Draft Report

on

OXIDATION RESISTANCE OF CORRUGATED HDPE PIPE

To

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Abstract

This report presents the study on the oxidation resistance (OR) of corrugated HDPE pipe. Two corrugated HDPE pipe, P-1 and P-2, manufactured by different companies were evaluated in the study. The oxidation process was carried out in three incubation conditions: forced air oven, water bath, and water/air cycles to simulate various field environments. In addition, three elevated temperatures (65, 75, and 85°C) were employed to accelerate the oxidation reactions so that Arrhenius equation can be applied to predict properties at site ambient temperature of 23°C.

The oxidation resistance of the HDPE pipe was assessed by the depletion of antioxidants (AO) and degradation of the polymer. The depletion AOs was measured by the oxidative induction time (OIT) test and the degradation of polymer was determined by the melt index (MI) and tensile tests. The AOs in both pipe samples decreased immediately as the incubation started. The AO depletion rate was the highest in water and the lowest in air condition. For the water/air cycle, the AO depletion mainly occurred in the water cycle, and thus the depletion rate was similar to that of the water condition. An exponentially decreasing trend with aging time was obtained for AO of P-1 and P-2 in air and P-1 sample in water and water/air conditions, indicating a first order reaction rate. Contrary, a second order reaction rate was found for the AO depletion of P-2 sample in water, reflecting a strong interaction between AOs and water.

The oxidation degradation of the HDPE pipe was gauged by the changes of MI and tensile break elongation. Both properties started to decrease after OIT reached a critical value. At 85°C water incubation, MI exhibited a consistent decreasing trend with time whereas the break elongation showed a large variation from test to test at different incubation periods. P-1 exhibited severe delamination of the pipe wall in all incubated specimens, leading to the large variation of tensile break elongation. Therefore, the tensile break elongation was considered to be unsuitable for accessing the oxidation degradation of the pipe sample, and the MI was the parameter used to define the boundaries of three oxidation stages of HDPE. In this study, a 90% MI retained value was selected to be the end of Stage A which represented the lifetime of AOs. The corresponding OIT value at the end of Stage A was found to be 3 minutes which was applied to predict the AO lifetime at 23°C at three incubation conditions. The predicted lifetime in a constant flow of air was over thousand years while it is approximately one hundred years in water and water/air cycle conditions.

Specification for OR of corrugated HDPE pipe was proposed based on the findings of this study.

1. Introduction

This report presents the test results of the oxidation resistance (OR) study on two corrugated high density polyethylene (HDPE) pipes. Polyethylene without stabilizers is highly susceptible to oxidative degradation, leading to deterioration in engineering properties. Antioxidants (AO) are added to polyethylene products, such as corrugated pipe, to retard the onset of the polymer oxidation. For a stabilized corrugated HDPE pipe, the oxidation process can be conceptually expressed in three stages, as shown in Figure 1 (Hsuan and Koerner, 1998). Stage A is the antioxidant depletion period in which engineering property remains essentially constant. Stage B refers to the induction time that contributed by the intrinsic polymer property, and Stage C is the oxidative degradation period during which there is significant reduction in engineering properties. In general, the lifetime of a material (t_{life}) is defined as the time for a selected property to drop to 50% of its initial value, i.e., durations of A+B+C. Since Stage A is the precursor of the oxidation, it would be a good indicator for the OR of corrugated HDPE pipe. It should note that the duration B cannot be ignored in the overall lifetime of corrugated HDPE pipe.

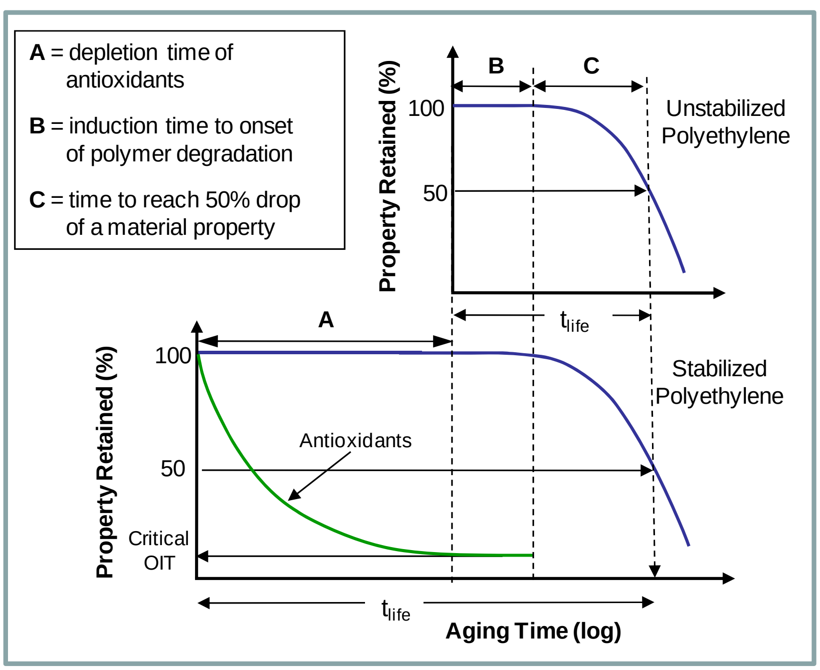

Figure 1 – Changes in antioxidants and tensile property with time

To assess the oxidation lifetime within a reasonable duration, target material is thermally aged at elevated temperature to accelerate the reaction rate. Multiple elevated temperatures are used so that the Arrhenius equation can be applied to predict the oxidation lifetime at a specific temperature which is lower than the test temperatures, as shown in Figure 2. In this study, two pipe samples were incubated in three different environments; air, water, and water/air cycle representing dry, wet, and water fluctuated zone, respectively. In addition, three elevated temperatures, at 65, 75, and 85°C were employed to accelerate the oxidation reactions in each of the incubation conditions.

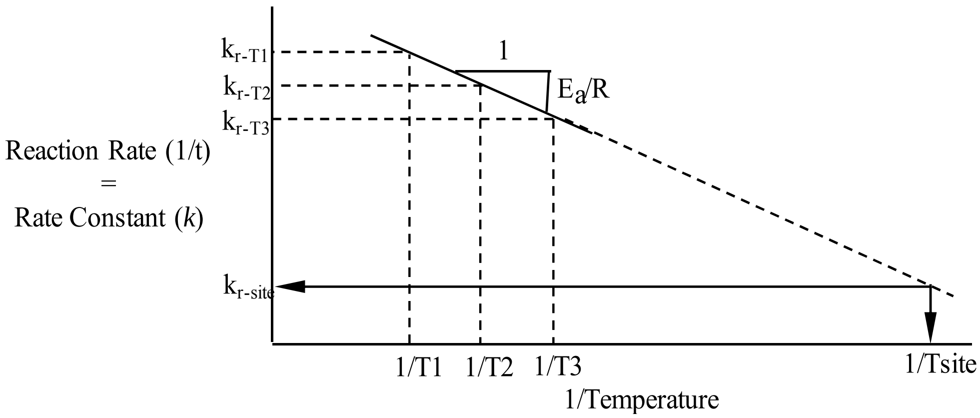

Figure 2 – Schematic illustration of Arrhenius plot to predict reaction rate at a specific site temperature based on results from elevated tests

2. Test Materials and Incubation Conditions

2.1 Test Materials

The two pipes used in this study were manufactured by two companies and pipe samples were supplied by FDOT. The pipe sample was separated into two parts, crown and liner; only the liner part of the pipe was used in this test. Coupons with length of 4 inches were cut from the liner.

2.2 Incubation Conditions

Table 1 shows the three incubation conditions and temperatures. The liner coupons were placed in each incubation conditions. The incubation procedures in each condition are described as follows:

- For the forced air oven series, the liner coupons were hanged with 1 inch spacing between coupons.

- For the bath incubation series, coupons were submerged in water bath at each test temperature. Air was constantly pumped into the water to maintain the saturated oxygen content at the incubation temperature.
- For the water/air cycle series, coupons were first submerged in the water bath for 30 days, and then switched to the forced air oven for 30 day to complete one cycle of incubation.

Table 1 – Incubation conditions for finished pipes

Pipe	Manufacturer	Incubation Conditions		
		Water (65, 75, 85°C)	Forced Air Oven (65, 75, 85°C)	Water/Air (65, 75, 85°C)
P-1	ADS (30-in)	X	X	X
P-2	Quality Culvert (36-in)	X	X	X

3. Test Methods

The properties of original and incubated pipe coupons were evaluated by the oxidative induction time (OIT) test, melt index (MI) test, and tensile test. The purpose of each test is described in Table 2.

Table 2 – Test methods and their function

Test	Standard	Purpose
OIT	ASTM D 3895	Qualitatively assessing the remaining amount of antioxidants
MI	ASTM D 1238	Onset of oxidation reaction by detecting the changes in molecular weight
Tensile	ASTM D 638, Type V	Onset of oxidation reaction by detecting the degradation in mechanical properties

A description of each test method is presented below:

3.1 <u>Oxidative Induction Time (OIT)</u>

OIT is a test method to detect the relative amount of antioxidants in the test specimen. The standard OIT was used in this study and the test procedure follows ASTM D3895. Using a differential scanning calorimeter (DSC), the specimen was heated to 200°C under nitrogen gas and was held at that temperature for 5 minutes. Oxygen was introduced into the cell and the test was terminated when the exothermal oxidation of the polymer took place. The time from introducing the oxygen to the onset of oxidation is defined as OIT. For the same antioxidant package, a higher OIT value indicates a greater amount of AO remaining in the test specimen.

3.2 Melt Index (MI)

MI is used to assess changes of molecular weight of the polymer. The test was performed according to ASTM D1238 under test condition of 2.16 kg/190^{o}C. Approximately 3 grams of material was heated to 190^{o}C for 8 minutes in the MI device. Then 2.16 kg load was applied to extrude the molten polymer out through an orifice. The extruded material in 6 minutes was weighed and the melt flow rate is reported in unit of g/10 minutes.

3.3 Tensile Test

Tensile test is used to measure the breaking properties of the pipe coupons. The test was performed according to ASTM D638 Type V which required a smaller specimen's dimensions than Type VI. Using a standardized Type V die, five specimens were cut from the incubated coupon. The tensile specimen was tested at a strain rate of 2 in/min. The tensile properties, including yield stress and strain, and breaking stress and strain, were recorded. However, the breaking strain will be used to assess changes in polymer chains.

