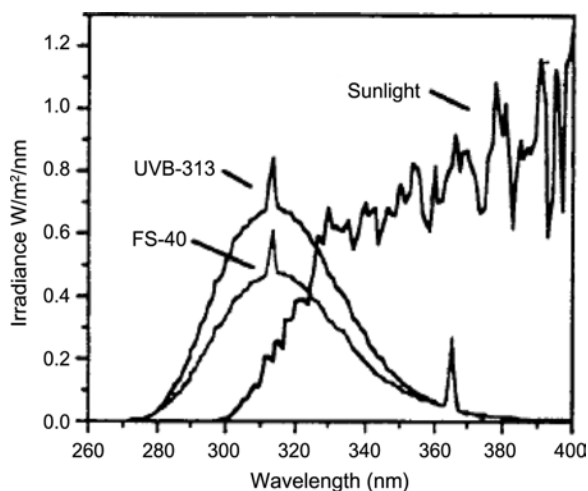


Figure 1. Spectral power distributions of UVB lamps and sunlight.¹¹

used that emit UV below the normal sunlight cut-on that can lead to rapid polymer degradation.

Experimental

Materials. Two types of GM were used for photo-degradation experiments: commercially available fPP GM (1.14 mm) and HDPE GM: black smooth (2.0 mm). fPP GM was supplied by Firestone specialty products and HDPE GM was supplied by Goldenpow Co., Ltd.

Aging Process. Using UVB-313 lamps in QUV accelerated weathering tester, three types of specimens were exposed at a customized cycle of 4 hrs UV ($IR = 1.23 \text{ Wm}^{-2}$) at 80, 70 & 60 °C and 4 hrs condensation at 60, 50 & 40 °C, respectively for 4320 hrs (upto 6 months). The test methods are described in the following section.

Tensile Properties. 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.⁷ 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 may be used like an indicator of oxidation. The oxidative degradation of the polymer induces either a crosslinking or a chain scission reaction in the polymer resulting in changes in molecular weight. Crosslinking reactions results an increase in molecular weight, whereas chain scission reactions produce a decrease in molecular weight. The MFI test measures the amount of molten polymer at 190 °C for PE and 230 °C for PP extruded through an orifice with a defined diameter under a load of 2.16 kg in 10 min. 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 crosslinking reactions and increase to chain scission reactions.⁷ In this study, 3 g 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 5 mg 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.

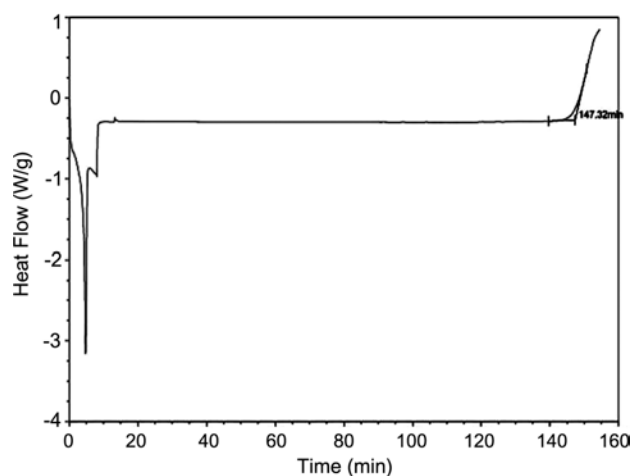


Figure 2. Thermal curve from Std-OIT test of HDPE GM.

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 50 mL/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 50 mL/min, respectively. The test was terminated after an exothermal peak, hence oxidation of the GM was detected. Figure 2 shows an example thermal curve with its identified OIT value.

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 5500 kPa. This type of cell is called a higher pressure cell and consequently the test is called high pressure OIT. 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 170 °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. (The ASTM standard requires the DSC cell to be saturated with oxygen at a pressure of 3500 kPa before heating is started). 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 3500 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 2 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. 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.¹² 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 170 °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 impractical. 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. In this study both Std-OIT and HP-OIT tests were conducted on all UV exposed samples, and the results will be compared to one another.

Fourier Transform Infrared Spectroscopy (FTIR). Fourier transform infrared spectroscopy (FTIR) is a spectroscopic method used to detect structural changes in polymeric materials at the molecular level. A polymer specimen is subjected to infrared radiation in successively decreasing frequencies. The amount of infrared radiation absorbed at each frequency is indicated in a spectrum. Peaks in the FTIR spectrum generally correspond to functional groups [e.g. methylene (-CH₂-) or methyl (-CH₃-)] that vibrate in a specific mode at a particular frequency. Polymer structure is determined by identifying the peaks using catalogues. Changes observed in the spectrum can be used as indicators of degradation.¹³ In this study, surface chemistry was characterized using a Perkin Elmer spectrum one Fourier transform infrared spectrometer (Waltham, MA).

