Predicting the depletion of antioxidants in high density polyethylene (HDPE) under sunlight using the reciprocity law

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ABSTRACT: In many applications, high density polyethylene (HDPE) geosynthetics are exposed to sunlight throughout their service life. In this study, the depletion of antioxidants in HDPE with 2.7% carbon black subjected to sunlight exposure was evaluated. The sunlight radiation was simulated using a laboratory xenon light weatherometer at three irradiation levels. Oxidative induction time (OIT) test was used to assess the depletion of antioxidant along the thickness of the test coupons to establish the antioxidant depletion profile throughout the exposure duration. The greatest decrease in OIT was obtained in the surface layer facing the sunlight irradiation, followed by the backside layer which was exposed to indirect reflected radiation. The core section showed a much slower decrease at the same irradiance level. Furthermore, the OIT depletion rate in the surface layer increased with radiation intensity. The study proved that the sunlight degradation of the tested HDPE material can be accelerated by increasing the irradiation intensity based on the reciprocity law, and prediction can be made for OIT depletion rate in the surface layer under the field conditions using the weatherometer test data.

Keywords: HDPE, Antioxidants, Sunlight, Degradation, Reciprocity law.

1 INTRODUCTION

HDPE is one of the widely used polymers in geosynthetics, including geomembranes, geogrids, and geonets due to its reasonable cost, low processing energy, and well balanced mechanical properties (Eith and Koerner 1992, Rowe and Sangam 2002).In many applications, HDPE geosynthetics are exposed to the sunlight. Solar radiation is known as a major environmental factor inducing HDPE degradation (Lodi, Bueno et al. 2010). Even though the high energy radiation with shortest wavelengths (UV-C) are mostly filtered by the earth’s atmosphere, the remaining photons still have enough energy to break the chemical bonds in HDPE, generating free radicals. In presence of oxygen, photo-oxidation reactions lead to production of highly reactive free radicals and hydroperoxides. Once the concentration of hydroperoxides reaches a critical level, they start to decompose, increasing the amount of free radicals as well as the oxidation rate, resulting in auto-accelerated reactions and subsequently degrading the polymer through chain-scission (Deanin, Orroth et al. 1970).

Antioxidants can be added to HDPE to interrupt these reactions and retard the degradation. However, regardless of the amount of antioxidants added to HDPE, they are eventually consumed as a result of reacting with oxygen, hydroperoxides, or free radicals (Gedde, Viebke et al. 1994). Consequently, sunlight degradation of HDPE product will take place. Therefore, the depletion time of antioxidant plays a major role in resistance of HDPE geosynthetics against sunlight degradation and it needs to be evaluated in order to predict their service life.

The photo-degradation of HDPE products can be accurately determined by exposing the product to the sunlight at the project site. However, antioxidant depletion under natural sunlight is a relatively slow process and it is therefore necessary to develop exposure methods that can accelerate the process. Several laboratory weatherometers are commercially available which are equipped with different artificial light sources to simulate the sunlight or the ultraviolet portion of the sunlight. In these weatherometers, the irradiance of the artificial sunlight can be increased to accelerate the photo-chemical reactions. Establishing a reliable correlation between accelerated laboratory test results and actual outdoor test results has been a challenge over the past few decades (Riedl 2003). An efficient method for making the correlation and obtaining a prediction on the outdoor results is to extrapolate the accelerated laboratory results based on reciprocity law. Reciprocity law concept was first introduced by Bunsen and Roscoe (Bunsen 1923) who showed that photo-chemical reactions depend only on the exposure dose, which is the product of the irradiance level and exposure time, and are independent of the individual values of irradiance level and exposure time. Therefore, the long term response of the material in the outdoor environment could be predicted by exposing the material to elevated irradiance levels in a weatherometer, if other environmental factors (moisture and air bonded impurities) do not play a significant role. However, since the introduction of reciprocity law, researchers have challenged its validity and reported experimental deviations from this law in different fields of application (Morgan 1944, Webb 1950). Reciprocity law failure in the field of material degradation can occur in two forms. If the irradiance level is too high, it can result in unnatural failure mechanisms and over-acceleration of the degradation (Gerlock, Kucherov et al. 2001). It is also possible that an increase in the irradiance does not result in the expected degradation rate due to cage effect (Loo, Ooi et al. 2005), such that the rate at which free radicals produced as a result of photo-initiated reactions is faster than the reaction rate in the degradation process.