4. Material Property

The material properties of the as-received pipe were evaluated by (OIT), melt index (MI), and tensile tests. Table 3 shows the OIT, MI, and tensile break elongation values. The reason for highlighting the tensile break elongation is because this property is often used as an indicator for the oxidation degradation of the polymer. The number of replicate tests performed on the OIT test was two, for the MI test was one, and for the tensile test was five. The same number of replicates was also performed on the incubated samples.

Table 3 – Material Properties of As-received Pipes

Pipe	Material Properties		
	OIT (Minute)	Melt Index (g/10 min)	Tensile Break Elongation (%)
P-1	22.2	0.12	1182
P-2	25.0	0.28	2423

5. Pipe P-1 Test Results

For P-1, the test duration of oven samples is exceeded 1000 days and is still on-going while water and water/air cycle incubations have been terminated after 344 days. This report provides the test results and the reason for the termination.

5.1 OIT Test Results

The OIT test data are presented in retained percentage calculated using Eq. 1. Figures 3(a) to (c) show the changes of OIT retained with time of pipe liner at incubation temperatures of 85, 75, and 65°C. In addition, the data are fit with equation, Eq. 2, representing a first order reaction.

$$OIT\ retained\ of\ aged\ sample(\%) = \frac{OIT\ value\ of\ aged\ sample}{original\ OIT\ value} \times 100\% \qquad (1)$$

$$OIT\ retained\ (\%) = 100e^{-kt} \qquad (2)$$

Where: "k" is the reaction rate which varies with polymer, AO package and incubation condition. "t" is aging time (day).

The OIT retained values in water bath exhibit the greatest decrease. Also the OIT retained values in the water/air cycle incubation condition are similar to those in water. A rapid initial decrease in OIT retained values can be seen in the water environment, Figure 3(a), and is suspected to be caused by the physical leaching and/or hydrolysis of antioxidants. At 65°C, the initial drop in OIT is less noticeable. In addition, the rapid initial decrease of OIT leads to a poor fitting with the first order reaction, particularly at 75 and 85°C.

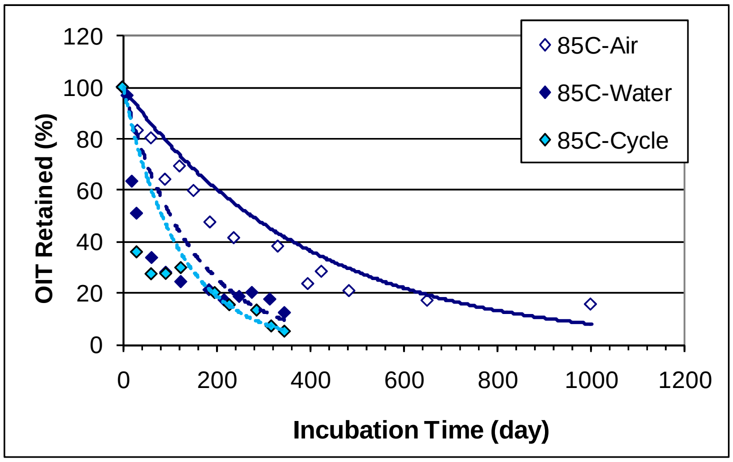

Figure 3(a) - OIT retained with time of P-1 in three incubation conditions at 85°C

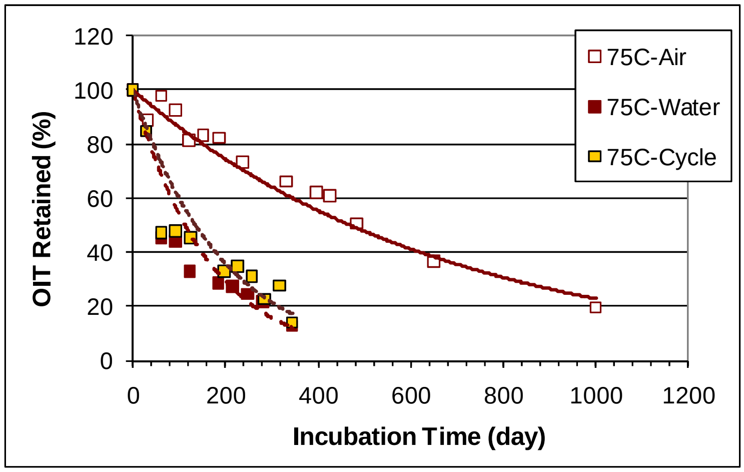

Figure 3(b) - OIT retained with time of P-1 in three incubation conditions at 75^{o}C

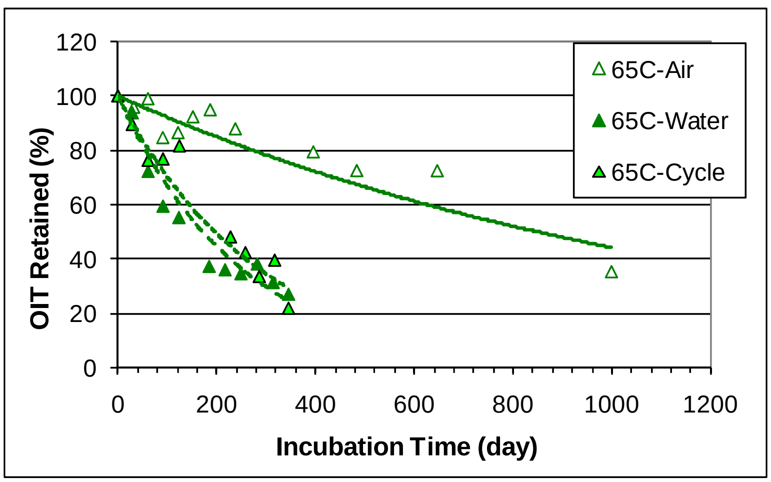

Figure 3(c) - OIT retained with time of P-1 in three incubation conditions at 65^{o}C

The effect of temperature on the depletion of antioxidants within a single incubation environment is presented below:

5.1.1 *Air Oven Condition*. Figure 4 shows the OIT value versus time plots of three temperatures. The OIT values decrease exponentially with time according to the first order reaction (Eq. 2) while the reduction rate increases with temperature.

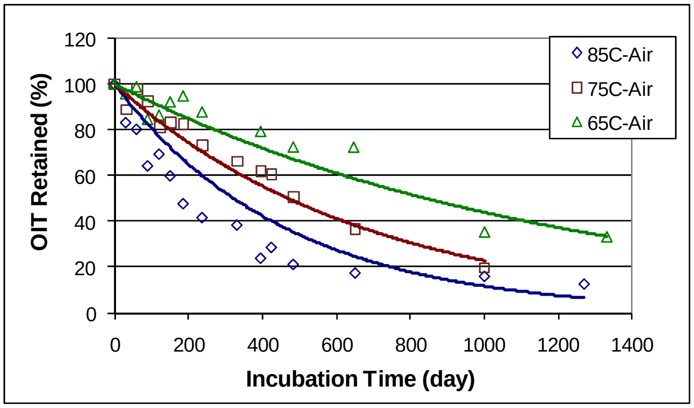

Figure 4 – Changes of OIT value in forced air ovens at three temperatures

5.1.2 *Water Bath Incubation*. Figure 5 shows the OIT versus time plots of three temperatures. At all three temperatures, the OIT values decrease significantly faster than those in air, particularly during the early incubation period. Multiple reactions are probably taken place during the incubation. Therefore equation represents a second order reaction (Eq. 3) is fit with the OIT data and the R square value at all three temperatures is greater than 0.9.

$$OIT\ retained\ (\%) = Ae^{k_1 t} + Be^{k_2 t} \tag{3}$$

Where: A and B are constants and B = (100-A); k_1 and k_2 are reaction rates of two simultaneous reactions, and *t* is incubation time.

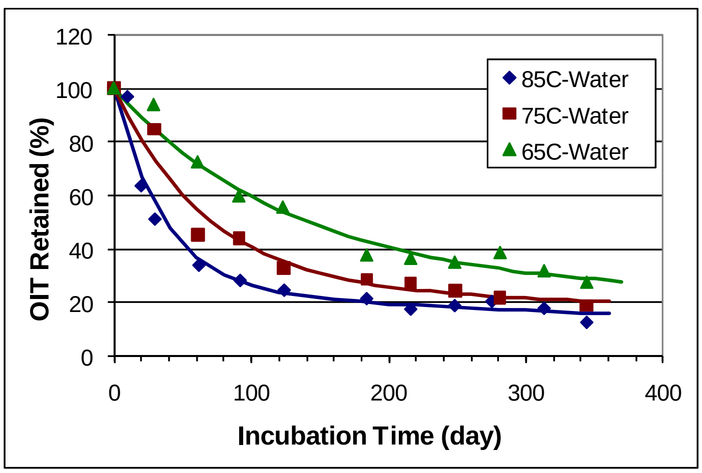

Figure 5 – Changes of OIT in water bath at three temperatures

5.1.3 *Water/Air Cycle Condition*. Figure 6 shows the OIT value against time plots of three temperatures. The OIT decreasing trends are similar to those in water. At 75 and 85°C, the OIT values drop rapidly in first cycle (30 days in water/30 days in air) and then decrease gradually with time. The depletion of antioxidants was primarily taking place during the water incubation period of the water/air cycle.

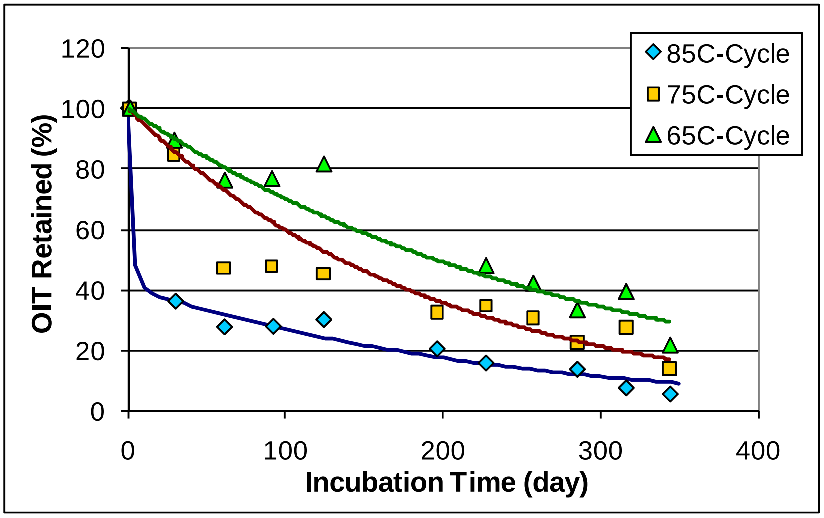

Figure 6 – Changes of OIT retained in water/air cycle at three temperatures

5.2 Melt Index (MI) Test Results

The MI test was performed on incubated liner coupons to detect changes in the molecular weight due to the oxidation. Results are presented in Figures 7(a) to (c). The MI retained value decreased to 80% after 1000 days at 85°C water while the MI retained values at 65 and 75°C water condition maintained above 80%.