Results and Discussion

Tensile Properties. The responses of tensile properties of the UV exposed samples are presented in the Figure 3. 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)

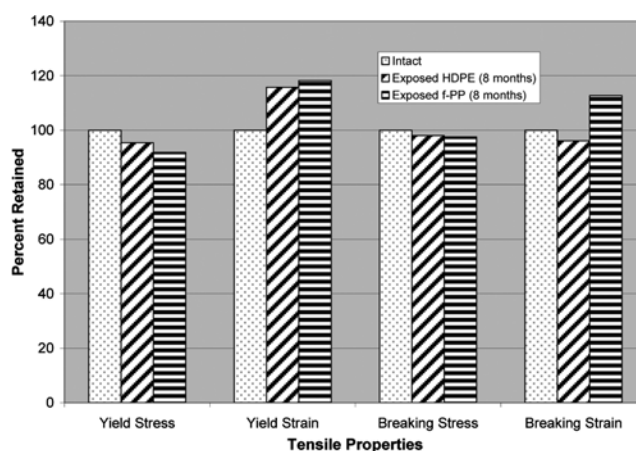


Figure 3. Tensile properties of geomembranes.

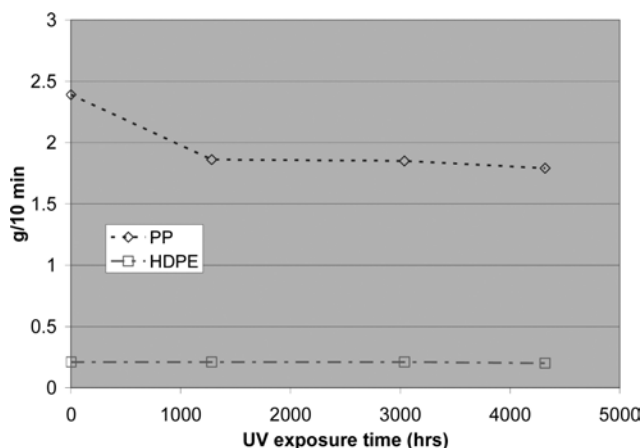


Figure 4. Melt flow index of GM.

break strain) do not appear to have any significant change over 8-month incubation period.

Melt Flow Index Test. MFI 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 crosslinking has occurred.

The MFI test results for the HDPE and f-PP GM were obtained in the laboratory (Figure 4). It was noted that there was no difference between the MFI value of the virgin and exposed HDPE 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 (22%~25%) in MFI of exposed f-PP GM samples is clearly the evidence of crosslinking. However, Crosslink after exposure is always an indicative of superficial degradation.

Std-OIT and HP-OIT Test. The OIT test results on specimens taken from the retrieved UV exposed samples are shown in Figures 5 & 8 for std-OIT and Figures 6 & 9 for HP-OIT. While some scatter is seen, the trend of exponential decrease at all incubation temperature is obvious except for Std-OIT of HDPE GM. On the contrast, Std-OIT value of HDPE GM decreases drastically that implies antioxidants in the GM consisted of hindered amines. It is also seen that the depletion rate increases with incubation temperature for all incubated samples.

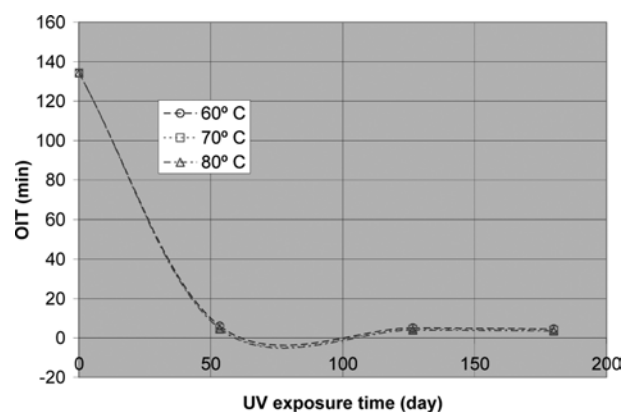


Figure 5. Std-OIT value vs. UV exposure time at different incubation temperature (HDPE GM).

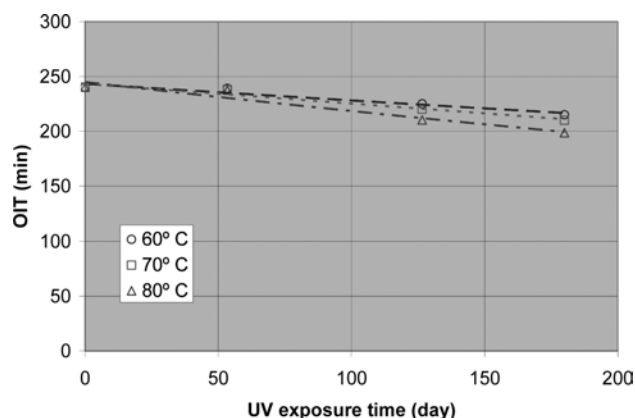


Figure 6. HP-OIT value vs. UV exposure time at different incubation temperature (HDPE GM).