The objective of this paper is to evaluate whether reciprocity law can be used to predict the depletion of antioxidants in HDPE at the field condition using accelerated weatherometer test. HDPE coupons which contained antioxidants and carbon black were exposed to three elevated irradiance levels in a laboratory xenon weatherometer to accelerate the depletion of antioxidants. The applicability of the reciprocity law was examined using the OIT test data obtained from these three exposure conditions. Also the predicted data were then compared to the actual values obtained by testing the coupons that were exposed to natural sunlight in Gainesville, Florida.

2 TEST SAMPLE AND SPECIMEN PREPARATION

HDPE coupons with dimensions of 5 cm × 15 cm × 0.25 cm were prepared for the exposure tests. The HDPE resin properties are listed in Table 1. Carbon black and antioxidants were added to the HDPE. However, the type of antioxidant was not revealed by the manufacturer. The amount of carbon black in the material was measured to be 2.7% based on themorgravimetry analysis.

Table 1- Material Properties of the HDPE Resin

Property	ASTM Test	Value
Specific Gravity	D6111	0.93
Compression Strength	D695	31 MPa
Tensile Strength	D638	25 MPa
Hardness	D4329	66 Shore D
Brittleness	D746	- 40 ^{0}C

3 EXPERIMENTAL

3.1 *Accelerated laboratory weathering*

To simulate the sunlight effect on antioxidant depletion, HDPE Coupons were exposed in an ATLAS Ci-4000 weatherometer equipped with a xenon lamp and inner and outer borosilicate filters. The exposure parameters were set according to ASTM D2565 “Standard Practice for Xenon-Arc Exposure of Plastics Intended for Outdoor Applications” [17]. Each cycle lasted 120 minutes and was composed of 102 minutes of irradiation followed by 18 minutes of irradiation and water spray. The temperature was set at 63 ± 2^{0}C, monitored by an uninsulated black panel. A standard irradiance of 41.5 W/m^2 between 300-400 nm (specified in ASTM D2565) and two additional irradiation levels of 60 and 80 W/m^2 were applied, named herein as conditions A, B, and C, respectively. Maximum exposure duration was 5000 hours for condition A, 4000 hours for condition B, and 3000 hours for condition C. To distinguish between the depletion caused by radiation and the depletion due to the elevated temperature, test coupons were also exposed to a constant temperature of 65^{0}C inside a forced air oven to simulate the thermal effect. Test coupons were periodically retrieved from weatherometer and oven to be tested for their retained antioxidant level via oxidative induction time test.

3.2 *Exposure to natural outdoor weathering*

HDPE coupons were exposed in Gainesville, Florida. According to ASTM D1435-13 "Standard Practice for Outdoor Weathering of Plastics", the coupons were mounted on a metal rack, facing south with an angle of 45° from horizontal. Coupons were removed every 4 month to be tested.

3.3 *Standard oxidative induction time (OIT) test*

To monitor the depletion of antioxidants under radiation, a TA instruments Q20 Differential Scanning Calorimeter (DSC) was used to perform the OIT test according to ASTM D3895-14. To assess the effect of irradiation along the thickness of the exposed coupons, OIT test was conducted on five thin layers sliced across the thickness of the exposed coupon (as illustrated in Figure 1).

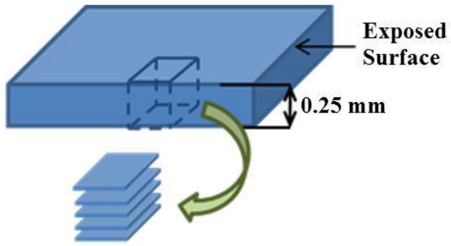


Figure 1. OIT specimens sliced across the thickness of exposed HDPE coupons

4 TEST RESULTS

4.1 *Unexposed coupons*

The OIT results of 5 layers of the unexposed coupon obtained from averaging two set of test results are presented in Table 2. A small gradient was detected in the OIT value across the thickness of the unexposed coupon.