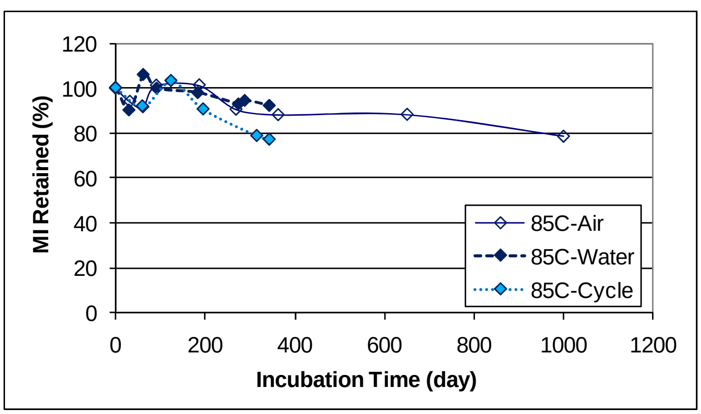

Figure 7(a) – MI value against time for pipe liner in three incubation conditions at 85°C

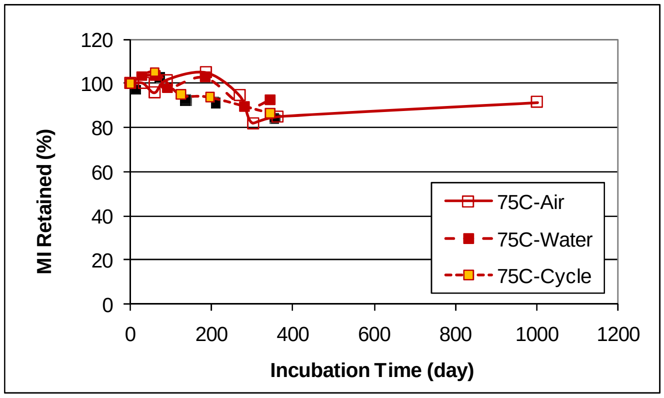

Figure 7(b) – MI value against time for pipe liner in three incubation conditions at 75°C

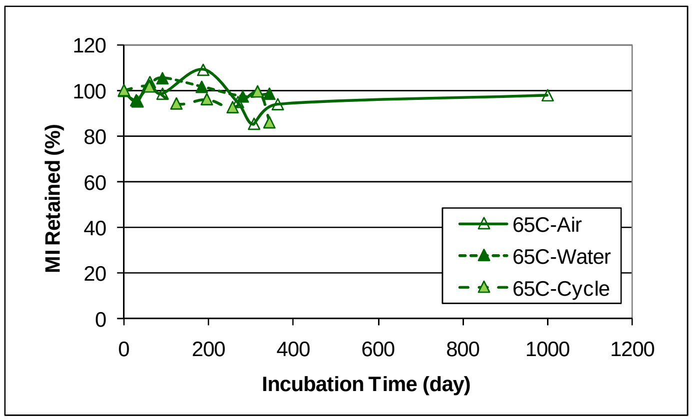

Figure 7(c) – MI value against time for pipe liner in three incubation conditions at 65°C

5.3 <u>Tensile Test Results</u>

Figures 8(a) to (c) show the changes of breaking elongation retained with time in different incubation environments at 85, 75 and 65°C. The breaking elongation retained values remain almost unchanged throughout 600 days in air incubation. In contrast, coupons incubated in water exhibit a large reduction in break elongation; the retained value drops to 20% within 150 days at 75 and 85°C and to 40% at 65°C. It should be emphasized that at the same incubation period the OIT retained values of these pipe coupons were still above 20%, and MI values remained unchanged. Similar behavior was also observed in samples exposed to water/air cycle. The reason for such large reduction in the breaking elongation is due to the *delamination* behavior, which will be discussed in the next section of the report. Figures 9 and 10 depict photos of delaminated specimens; separation occurred along the thickness of the tensile test specimen. The delamination led to large variation in the breaking strain among five replicate tests, as illustrated in Figures 11 and 12.

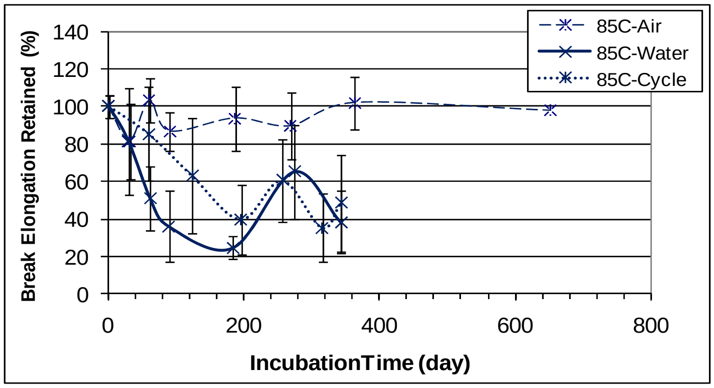

Figure 8(a) – Tensile break elongation against time in different conditions at 85^{o}C

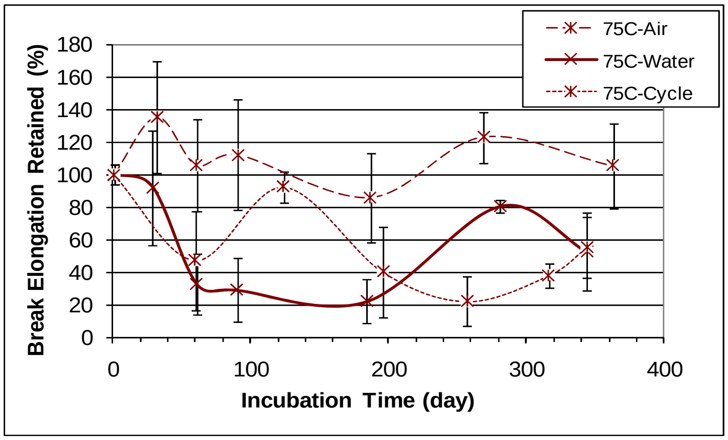

Figure 8(b) – Tensile break elongation against time in different conditions at 75^{o}C

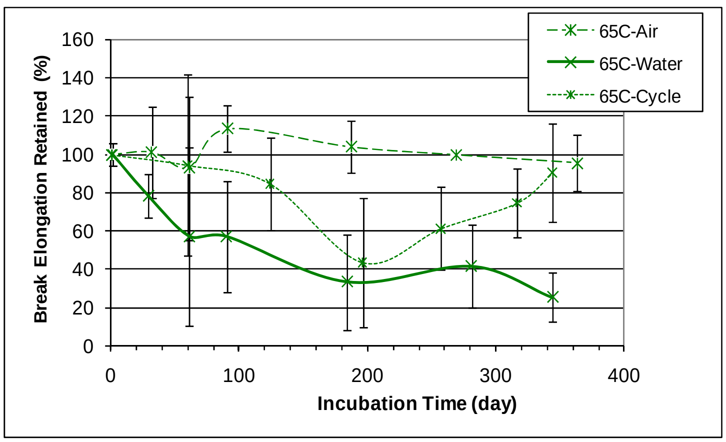

Figure 8(c) – Tensile break elongation against time in different conditions at 65^{o}C

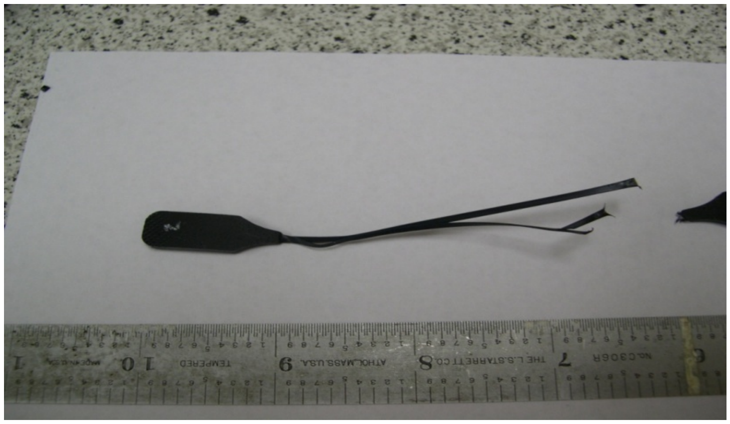

Figure 9 – A failed tensile specimens that exhibited delamination

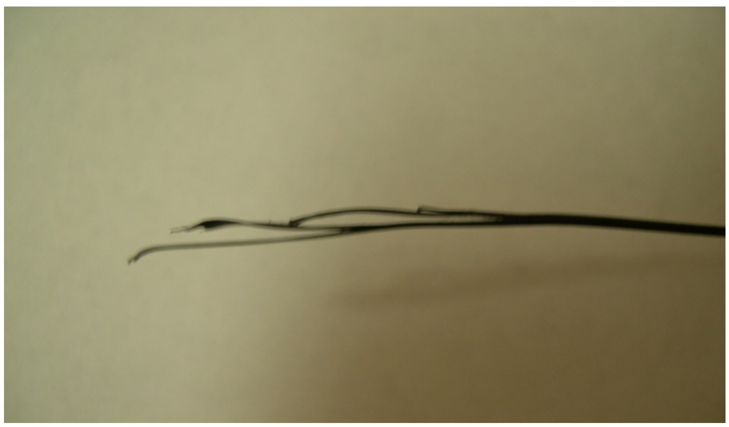

Figure 10 – A close view of the delamination revealing four layers of separation along the thickness of the specimen

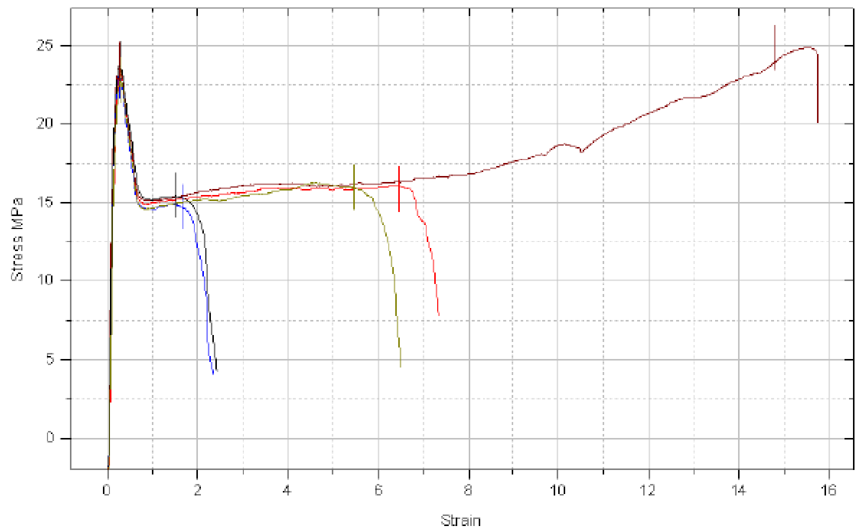

Figure 11 – Stress/strain curves of five test specimens exposed to water bath at 65°C after 60days