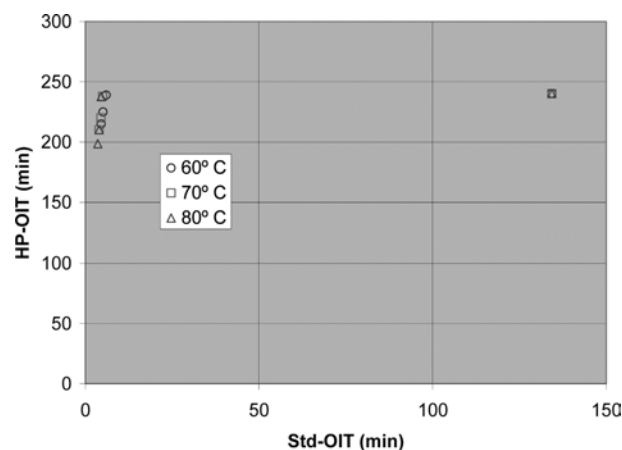


Figure 7. Correlation between Std-OIT and HP-OIT values of HDPE GM.

The behavior in each test indicates that the OIT reduction occurred continuously and gradually as incubation time increased in HP-OIT (for HDPE GM) and both (for f-PP GM)

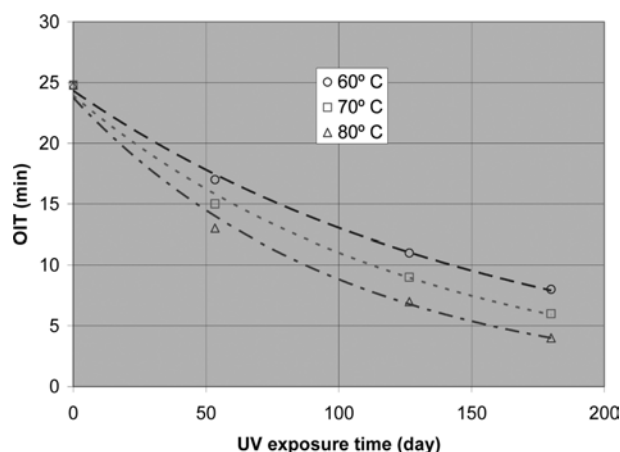


Figure 8. Std-OIT value vs. UV exposure time at different incubation temperature (f-PP GM).

tests but sudden fall in Std-OIT test of HDPE GM.

In case of HDPE GM, HP-OIT values exhibited very slow depletion trends. No linear correlation was found between these two sets of OIT values, as shown in Figure 7. This suggests that only HP-OIT should be used to evaluate the depletion of antioxidant for this particular GM formulation which also implies that the major antioxidants in this GM probably consisted of hindered amines.¹² On the other hand, in case of f-PP GM, 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, as shown in Figure 10. This suggests that either Std-OIT or HP-OIT can be used to evaluate the depletion of antioxidant for this particular GM formulation. However, it implies that there are no hindered amines in this GM. The major antioxidants in this GM probably consisted of phosphites and hindered phenols, as observed.¹⁹ The antioxidant packages are the common types used by many GM manufacturers to stabilize the HDPE and the f-PP GM.

Lifetime Prediction of Antioxidants. In the introduction part, the importance of antioxidants to the longevity of the GM has been illustrated. Here the discussion will focus to quantify the antioxidant depletion lifetime of the GM. For this quantification, the lifetime of the antioxidant is determined based on the depletion rate of the OIT values. Figures 11, 12 and 13 reproduce the OIT data in Figures 6, 8 and 9 respectively, by plotting natural log of OIT against incubation time. A set of linear response curves result. The slope of the lines represents the OIT depletion rate at each particular temperature. It should be noted that due to some deviations from the exponential rela-

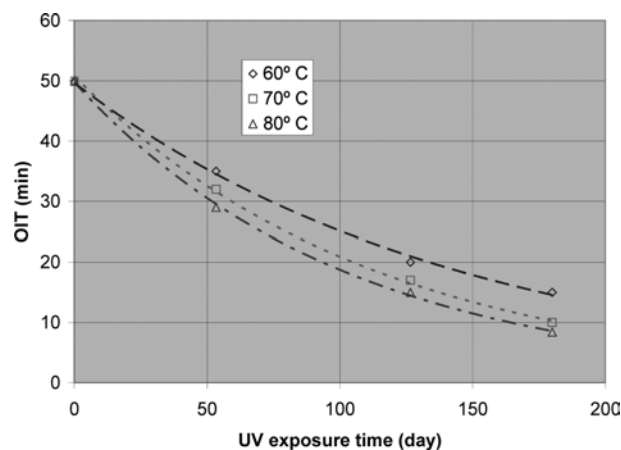


Figure 9. HP-OIT value vs. UV exposure time at different incubation temperature (f-PP GM).