Table 2 – OIT value for different layers of the unexposed HDPE coupons

Layer Number	*Average Thickness (mm)*	*OIT-1 (min.)*	*OIT-2 (min.)*	*OIT-Average (min.)*
Layer-1	0.37±0.11	8.95	10.64	9.80
Layer-2	0.47±0.09	8.95	9.86	9.40
Layer-3	0.54±0.08	7.87	8.82	8.35
Layer-4	0.45±0.02	6.64	8.46	7.55
Layer-5	0.75±0.12	6.40	7.82	7.11

The retained OIT percentage was used instead of the absolute OIT value for evaluating the OIT change in each layer throughout the exposure. Retained OIT percentage was calculated for each layer at different exposure times using Equation 1:

$$\text{Re}\mathit{tained\ OIT}\,(\%) = \frac{OIT_{i,t}}{OIT_{i,0}} \times 100 \tag{1}$$

where i = layer number and t = exposure time.

4.2 *Coupons exposed to accelerated laboratory weathering*

Figure 2 provides the retained OIT percentage values for different layers of test coupons exposed to a constant temperature of 65^{0}C in a forced air oven, and exposed to conditions A, B, and C in the weatherometer. For coupons exposed in the weatherometer, the surface layer (layer 1), facing the xenon lamp, showed a significant decrease in the OIT value (Figure 2a). In contrast, OIT values of core layers (layers 2-4) decreased much less than the corresponding surface layers, particularly for layers 3 and 4.

The backside layer of the test coupon (layer 5) experienced a higher drop in OIT in comparison to the core layers. This could be attributed to the radiation deflected from the wall of the weatherometer chamber. The lowest OIT values were measured under condition C, suggesting that the greatest radiation penetration was occurred at the highest irradiance level. On the other hand, OIT values obtained from the oven-aged coupons remained relatively constant in all layers throughout the incubation period (Figure 2a-d). The drastic difference of the OIT decreasing trends between xenon exposure and oven aging verifies that the decrease of OIT measured in the weatherometer-aged coupons was solely attributed to the radiation, and the effect of the elevated temperature (63± 2^{0}C) is negligible.