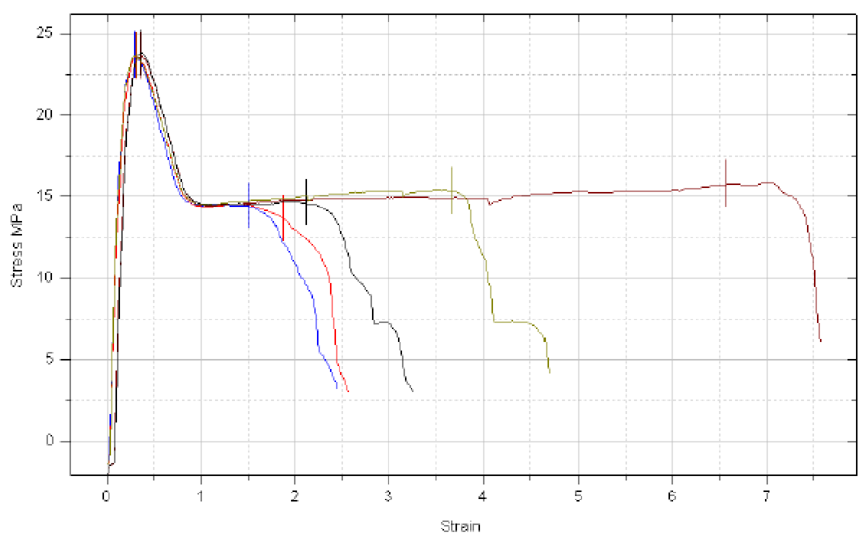

Figure 12 – Stress/strain curves of five test specimens exposed to water bath at 75°C after 60days

5.4 Delamination Behavior of P-1

The delamination phenomenon occurred during the tensile test was observed in most of the incubated specimens, even through the severability varied among specimens. In general, delamination started at the base/transition part of the dumbbell specimen and then extended to the necking region. In some specimens, delamination extended to the entire length of elongated region, resulting in multiple layers of separation. In order to quantify the delamination, a ranking system was developed based on the length of delamination, as shown in Table 3. Since five specimens were tested at each incubation period, the highest possible ranking point is 100 (i.e., 5 * 20 = 100).

Table 3 – Ranking point referring to the length of delamination

Delaminated Length	**Ranking point**
Severe: ≥ 90%	20
High: 89% to 50%	15
Medium: 49% to 11%	10
Low: ≤ 10%	5
No delamination	0

The comparison among different temperatures in each incubation environment is presented in a bar chart format, as shown in Figures 13 to 15. However, there is no definite relationship between the delamination and temperature. Coupons incubated in the water environment generally show a higher degree of delamination than those in other two incubation environments. Also a higher degree of delamination was observed for coupons incubated at the higher temperatures.

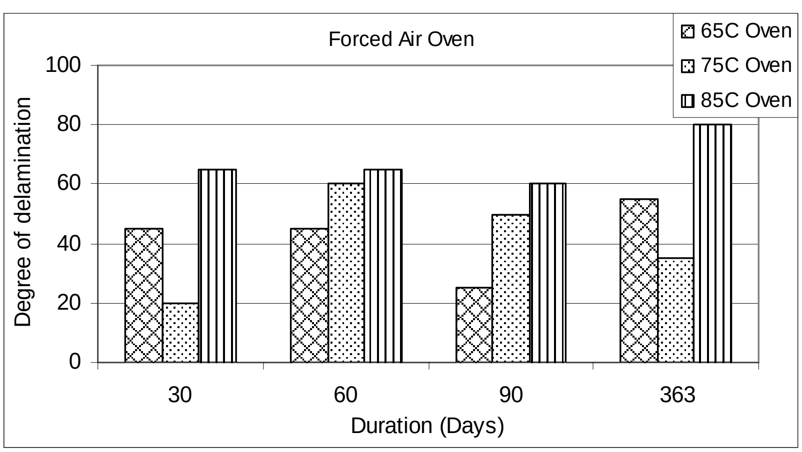

Figure 13 – Delaminated of Forced Air Oven Samples

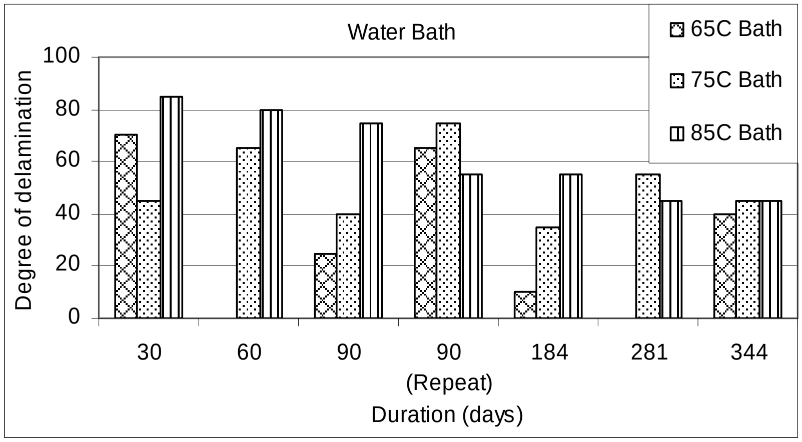

Figure 14 – Delaminated of Water Bath Samples

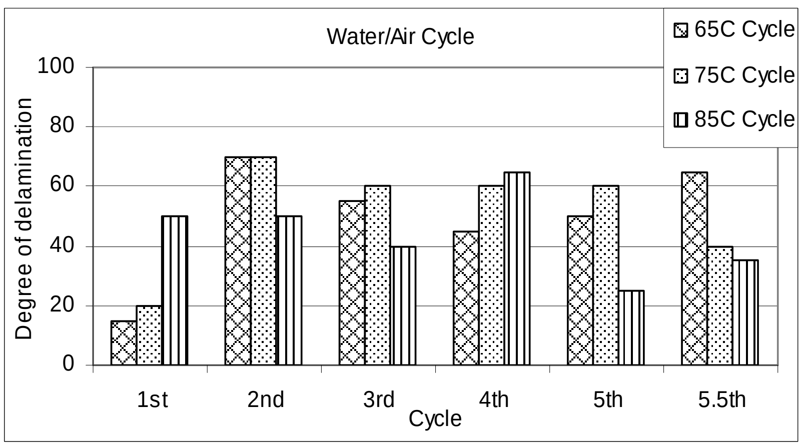

Figure 15 – Delaminated of Water/Air Cycle Samples

6. Pipe P-2 Test Results

6.1 <u>OIT Test Results</u>

The OIT test data are presented as the retained percentage. Figures 16(a) to (c) shows changes of OIT retained value with time at incubation temperatures of 65, 75, and 85°C. It should note that the initial rapid decrease of OIT values is much less pronounced in both water and water/air cycle environments in comparison to P-1. The OIT retained values decrease exponentially with time in all three incubation environments indicating a first order reaction. In addition, the OIT retained values in water/air cycle environment are slightly higher than those in the water environment at all three incubation temperatures.

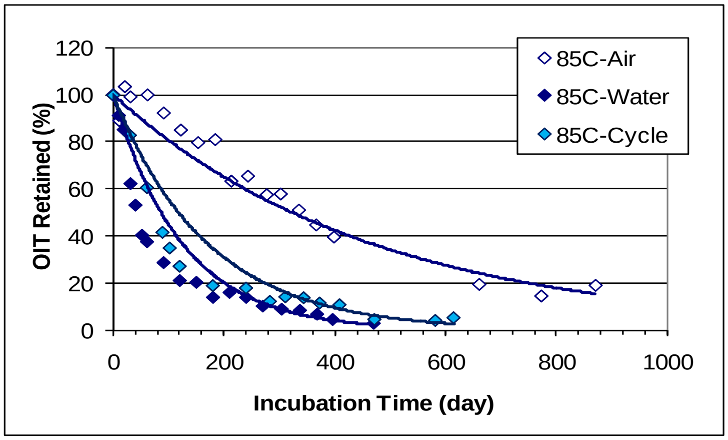

Figure 16(a) - OIT retained with time of P-2 in three incubation conditions at 85°C

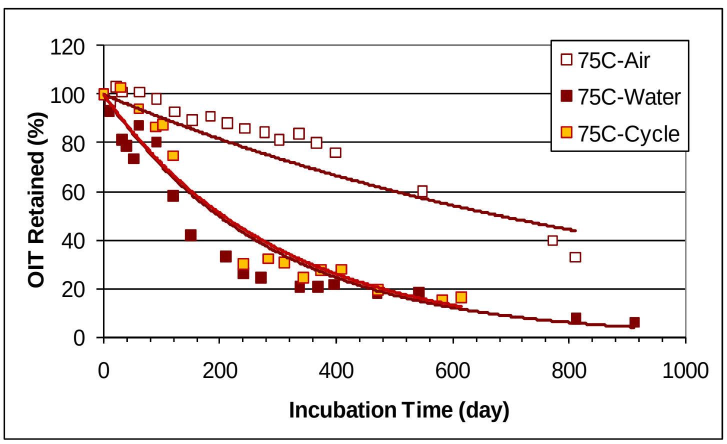

Figure 16(b) - OIT retained with time of P-2 in three incubation conditions at 75°C

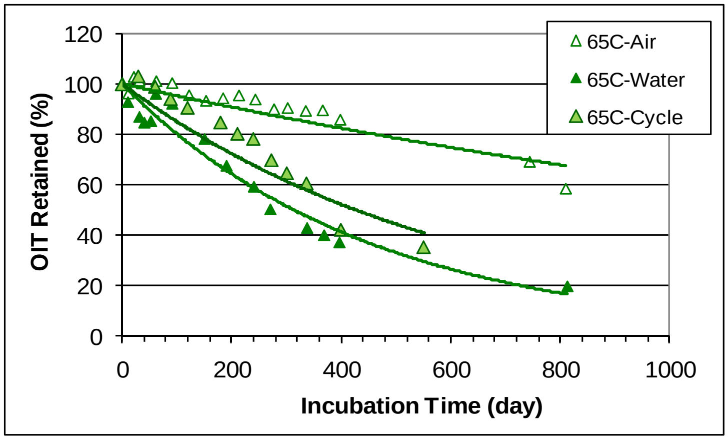

Figure 16(c) - OIT retained with time of P-2 in three incubation conditions at 65^{o}C

The effect of temperature on the depletion of antioxidants in the same incubation environment is presented below:

6.1.1 *Air Oven Condition*. Figure 17 shows the OIT value versus time plots of three temperatures. The OIT values decrease exponentially with time. However the reduction rates are relatively slow. At 85^{o}C, the OIT value drops to 10 min. (60%) after 400 days.