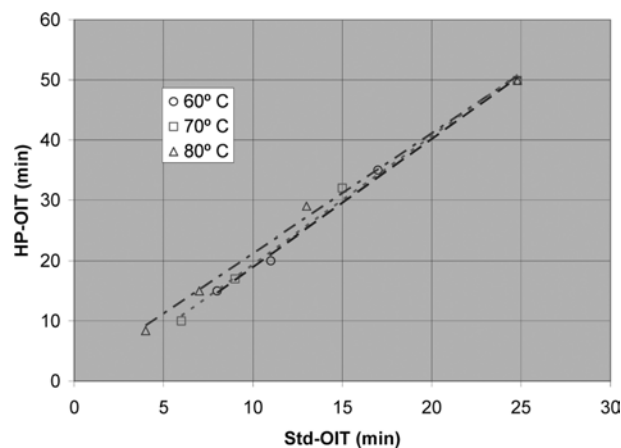


Figure 10. Correlation between Std-OIT and HP-OIT values of f-PP GM.

tionship in the OIT values, extrapolation based on the OIT data may result some errors.

Based on Figures 11, 12 and 13, the generalized equation for each of the straight lines is expressed by

$$\ln(OIT) = \ln(P) - (S)(t) \quad (1)$$

where OIT = OIT time (min); S = OIT depletion rate (min/day); t = incubation time (days); and P = constant (the original value of OIT of the GM). The depletion rate of OIT in each test at each incubation temperature can be obtained and listed in Table 1.

The next in the analysis is to extrapolate the OIT depletion rate to a lower temperature, such as the site specific temperature. Arrhenius equation can be used in such prediction.¹⁴ The Arrhenius equation can be expressed by

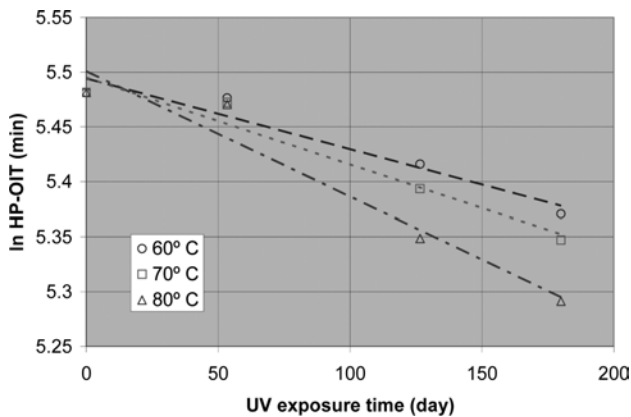


Figure 11. Ln(OIT) vs. incubation time for HP-OIT (HDPE GM).

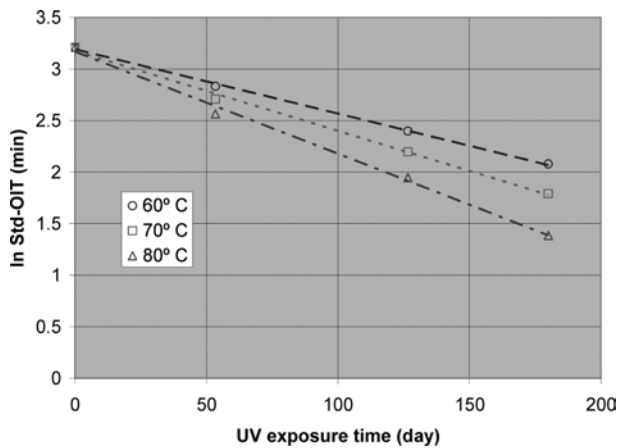


Figure 12. Ln(OIT) vs. incubation time for Std-OIT (f-PP GM).

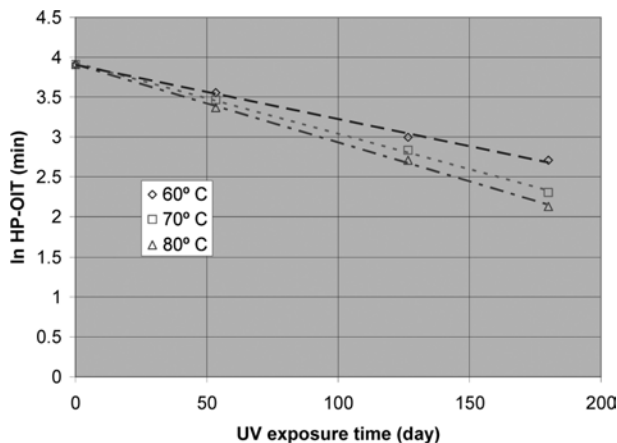


Figure 13. Ln(OIT) vs. incubation time for HP-OIT (f-PP GM).