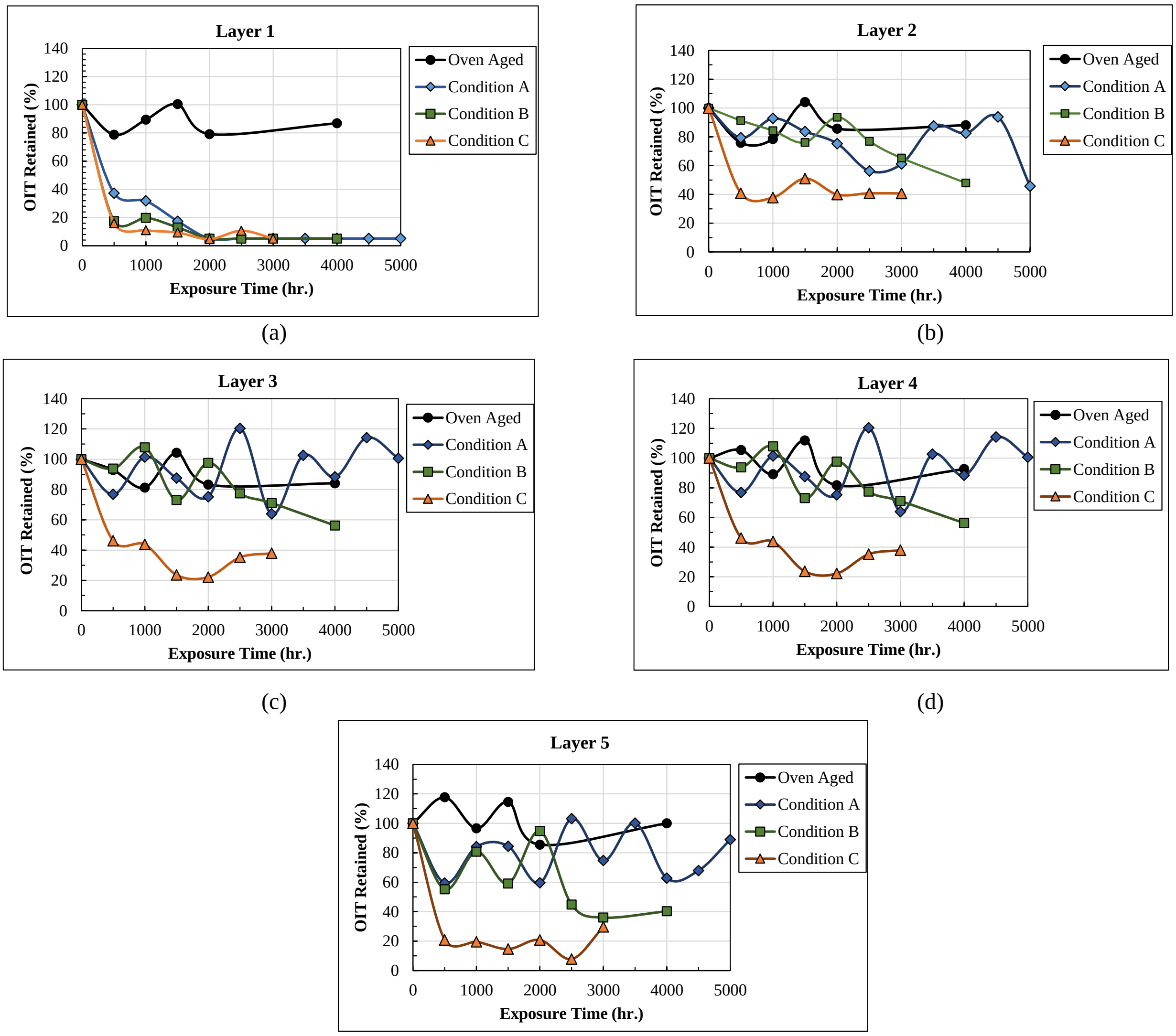


Figure 2. Retained OIT percentage for HDPE coupons exposed inside oven and weatherometer
a) Layer 1,b) Layer 2, c) Layer 3, d) Layer 4, e) Layer 5

4.3 *Coupons exposed to natural outdoor weathering*

The OIT retained percentages for coupons exposed to the outdoor weathering in Florida are shown in figure 3. Similar to the laboratory aged coupons, the greatest OIT decrease was measured in the surface layer, followed by the back layer (layer 5). The core layers (2 to 4) were relatively less affected.

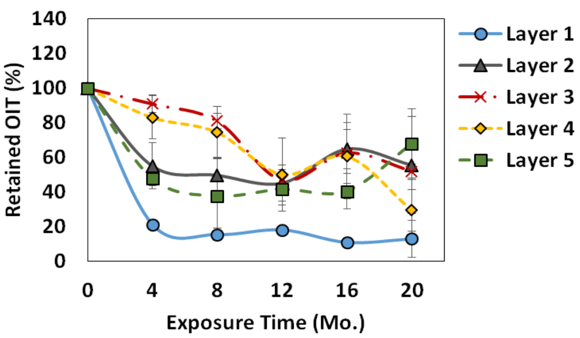


Figure 3. Retained OIT values for HDPE coupons exposed to the sunlight in Gainesville, Florida

5 DISCUSSION

5.1 *Reciprocity law examination*

Photo-chemical reactions are mainly confined to the surface due to radiation penetration depth (Gijsman, Meijers et al. 1999). OIT results in this study confirm that the surface layer was impacted the most by the sunlight radiation in comparison to interior layers. Therefore, the discussions are hereafter focused on the surface layer.