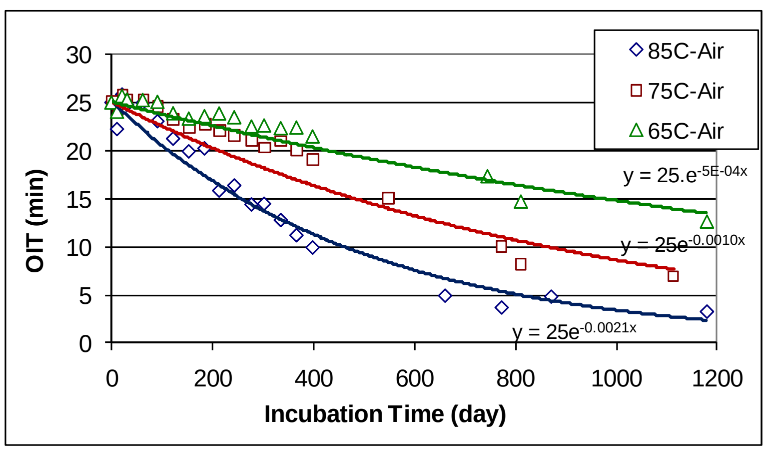

Figure 17 – The OIT retained versus time in oven incubation environment

6.1.2 *Water Bath Incubation*. Figure 18 shows the OIT value versus time plots of three temperatures. The OIT data can be fitted with an exponential equation reasonably well. Compared to the air incubation, the OIT reduction rates in water are significantly faster at all three temperatures. At 85^{o}C, the OIT value drops to 1 min. after 400 days.

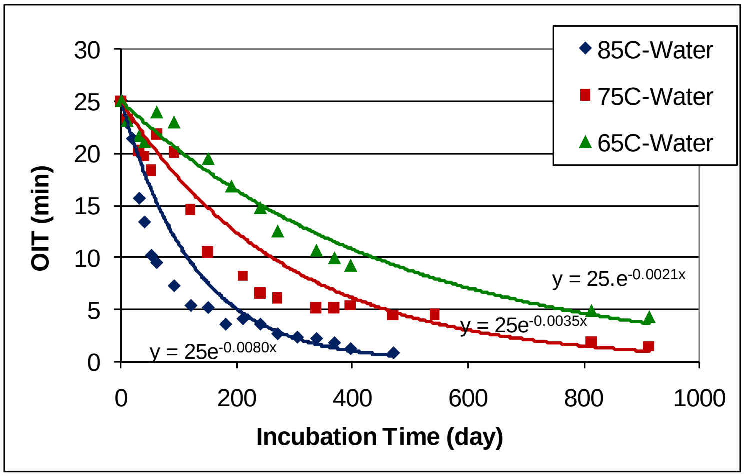

Figure 18 – The OIT retained versus time in water incubation environment

6.1.3 _Water/Air Cycle Condition_. Figure 19 shows the OIT value against time plots of three temperatures. The OIT decreasing trends are very similar to those in water. The data can also be fitted with an exponential equation. At 85°C, the OIT value drops to approximately 1.3 min. after 470 days.

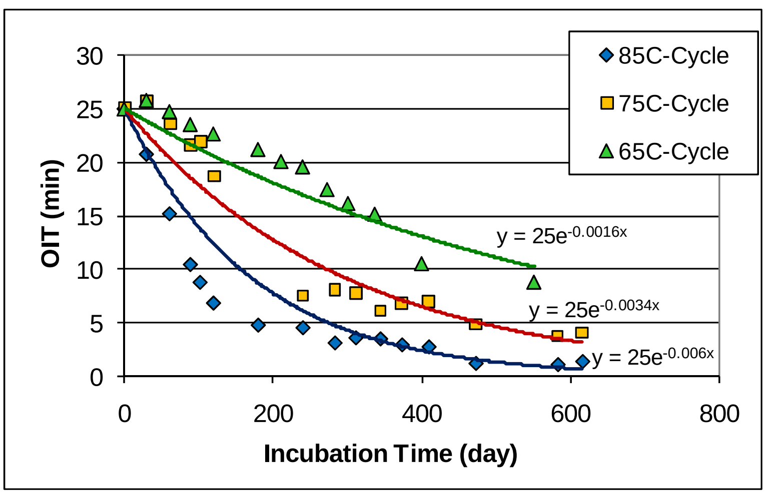

Figure 19 – The OIT retained versus time in air/water incubation environment

6.2 Melt Index (MI) Test Results

The MI test was performed on the incubated coupons to detect changes in the molecular weight. Test results are presented in Figure 20(a) to (c). The MI values remain above 90% at 65°C after 800 days. However, MI value starts to decrease after 210 days at 85°C after in the water and water/air incubated coupons.

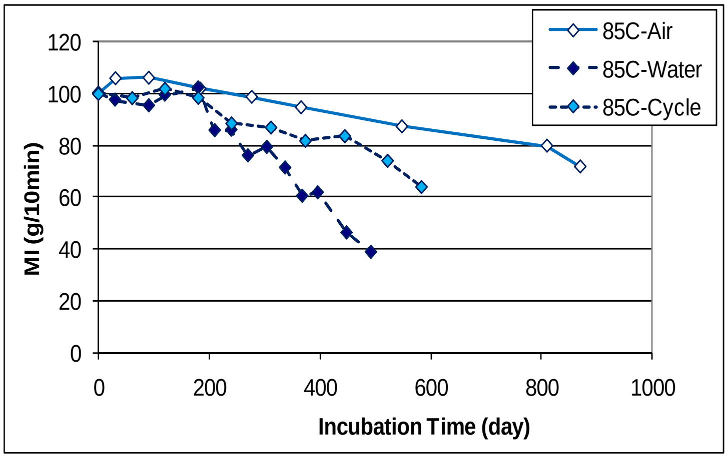

Figure 20(a) – MI value against time for pipe liner in three conditions at 85°C

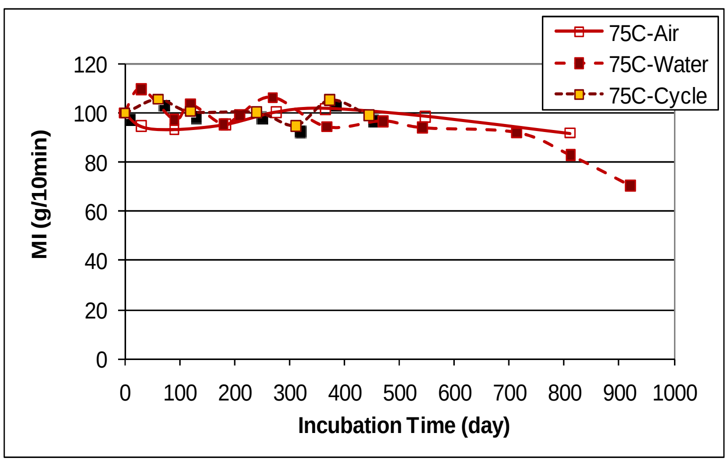

Figure 20(b) – MI value against time for pipe liner in three conditions at 75°C

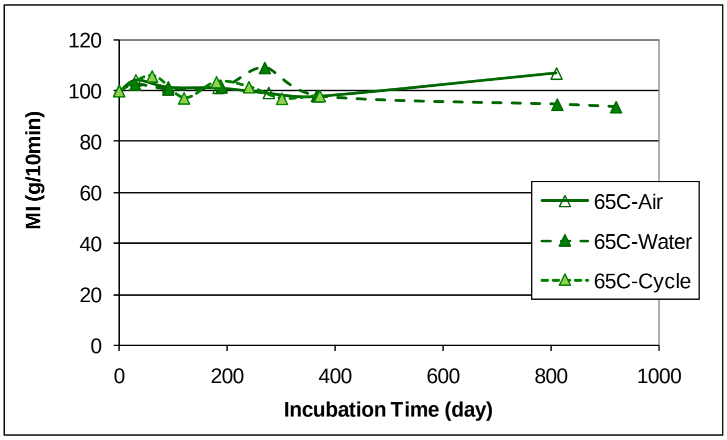

Figure 20(c) – MI value against time for pipe liner in three conditions at 65°C

6.3 <u>Tensile Test Results</u>

Figures 21(a) to (c) show the changes of breaking elongation retained with time in three incubation conditions at 85, 75 and 65°C. Overall, coupons incubated in water exhibit the greatest reduction in the breaking elongation. In the air incubation, the breaking elongation retained values remain relatively constant throughout 800 days of incubation at all three temperatures. In the water environment, the breaking elongation begins to decrease after 210 days at 85°C which coincides with the decrease of MI value. However, increase in standard deviation was also detected. From 210 to 400 days, the breaking elongation varies between 60% and 80%. At 480 days of incubation, the breaking elongation decreases to 13%. For the air/water cycle condition, a small decrease in the tensile breaking elongation values can be observed after 400 days of incubation at 85°C, while the corresponding OIT retained value is at 2.5 minutes (10%). There was no *delmaination* observed in any of the specimens during the tensile test.