$$S = (A)\exp(-E_a/RT) \quad (2)$$

$$\ln(S) = \ln(A) + (-E_a/R)(1/T) \quad (3)$$

where S = antioxidant depletion rate (values listed in Table 1);

Table 1. Antioxidant Depletion Rates (Day-1) at Different Incubation Temperatures

Temperature (°C)	HP-OIT (for HDPE)	Std-OIT (for f-PP)	HP-OIT (for f-PP)
80	0.00114 (0.9464)	0.00990 (0.9955)	0.00977 (0.9988)
70	0.000793 (0.9522)	0.00776 (0.9963)	0.00889 (0.9986)
60	0.000645 (0.9391)	0.00624 (0.9985)	0.00682 (0.9963)

Note: The numbers in parenthesis represents coefficient of determination R^2 .

E_a = activation energy of the antioxidant depletion reaction under this set of test conditions (kJ/mol); R = gas constant ($8.31 \text{ J mol}^{-1}\text{K}^{-1}$); T = absolute temperature (K) and A = constant.

A linear relationship is established between $\ln(S)$ and inverse temperature, as shown in Figures 14 and 15. The activation energy is taken from the slopes of the lines, which results in values 27.76 kJ/mol for the HP-OIT of HDPE GM, 22.54 kJ/mol for the Std-OIT of f-PP GM, and 17.65 kJ/mol for the HP-OIT of f-PP GM. The corresponding Arrhenius equations are expressed by

$$\ln(S) = 2.6526 - 3340.5/T \quad (\text{for HP-OIT of HDPE GM}) \quad (4)$$

$$\ln(S) = 3.0601 - 2712.9/T \quad (\text{for Std-OIT of f-PP GM}) \quad (5)$$

$$\ln(S) = 1.4126 - 2123.7/T \quad (\text{for HP-OIT of f-PP GM}) \quad (6)$$

Using 4, 5 and 6, the OIT depletion rates at a typical site specific (and lower) temperature can be obtained. Let, the site specific temperature is 20 °C. Thus we are using 20 °C to demonstrate the extrapolation calculation. The extrapolated OIT rates (per day) at 20 °C are as follows: $S = 0.00015964$ (for HP-OIT of HDPE GM); $S = 0.002041222$ (for Std-OIT of f-PP GM); and $S = 0.002932752$ (for HP-OIT of f-PP GM).

Using eq. (1), the calculation procedures to obtain the depletion time at 20 °C are as follows.

For HP-OIT test of HDPE GM: The OIT value for a pure unstabilized HDPE resin was found to be 20 min by Hsuan and Koerner (1998), which is taken to be the OIT value when the antioxidants are essentially consumed.⁷

$$\ln(20) = \ln(240.2) - (0.00015964)(t)$$

$$t = 43.25 \text{ years}$$

For Std-OIT test of f-PP GM: The OIT value for a pure

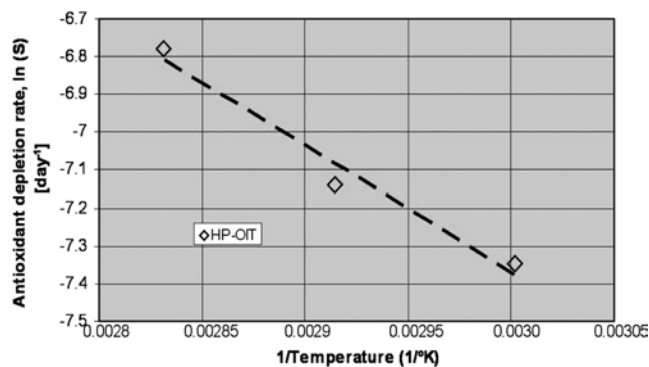


Figure 14. Arrhenius plot of antioxidants depletion rate for HDPE GM.

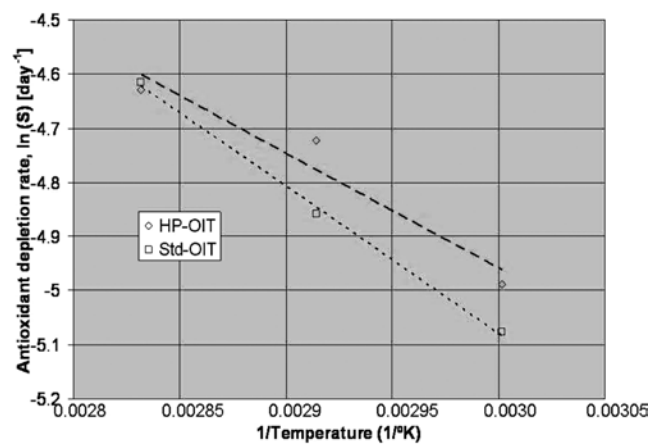


Figure 15. Arrhenius plot of antioxidants depletion rate for f-PP geomembrane.