Two elevated irradiance levels of 60 and 80 W/m^2 were used in this study in addition to the standard irradiance of 41.5 W/m^2 between 300 and 400nm suggested by ASTM D2565-16. Figure 4a presents OIT retained in the surface layer versus the exposure time under three exposure conditions. The OIT decreased faster as irradiance level increased.

In order to ensure that the results obtained under the two elevated irradiance levels (conditions B and C) are not affected by unnatural chemical reactions or cage effect, the validity of reciprocity law at the three levels were examined. The total irradiation energy was calculated at each exposure time for all conditions using Equation 2:

$$E_{total,weatherometer} = I_{300-400} \times \alpha \times t \times 0.0036 \times \beta \tag{2}$$

Where $E_{total,weatherometer}$ = Total radiation energy in weatherometer (MJ/m^2), $I_{300\text{-}400}$ = Irradiance level (W/m^2), $\alpha = I_{300\text{-}800}/I_{300\text{-}400}$, t = Exposure time and $\beta = I_{300\text{-}2500}/I_{300\text{-}800}$.

Conversion factor α was provided by the manufacturer of the weatherometer and was used to convert the irradiance in the of 300-400 nm bandpass to irradiance in the 300-800 nm bandpass. β was obtained by calculating the total irradiation from the reference solar spectrum provided by ASTM G173-12 and dividing it by the irradiation in the 300-800nm bandpass on the same spectrum. Figure 4b shows the retained OIT values versus radiation energy under the three irradiance levels. The results demonstrate that the three OIT curves were converged, suggesting that the reciprocity law is valid.

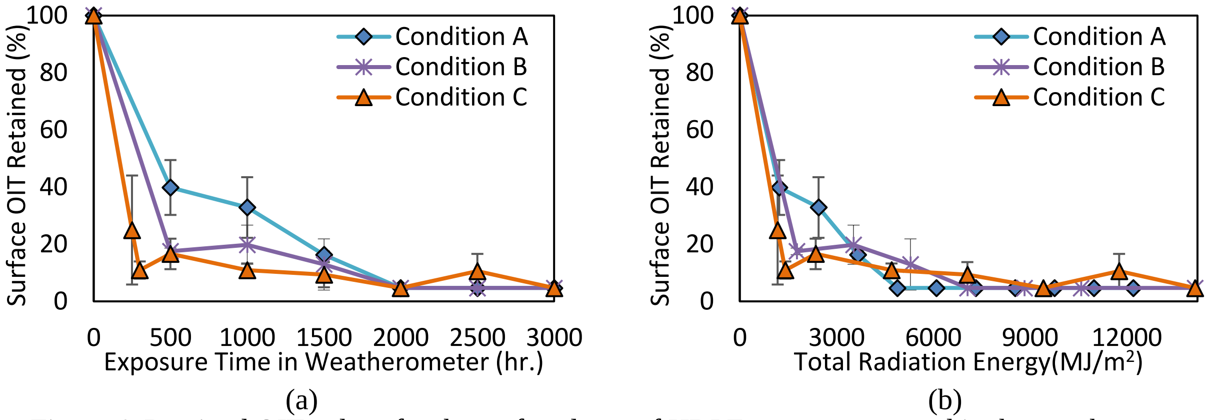


Figure 4. Retained OIT values for the surface layer of HDPE coupons exposed in the weatherometer.
a) versus the exposure time, b) versus the radiation energy

5.2 *Predicting the antioxidant depletion under outdoor exposure*

Since reciprocity law was validated for the three irradiance levels, all OIT test data can be normalized to generate a master curve presenting the retained OIT values versus the total irradiation energy. The master curve can then be used for predicting the antioxidant depletion under natural sunlight at a specific location as long as the radiation energy data for that location are available. In this study, the outdoor exposure site was located at Gainesville, Florida. The closest location for which the radiation energy data are available is Miami, FL where Atlas Weathering Services Group provides annual reports for total and UV solar radiation at an angle of 45° with horizontal. The results for the past 10 years are summarized in Table 3 below.

Table 3. Annual Solar Radiation Energy Summary in Miami, FL.