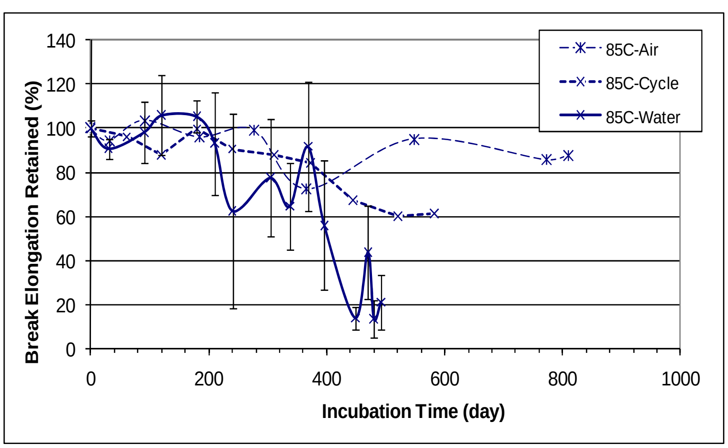

Figure 21(a) – Tensile break elongation against time in different conditions at 85°C

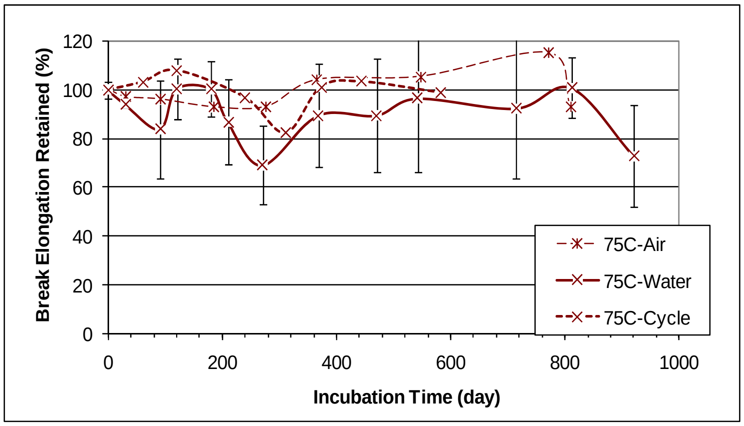

Figure 21(b) – Tensile break elongation against time in different conditions at 75^oC

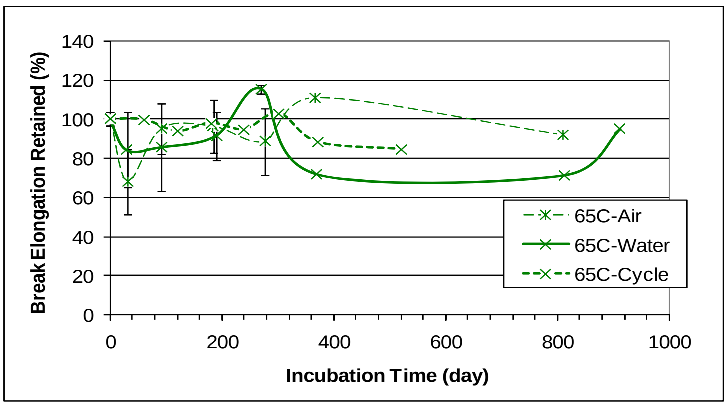

Figure 21(c) – Tensile break elongation against time in different conditions at 65^oC

7. Correlating OIT to MI and Tensile Break Elongation

For P-1, the delamination behavior led to prematurely decrease in tensile break elongation. The incubation series in water and water/air cycle were terminated after 344 days while the air incubation is still on-going. For P-2, the incubation in water/air cycle condition has been terminated after 521 days since coupons exhibited slower depletion of AO than those in water condition. The incubations in water and air are still on-going.

P-2 in water condition shows the most pronounced changes and thus the test data are used for the correlation evaluation. Figures 22 (a), (b), and (c) are graphs of plotting property retained versus incubation time of P-2 in water at temperatures of 85, 75, and 65^oC. The immediately decrease in OIT can be observed at all three temperatures while MI and tensile break elongation maintains essentially unchanged. After OIT reaches a critical value at which MI gradually decreases as well as the tensile break elongation.

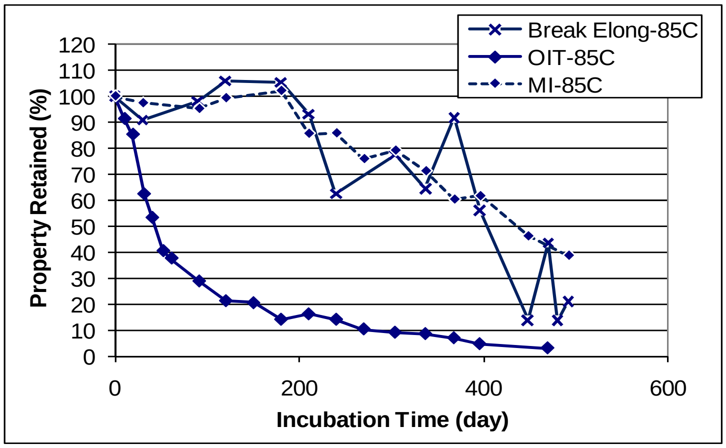

Figure 22(a) – Property retained versus time of P-2 at 85°C water incubation

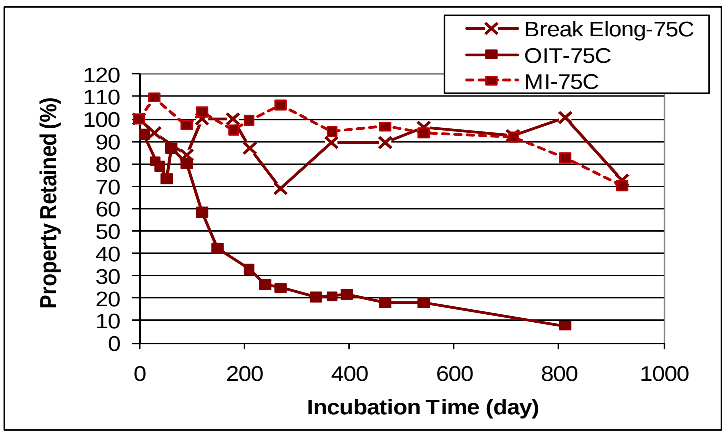

Figure 22(b) – Property retained versus time of P-2 at 75°C water incubation

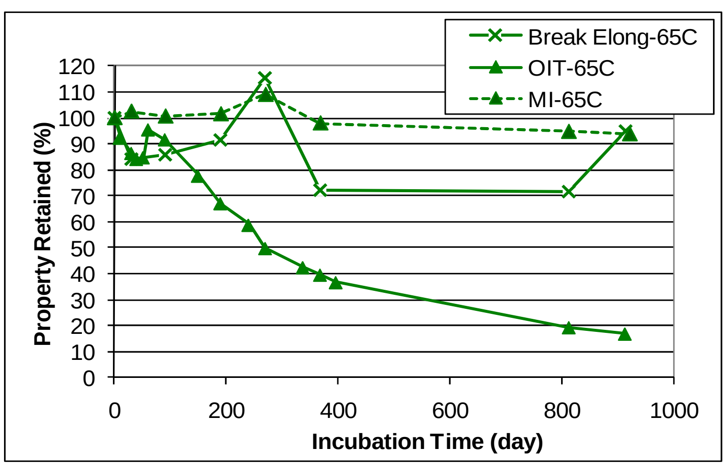

Figure 22(c) – Property retained versus time of P-2 at 65°C water incubation

Based on these three sets of data, the boundary conditions of the three stages (Stages A, B, and C) in Figure 1 are identified. Since the tensile break elongation does not change consistently with increasing incubation time, MI is used as the guide for setting the boundaries of three stages, while the tensile break elongation is still considered as a reference. The MI retained value for each stage of the oxidation process is as follows:

i) Stage A – MI retained value at 90%

ii) Stage B – MI retained value at 80%

iii) Stage C – MI retained value at 50%.

Table 4 shows the corresponding OIT values and tensile break elongation retained values for P-1 and P-2 in all incubation conditions. Coupons incubated in water have the most pronounced changes in material properties in comparison to air and water/air cycle conditions. P-2 coupons in water have reached Stage C after 337 and 921 days at 85 and 75^{o}C, respectively. The OIT value at the boundary of Stage A in water incubation condition ranges from 2 to 4 min.

Table 4 – Summary of boundary values for the three stages of oxidation process

85°C

Condition	Test	P-1 Stage A	P-1 Stage B	P-1 Stage C	P-2 Stage A	P-2 Stage B	P-2 Stage C
Oven	MI	> 90% upto 269 days	80-90% upto 650 days[1]	N/A	> 90% upto 548 days	80-90% upto 810 days[2]	< 80% NYR
	OIT	8 - 9 min.	4 - 5 min.	3 - 4 min.	5 - 6 min.	3 - 4 min.	NYR
	Tensile	na	na	na	~ 90%	80- 90 %	NYR
Bath	MI	> 90% upto 344 days[3]	N/A	N/A	> 90% upto 210 days	80-90% upto 304 days	< 80% after 337 days[2]
	OIT	2 - 3 min.	N/A	N/A	3 - 4 min.	2 -3 min.	1 - 2 min.
	Tensile	na	na	na	~ 90%	~ 80%	< 60%
Cycle	MI	> 90% upto 169 days	80-90% upto 257 days	< 80% after 316 days[3]	> 90% upto 240 days	80-90% upto 444 days	< 80% after 521 days[4]
	OIT	4 - 5 min.	4 - 5 min.	3 - 4 min.	4 - 5 min.	2 - 3 min.	1 - 2 min.
	Tensile	na	na	na	~ 90%	~ 65%	60%

75°C

Condition	Test	P-1 Stage A	P-1 Stage B	P-1 Stage C	P-2 Stage A	P-2 Stage B	P-2 Stage C
Oven	MI	> 90% > 650 days[1]	NYR	NYR	> 90% upto 810 days[2]	NYR	NYR
	OIT	4 - 5 min.	NYR	NYR	8 min.	NYR	NYR
	Tensile	na	na	na	above 90%	NYR	NYR
Bath	MI	> 90% upto 344 days[3]	N/A	N/A	> 90% upto 714 days	80-90% upto 812 days	< 80% after 921 days[2]
	OIT	2 - 3 min.	N/A	N/A	3 - 4 min.	2 - 3 min.	1 - 2 min.
	Tensile	na	na	na	~ 90%	80- 90 %	~ 70%
Cycle	MI	> 90% upto 196 days	80-90% upto 344 days[3]	N/A	> 90% > 521 days[4]	N/A	N/A
	OIT	7 -8 min.	2 -3 min.	N/A	5 min.	N/A	N/A
	Tensile	na	na	na	unchange	N/A	N/A

65°C

Condition	Test	P-1 Stage A	P-1 Stage B	P-1 Stage C	P-2 Stage A	P-2 Stage B	P-2 Stage C
Oven	MI	> 90% > 650 days[1]	NYR	NYR	> 90% > 810 days[2]	NYR	NYR
	OIT	~ 8 min.	NYR	NYR	~ 15 min.	NYR	NYR
	Tensile	na	na	na	unchanged	NYR	NYR
Bath	MI	> 90% > 344 days[3]	N/A	N/A	> 90% upto 912 days[2]	NYR	NYR
	OIT	6 min.	N/A	N/A	4 min.	NYR	NYR
	Tensile	na	na	na	~ 90%	NYR	NYR
Cycle	MI	> 90% > 344 days[3]	N/A	N/A	> 90% > 521 days[4]	NYR	NYR
	OIT	~ 5 min.	N/A	N/A	~ 9 min.	NYR	NYR
	Tensile	~ 90%	NYR	NYR	~ 90%	NYR	NYR

[1] incubation terminated after 650 days
[2] incubation is still on-going
[3] incubation terminated after 344 days
[4] incubation terminated after 521 days
na - not applicable
N/A = Not Available
NYR = Not Yet Reach

8. Predicting the Lifetime of Antioxidants

In this section of the report, the lifetime of antioxidants, which represents the duration of Stage A in Figure 1, is predicted based on the OIT reduction rate. The lifetime of antioxidants is defined by the duration that it takes the OIT value to reach 3.0 minutes, which is the average value at the boundary between Stages A and B.