unstabilized f-PP resin was found to be 0.2 min by Jing Chen *et al.* (2011), which is taken to be the OIT value when the antioxidants are essentially consumed.¹⁵

$$\ln(0.2) = \ln(24.8) - (0.002041222)(t)$$

$$t = 6.56 \text{ years}$$

For HP-OIT test of f-PP GM: The OIT value for a pure unstabilized f-PP resin was found to be about 1 min by Qin Xiang (2002), which is taken to be the OIT value when the antioxidants are essentially consumed.¹⁶

$$\ln(1) = \ln(49.9) - (0.002932752)(t)$$

$$t = 3.7 \text{ years}$$

It should be noted that there is uncertainty in determining OIT for a pure unstabilized resin. This may be due to the difficulty of measuring such low value, since one can get different values depending on where exactly the tangents are taken on the baseline and exothermic portion of the curve, or

it may be that the residual value varies from one resin to another. In any event, in the present tests consistent OIT values below 1 min were not typically observed even after prolonged ageing and it may well be that for the GM tested the residual value of OIT, is of the order of 1 min.⁸

FTIR Spectra of HDPE GM. Since the PE is composed almost completely of methylene groups, its infrared spectrum would be expected to consist solely of methylene stretches and bends. Four sharp peaks dominate the spectrum: The methylene stretches nearly at 2920 and 2850 cm^{-1} and the methylene deformations at 1464 and 719 cm^{-1} . Due to the crystallinity of polyethylene, the 1464 and 719 cm^{-1} peaks are split, and additional peaks are seen at 1473 and 731 cm^{-1} . HDPE is very regular and is about 70% crystalline. Similar spectra were observed by other researchers.^{20,27} Spectra for the geomembrane samples exposed to UVB-313 for (b) 2 months, (c) 4 months, (d) 6 months at 80 °C are shown in Figure 16 along with the spectrum of the (a) unexposed GM. UV exposure at 80 °C was expected to be the most aggressive treatment and therefore was chosen for FTIR testing. Other exposure times and treatments were not tested owing to budget limitations.

The spectra at 2, 4 and 6 months of UV exposure at 80 °C (Figure 16(b), 16(c) and 16(d)) are consistent with the spectrum of the unexposed GM (Figure 16(a)), except for one small absorption peak below 1750 cm^{-1} and two additional small absorption bands: most significant of which appear near 1100 cm^{-1} ; other band appears near 3300 cm^{-1} in the 6-month spectrum.

It is known that oxidation of PE would be indicated by new bands emerging within the range 1600-1800 cm^{-1} wave number. However, we did not identify any new band in the above range in 2-month and 4-month specimen and taking into account that FTIR is claimed to be a sensitive and reliable method for the identification of the changes occurring on the surface of a GM, we can conclude that within the experimental conditions (2-month and 4-month) of this work no degradation of the GM took place.

The small peak (near 1750 cm^{-1}) observed in the 6-month spectrum corresponds to a carbonyl (C=O) linkage, which suggests that oxidation has occurred in the polymer structure. The extra peak at 6-month may be a local effect, but a definitive conclusion cannot be made because replicate FTIR analyses were not conducted. Nevertheless, the absence of major changes in the spectra suggests that exposure to UV at 60 °C did not significantly change the bulk polymer structure over 6 months.

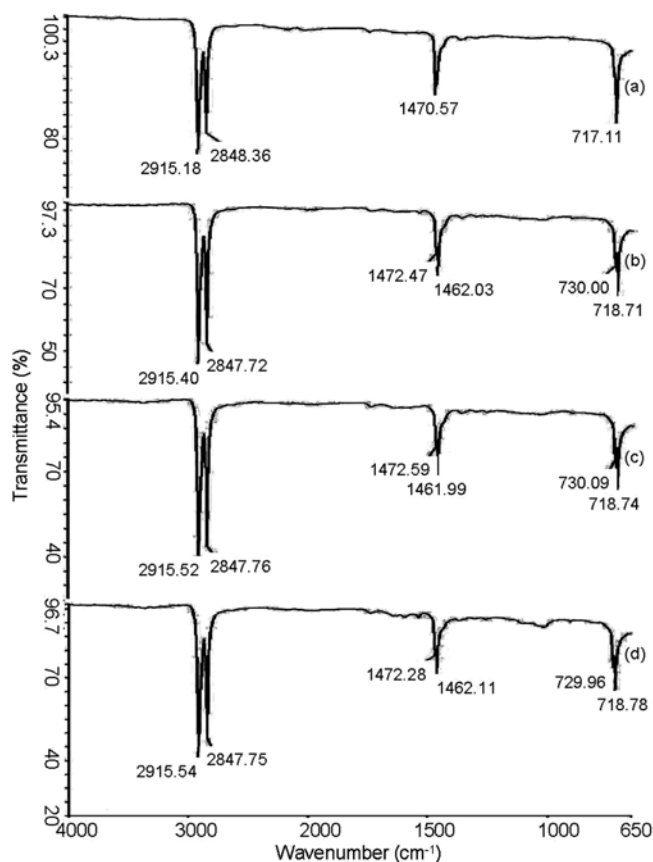


Figure 16. FTIR spectra of HDPE GM (a) intact and UV incubated sample after; (b) 2 months; (c) 4 months; (d) 6 months at 80 °C.