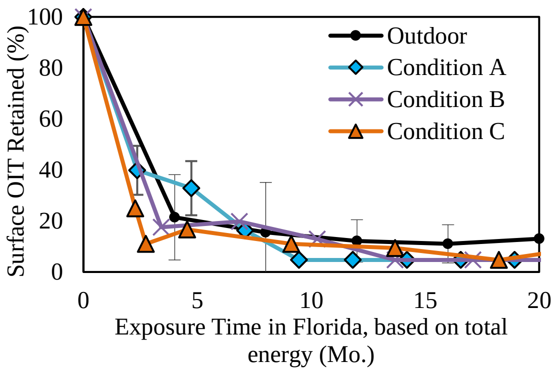
Year	Total Solar Radiation, MJ/m² (295-2500nm)	Year	Total Solar Radiation, MJ/m² (295-2500nm)
2007	6345.3	2012	6316.3
2008	6259.0	2013	6017.5
2009	6446.4	2014	6452.7
2010	6181.9	2015	6306.1
2011	6568.1	2016	6309.2
		Average	**6320.3**

Using the average value for the past 10 years, the equivalent outdoor exposure time was calculated for every coupon using Equation 3:

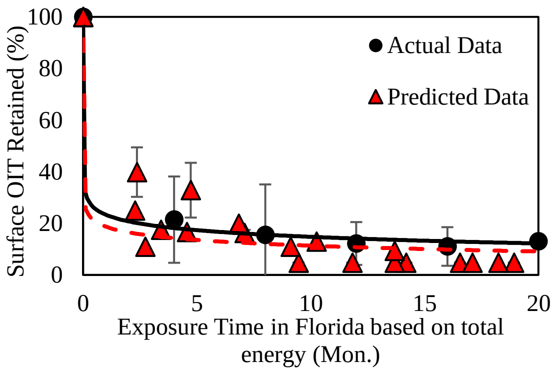
$$t_{Outdoor} = \frac{E_{total,Weatherometer}}{E_{total,Outdoor}} \times 12 \tag{3}$$

where $t_{outdoor}$ = Equivalent outdoor exposure time in Months, $E_{total.weatherometer}$ = Total absorbed energy in inside the weatherometer (MJ/m^2), and $E_{total.outdoor}$ = Total absorbed energy in the outdoor environment (MJ/m^2).

OIT percentage retained were plotted against the equivalent time in Figure 5a to be compared with the outdoor results. A close agreement was observed between the actual outdoor values and values predicted under three exposure conditions in the xenon weatherometer. Figure 5b shows a comparison between the actual outdoor values and the master curve for the predicted outdoor values.



(a)



(b)

Figure 5. Comparison between actual retained OIT values and the values predicted based on total radiation energy.

Since the UV region has the photons with highest energy levels, OIT depletion is expected to be correlated to the UV dosage. To examine that hypothesis, a prediction was also made using equations 4 and 5 as well as the average UV solar radiation in Florida summarized in Table 3.

$$E_{UV,Weatherometer} = \frac{I_{300-400} \times \eta \times t \times 0.0036}{\gamma} \tag{4}$$

where $E_{UV,weatherometer}$ = Total radiation energy in the UV region from the Xenon weatherometer (MJ/m^2), $I_{300-400}$ = Irradiance level (W/m2), $\eta = I_{340} / I_{300-400}$, $\gamma = I_{340}/I_{UV}$, t= exposure time (hr)

The conversion factor η is provided by the manufacturer of the weatherometer and is used to convert the irradiance in the of 300-400 nm bandpass to the irradiance at 340 nm. For the weatherometer used in this study, energy at 340 nm is approximately 1.1% of the energy integrated in the UV spectrum. Therefore, γ = 0.011 was used in the calculations.

Table 4. Annual UV Dosage Summary in Miami, FL.