8.1 Lifetime Prediction of Antioxidants in P-1

The lifetime prediction is carried out on P-1 in air and water incubated environments. The prediction was not carried out for the water/air incubation due to the scattering of the OIT data. However, it is anticipated that the predicted lifetime of AO in water/air environment would be slightly longer than that in water. As indicated in Figure 3(b) and (c), the reduction rates of AO at 65 and 75°C in water/air cycle is slower than in water.

8.1.1 *AO lifetime in air.* As shown in the Figure 4 of this report, the OIT reduction rate can be obtained by fitting Eq. 2 to the OIT versus time data at each temperature. Figure 23 shows the AO reaction rates at three incubation temperatures by plotting OIT value versus time.

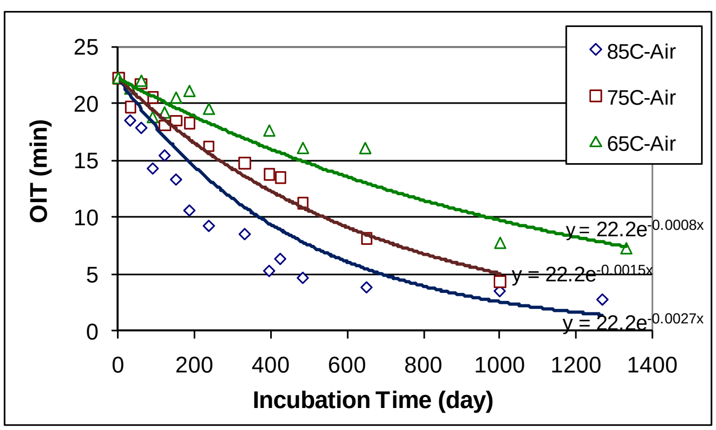

Figure 23 – Plotting OIT versus incubation time for oven incubated samples

By applying the Arrhenius equation, the OIT reduction rate at 23°C can be predicted according to Eq. (4).

$$k = Ae^{-E/RT} \quad (4)$$

Where: k is OIT reduction rate or AO reaction rate (1/day), E is activation energy (kJ/mole), R is gas constant (8.314 J/mol-K), T is absolute temperature (K), and A is material constant.

Figure 24 shows the Arrhenius plot of *ln(k)* versus *1/T*. The activation energy is deduced from the slope of the curve and is equal to 61 kJ/mol. The calculation to obtain the time for OIT to reach 3.0 minutes at 23°C is illustrated in Eq. (5) and (6):

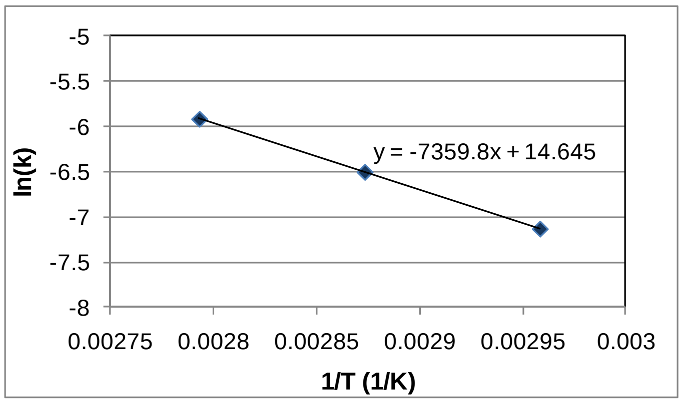

Figure 24 – Arrhenius plot of OIT reduction rate in air for P-1

$$ln(k_{23^oC}) = 14.645 - 7359.8\left(\frac{1}{23+273}\right) = -10.22 \quad (5)$$

$$k_{23^oC} = 3.65x10^{-5}$$

$$\ln(3) = \ln(22.2) + (-3.65x10^{-5}) * (t) \quad (6)$$

$$t = \frac{(3.1-1.1)}{3.65x10^{-5}} = 54794\ days = 150\ years$$

The predicted lifetime of antioxidants in terms of OIT is well over hundred years at 23°C in completely dry environment simulated by using forced air ovens.

8.1.2 *<u>AO lifetime in water.</u>* As shown in the Figure 3 of this report, the OIT reduction rate can be expressed by the second order reaction, as shown in Eq. 3. The four parameters of Eq. 3 at each incubation temperature are shown in Table 5. At 65°C, the depletion of AO is still governed by the first term after 340 days of incubation.

Table 5 – Parameters of Eq. 3 deduced from Figure 3

Temperature (°C)	*A*	*B*	k_1	k_2
85	75.25	24.75	0.0283	0.00125
75	75.02	24.98	0.0148	0.00064
65	77.15	22.85	0.0074	0.00000

The analytical procedure to predict AO lifetime in water is different than that used in the air because the reaction is governed by two separate terms instead of a single term. The step-by-step procedure is described as follows:

i. Determine k_1 and k_2 at 23°C using the slope value obtained from the Arrhenius plot in Figure 25. The predicted k_1 and k_2 values are 2.44 x10^{-4} and 8.81 x10^{-6}, respectively.

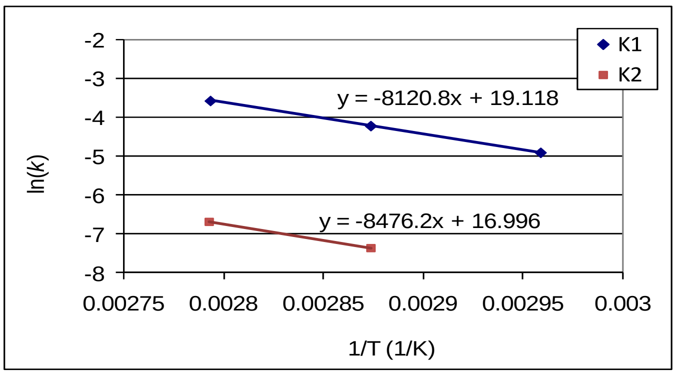

Figure 25 – Arrhenius plot of k_1 and k_2

ii. Identify the boundary separating the first and second term in each of the curve, by plotting the first and second term separately, as illustrated in Figure 26.

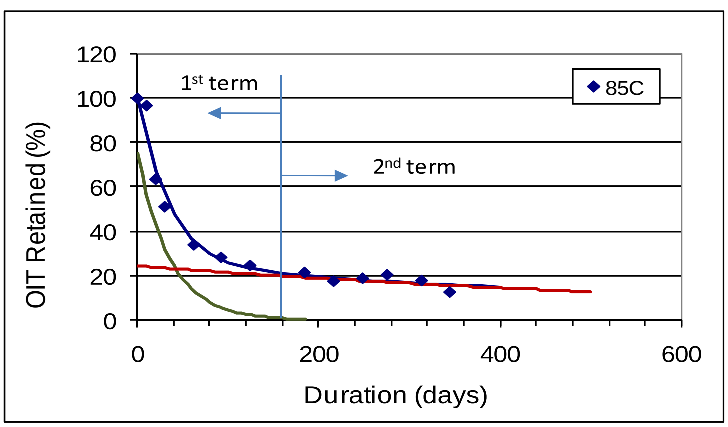

Figure 26 – Identifying the boundary separating the first and second term

iii. Shift data from 85, 75 and 65°C to 23°C using Eq. (7) and Eq. (8) to generate the AO depletion master curve at 23°C, as shown in Figure 27.

$$a_{T_{(k_1)}} = e^{\frac{-E_1}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \tag{7}$$

$$a_{T_{(k_2)}} = e^{\frac{-E_2}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \tag{8}$$

Where: $a_{T(k1)}$ and $a_{T(k2)}$ are shift factors for first and second terms, respectively; E_1 and E_2 are activation energy for k_1 and k_2; T_1 is the reference temperature at 23°C, and T_2 is the incubation temperature.

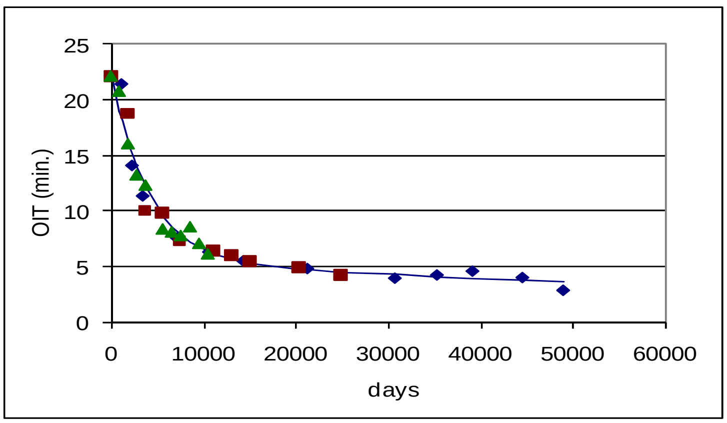

Figure 27 – Master curve at 23°C of AO depletion

iv. Establish the second order reaction equation to represent the master curve at 23°C, as expressed in Eq. (9).

$$OIT_{23^oC} = 16.75e^{2.44x10^{-4}t} + 5.25e^{8.8x10^{-6}t} \tag{9}$$

Where: The sum of A and B (16.75 + 5.25) is equal to the initial OIT value of 22 minutes; t is the duration (day).

v. Determine time to reach 3 minutes of OIT value using Eq. (9), which is the lifetime of AO in the pipe P-1 under water incubation condition. The value is 187 years.

In order to verify the validity of this extrapolation analysis, the OIT depletion curves at 85 and 75^{o}C are shifted to 65^{o}C using Eq. (7) and (8). The equation representing the master curve at 65^{o}C is expressed in Eq. (10).

$$OIT_{65^oC} = 16.75e^{0.0074t} + 5.25e^{0.00031t} \qquad (10)$$

The predicted time to reach an OIT value of 8.5 minutes is 209 days which is reasonable close to the experimental value of 280 days from the 65^{o}C OIT curve.