The small absorption bands observed at 3300 and 1100 cm^{-1} in the 6-month spectrum are not associated with the wavelengths at which polymer oxidation peaks occur, and are believed to be associated with mixed metal oxides.¹³ The source of these elements usually comes from residual catalysts used to polymerize the resin. Although, the concentration of these elements is very low, they are still a concern regarding the long-term durability of the polymer.¹⁸ However, types of metal oxides cannot be identified by FTIR.

FTIR Spectra of f-PP GM. The addition of a methyl side group on every other carbon atom in polyethylene gives polypropylene and quickly complicates the infrared spectrum. In addition to the methylene, we now have methyl and methine groups present. The methyl peaks appear at 2950/2917 (split peak), 2850 and 1375 cm^{-1} . A methyl deformation is also overlapped with the methyl and methylene deformation, and this peak has shifted slightly to 1475 cm^{-1} . The methine peaks are weak and of no analytical value.¹⁷ FTIR spectra can be of the utmost importance in the analysis of industrial products for the detection of surface modifications caused by aging or a chem-

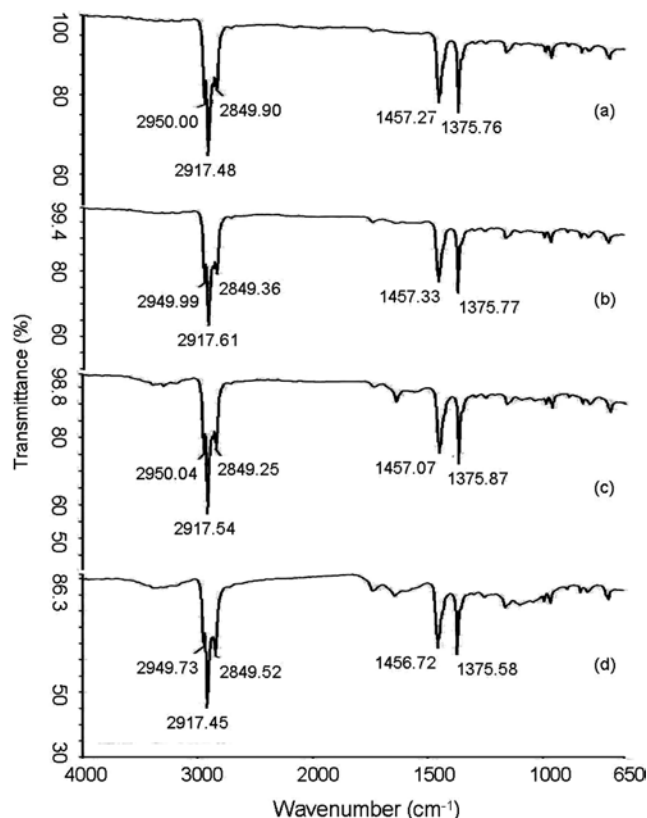


Figure 17. FTIR spectra of PP GM (a) intact and UV incubated sample after; (b) 2 months; (c) 4 months; (d) 6 months at 60 °C.

ical reaction.¹⁹ Spectra for the PP GM samples exposed to UVB-313 for (b) 2 months, (c) 4 months, and (d) 6 months at 80 °C are shown in Figure 17 along with the spectrum of the (a) unexposed GM. UV exposure at 80 °C was expected to be the most aggressive treatment and therefore was chosen for FTIR testing. Other exposure times and treatments were not tested owing to budget limitations.

As expected, intact specimen (Figure 17(a)) consists of the characteristic bands of PP¹⁹: a broad and intense band that extends from 2850 to 3000 cm^{-1} is attributed to the valence vibrations of the C-H bonds, a band located at 1457 cm^{-1} is characteristic of methylene CH_2 groups, and a band at around 1375 cm^{-1} is attributed to the methyl CH_3 group. There are two other types of bands present: C-C vibrations are found in the lower frequency region (from 1000 to 840 cm^{-1}), and another band of intensity comparable to the former, which characterizes dialkyl ether bonds, C-O-C, is found at 1168 cm^{-1} . Note also the emergence of a very low intensity band at 1646 cm^{-1} that corresponds to C=C bonds, as well as the existence of another band, also of very weak intensity, in the region of 3114-3255 cm^{-1} that is attributed to the valence vibrations of an

alkene C-H bond.