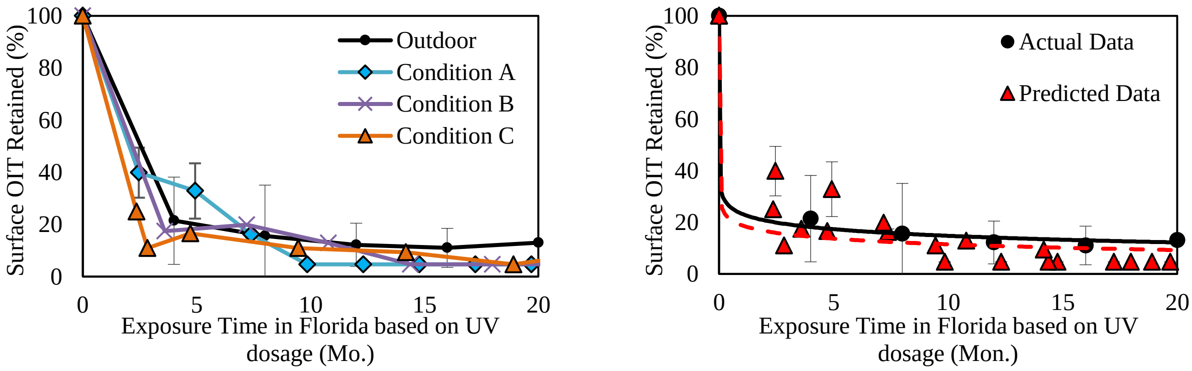
Year	Total Solar Radiation, MJ/m^2 (295-2500nm)	Year	Total Solar Radiation, MJ/m^2 (295-2500nm)
2007	305.8	2012	264.0
2008	297.8	2013	296.6
2009	311.9	2014	295.9
2010	323.9	2015	280.8
2011	288.1	2016	292.4
		Average	**295.7**

The equivalent outdoor exposure time was obtained from equation 5.

$$t_{Outdoor} = \frac{E_{UV,Weatherometer}}{E_{UV,Outdoor}} \times 12 \tag{5}$$

where $t_{outdoor}$ = Equivalent outdoor exposure time (Mon.), $E_{UV,weatherometer}$ = Total absorbed energy in the UV region inside the weatherometer (MJ/m2), $E_{UV.outdooor}$ = Total absorbed energy in the UV region in an outdoor environment (MJ/m2).

Results were plotted in Figure 6 and it was observed that predictions made based on the energy radiated in the UV region can also predict the OIT depletion sufficiently. It should be noted that this observation was made for xenon weatherometer which simulates the entire sunlight spectrum very closely. Result might differ for other types of weatherometers that use other artificial light sources such a fluorescent weatherometers that only simulates the UV portion of the spectrum.



(a) (b)

Figure 6. Comparison between actual retained OIT values and the values predicted based on UV dosage.

The predictions made here were based only on a comparison between the radiation energy inside weatherometer and outdoor solar radiation energy. While other weathering factors such as temperature and moisture, pollution also affect the antioxidant depletion in HDPE, their effect is believed to be less significant compared to radiation. This was confirmed for temperature in this study, where the OIT value of the coupons exposed to the elevated temperature of 65°C remained almost unchanged during the exposure time.

6 CONCLUSION

In this paper, HDPE coupons that contained antioxidant and 2.7% carbon black were exposed to xenon weatherometer at three irradiance levels, and natural sunlight. The relative amount of antioxidant in the exposed coupons was assessed using the OIT test. The effect of sunlight on exposed coupons was evaluated by monitoring the OIT profile along the thickness of the coupons throughout the exposure time.

- For both the weatherometer-aged and the outdoor-aged coupons, the surface layer showed the greatest decrease in OIT.
- Relative to the surface layer, the OIT value of the backside layer which was exposed to indirect radiation was less influenced. The least decrease in the OIT was measured in the core layers.
- Increasing the radiation intensity resulted in faster depletion of antioxidants in the surface layer.

- Applicability of the reciprocity law was evaluated and confirmed using OIT data in the surface layers under irradiance levels of 41.5, 60, and 80 W/m^2 in xenon weatherometer.
- The results obtained from the laboratory weatherometer testing were used to predict the OIT values of the surface layer under the natural sunlight, and the predicted values were in close agreement with the actual values obtained from outdoor exposure testing.

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