Figure 17(c), (d) shows the spectrum of the sample exposed to UV at 60 °C for 4 and 6 months. In addition to the characteristic bands next to the bands corresponding to the PP bonds (C-H, CH₂, CH₃), the spectrum reveals the existence of a new band centered nearly at 1712 cm⁻¹ that corresponds to a carbonyl bond C=O. Also, another new band between 3100 and 3500 cm⁻¹ is attributed to a hydroxyl bond and/or hydroperoxide bond. Note the significantly increased intensity of the band located nearly at 1168 cm⁻¹, which characterizes the C-O bond and the decreased intensity of the band, corresponding to methylene -CH₂- groups. Henceforth, FTIR spectroscopy allowed us to clearly determine the site of oxidative attack, as corroborate by result.

Conclusions

The service life of a GM in UV exposure condition is important issue since there are many applications where it may be exposed to the sun. Since actual field performance observation takes a long time, accelerated laboratory simulation test can be a good option to have some knowledge to quantify the lifetime in similar condition. In this paper, the changes in chemical and physical properties resulting from accelerated laboratory UV degradation of HDPE and f-PP GM were studied, by exposure to Q-UV weatherometer at elevated temperature for a period of 6 months. Also, depletion lifetime of the antioxidant in the GM due to UV exposure was discussed where the GM went through the first stage of the degradation.

Arrhenius modeling was conducted to provide estimates of the antioxidant depletion time (Stage I) for the GM at typical liner temperatures in UV-B exposure condition. The calculated Stage I at a typical liner temperature of 20 °C was 43 years for HDPE and 6.5 years for f-PP GM. The mechanical properties of the polymer remained unaffected. 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 crosslinking. OIT decreased with exposure time for all exposed specimen. FTIR spectra did not reveal any significant change in physicochemical properties of the examined specimens. 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. This present study did not explicitly consider the effect of stress and other issues that would be expected in a real field. Therefore, more intensive investigation is required to make a clear statement.

Acknowledgement: This work was supported by the 2007 Yeungnam University Research Grant.

References

1. P. C. Lodi, B. S. Bueno, C. L. M. Costa, and J. G. Zornberg, *The first Pan Geosynthetics Conference & Exhibition*, GeoAmericas, p 681 (2008).
2. P. C. Lodi, B. S. Bueno, and O. M. Vilar, *4th Asian Regional Conference on Geosynthetics*, Geosynthetics Asia, p 40 (2008).
3. H. Haxo and N. Nelson, *International Conference on Geomembranes*, Denver, p 287 (1984).
4. A. L. Rollin, *57th Canadian Geotechnical Conference*, Geo Quebec, p 15 (2004).
5. L. D. Suits and Y. G. Hsuan, *Geotext. Geomembranes*, **21**, 111 (2003).
6. W. Wang and B. Qu, *Polym. Degrad. Stabil.*, **81**, 531 (2003).
7. Y. G. Hsuan and R. M. Koerner, *J. Geotech. Geoenviron.*, **124**, 532 (1998).
8. R. K. Rowe, S. Rimal, and H. Sangam, *Geotext. Geomembranes*, **27**, 137 (2009).
9. X. Hu, *Polym. Degrad. Stabil.*, **55**, 131 (1997).
10. Z. Zhang, X. Hu, and L. Zubo, *Polym. Degrad. Stabil.*, **51**, 93 (1996).
11. *ASTM G154 Standard Practice for Operating Fluorescent Light Apparatus for Exposure of Nonmetallic Materials* (2006).
12. Y. G. Hsuan and Z. Guan, *ASTM STP 1326*, 76 (1997).
13. S. B. Gulec, T. B. Edil, and C. H. Benson, *Geosynth. Int.*, **11**, 60 (2004).
14. R. M. Koerner, A. E. Jr. Lord, and Y. H. Hsuan, *Geotext. Geomembranes*, **11**, 151 (1992).
15. J. Chen, M. S. Yang, and S. M. Zhang, *Compos. Part A: Appl. S.*, **42**, 471 (2011).
16. Q. Xiang, Ph.D. Thesis, Department of Chemistry and Environment Science, The State University of New Jersey - Newark, p 91 (2002).
17. Jerome F. O'Keefe, *Rubber World*, **230**, 27 (2004).
18. R. Rowe, K. Sangam, and P. Henri, *Geotext. Geomembranes*, **20**, 77 (2002).
19. A. Rjeb, L. Tajounte, M. Chafik El Idrissi, S. Letarte, A. Adnot, D. Roy, Y. Claire, A. Pe'Richaud, and J. Kaloustian, *J. Appl. Polym. Sci.*, **77**, 1742 (2000).