8.1.3 Summary

The predicted AO lifetimes of P-1 pipe in air and water are 150 years and 187 years, respectively. The predicted lifetime of this AO package in water and air is very similar. However, a rapid depletion of AO was detected in the first six months of water incubated samples; after that the AO depletion rate slowed down significantly. The rapid depletion was probably caused by the physical leaching and/or hydrolysis of AO rather than the oxidative free radical reactions which corresponded to the secondary reaction as the concentration of oxygen in water at elevated temperature is limited.

8.2 Lifetime Prediction of Antioxidants in P-2

The lifetime prediction is carried out on P-2 in air, water, and air/water cycle incubated environments.

8.2.1 *AO lifetime in air*. As shown in the Figure 17 of this report, the OIT reduction rate can be obtained by fitting an exponential equation to the OIT versus time data at each temperature. Figure 28 shows the Arrhenius plot based on the OIT reduction rate. The activation energy deduced from the slope of the curve is 72 kJ/mol which is higher than the value obtained from P-1 under the same incubation condition.

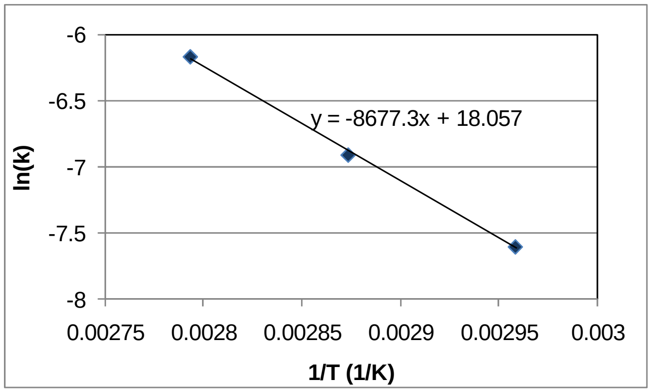

Figure 28 – Arrhenius plot of OIT reaction rate in air for P-2

The calculation to obtain the predicted time for OIT to reach 3.0 minute at 23°C under constantly flow of air is illustrated in Eq. (10) and (11):

$$ln(k_{23^oC}) = 18.057 - 8677.3\left(\frac{1}{23+273}\right) = -11.26 \quad (10)$$

$$k_{23^oC} = 1.29x10^{-5}$$

$$ln(3) = ln(25) + (1.29x10^{-5})(t) \quad (11)$$

$$t = \frac{3.21 - 1.1}{1.29x10^{-5}} = 163553\ day = 448\ years$$

8.2.2 *AO lifetime in water.* As shown in Figure 18, the OIT reduction rate can be expressed by the first order reaction, as shown in Eq. 2. Figure 29 shows the Arrhenius plot based on the OIT reduction rate. The activation energy deduced from the slope of the curve is 67 kJ/mol.

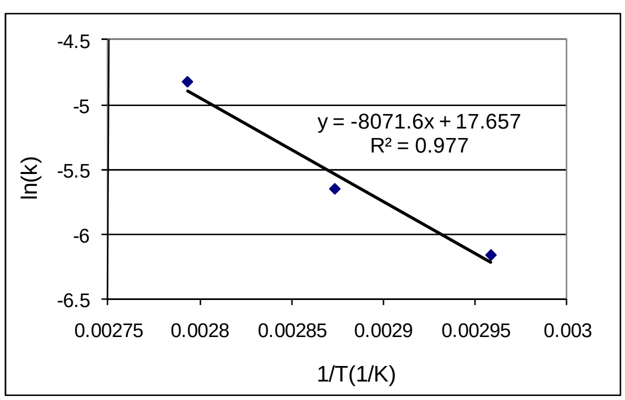

Figure 29 – Arrhenius plot of OIT reaction rate in water for P-2

The calculation to obtain the predicted time for OIT to reach 3.0 minute at 23°C water is illustrated in Eq. (12) and (13):

$$ln(k_{23^oC}) = 17.657 - 8071.6\left(\frac{1}{23+273}\right) = -9.6 \quad (12)$$

$$k_{23^oC} = 6.69x10^{-5}$$

$$ln(3) = ln(25) + (6.69x10^{-5})(t) \quad (13)$$

$$t = \frac{3.21-1.1}{6.69x10^{-5}} = 31527\ day = 86\ years$$

The duration of Stage A in water can also be predicted based on the times to reach 90% MI retained value at three different incubation temperatures. From Table 4, these times are 210, 714, and 912 days at 85, 75, and 65°C, respectively. The reaction rates are equal to the inverse of times which are then applied to the Arrhenius plot to predict the reaction rate at 23°C, as shown in Figure 30.

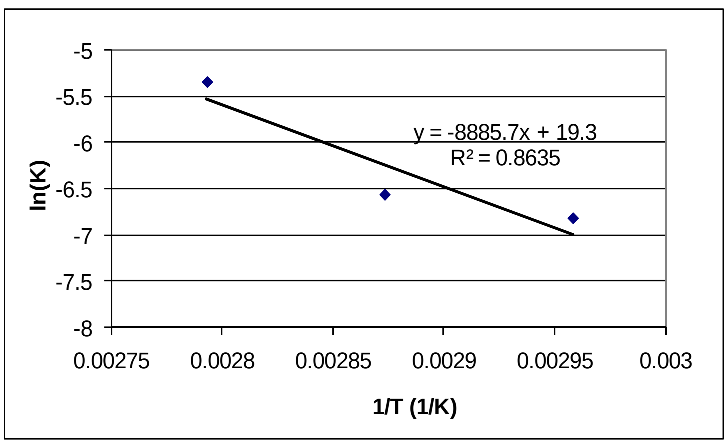

Figure 30 – Arrhenius plot of reaction rate based on time to reach 90% MI in water

The calculation to obtain the duration of Stage A at 23°C based on 90% MI value is illustrated in Eq. (14):

$$ln(k_{23^oC}) = 19.3 - 8885.7\left(\frac{1}{23+273}\right) = -10.72 \quad (14)$$

$$k_{23^oC} = 2.21x10^{-5}$$

$$t_{23oC} = \frac{1}{k} = 45218 \text{ days} = 124 \text{ years}$$

The predicted value is slightly higher than that obtained from the OIT. However, considering the accuracy of the Arrhenius plot (R^2 value is 0.8635), the discrepancy between the two predicted values is acceptable.

8.2.3 _AO lifetime in water/air._ The OIT reduction rates in water/air cycle are slightly slower than those in the water environment. The OIT data decrease exponentially with the incubation time, as shown in Figure 19. Figure 31 shows the Arrhenius plot based on the OIT reduction rate. The activation energy deduces from the slope of the curve is 67 kJ/mol which is same as that of the water incubation.

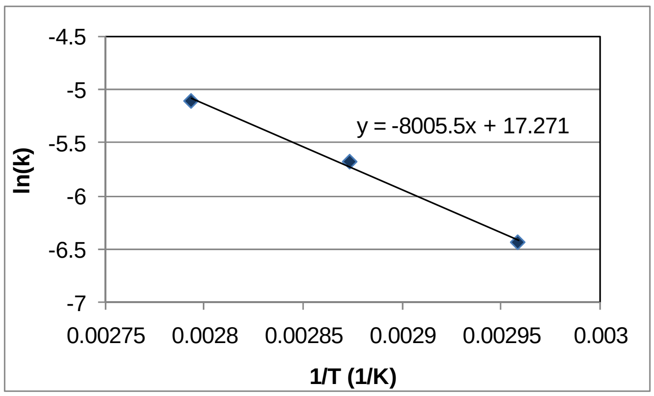

Figure 31 – Arrhenius plot of OIT reduction rate in water/air cycle

The calculation to obtain the predicted time for OIT to reach 3.0 minute is illustrated in Eq. (12) and (13):

$$ln(k_{23^oC}) = 17.271 - 8005.5\left(\frac{1}{23+273}\right) = -9.77 \qquad (12)$$

$$k_{23^oC} = 5.69x10^{-5}$$

$$ln(3) = ln(25) + (5.69x10^{-5})(t) \qquad (13)$$

$$t = \frac{3.21-1.1}{5.69x10^{-5}} = 37097\ day = 101\ years$$

The predicted antioxidant's lifetime in water/air cycle is twice longer than that in the water environment at 23°C.

8.2.4 Summary

The predicted AO lifetimes in P-2 pipe in air and water are 448 and 86 years, respectively. For the AO package of this pipe, a strong interaction with water was observed at the 85°C water environment but such interaction was less pronounced at 75 and 65°C. For the water/air cycle environment, the predicted AO lifetime (101 years) is closer to that of the water than air.

9. Summary

This report presents the test results of OR evaluation of two pipes, P-1 and P-2. Test coupons were taken from the pipe liner and were exposed to three incubation conditions: forced air oven, water bath with constant air percolation, and water/air cycle to simulate various field service conditions. In each of the incubation condition, three elevated temperatures at 65, 75, and 85°C were employed to accelerate the oxidation process. The changes in material properties were monitored using OIT, MI and tensile tests.

For P-1, test results show that OIT retained values decreased exponentially with time in air environment at all three temperatures. In contrast, the change of OIT with time of water incubated coupons was expressed by an equation with summation of two exponential terms to present two separate reaction mechanisms which are likely to be physical leaching and/or hydrolysis together with free radical reactions of the antioxidants. The OIT decreasing trends of samples exposed to water/air cycles are very similar to those exposed to the water, but at a slower rate. The average OIT value corresponds to 90% MI retained value was found to be approximately 3 minutes in the water incubation.

Regarding the tensile properties of P-1, the breaking elongation exhibited the greatest changes with incubation time. A delamination along the thickness of the pipe liner was observed in most of the incubated specimens regardless the incubation environment. In general, the delamination is more severe for samples incubated in water than the other two environments. It is believed that the premature decrease of the break elongation detected in water and water/air cycle environments was caused by the delamination, and not by the oxidation degradation, since the OIT retained values still above 20% and MI retained values remained above 90%.

For the P-2 coupons, the OIT value decreased exponentially with time in all three incubation conditions, while MI and tensile break elongation retained within 90% for some period of times before starting to decrease. The average OIT value corresponds to 90% MI retained value was found to be approximately 3 minutes in water incubation which was similar to that found in P-1. Coupons in 85°C water incubation condition yielded a greater than 50% decrease in MI and tensile break elongation, indicating that polymer degradation has already occurred (i.e., pipe samples have reached Stage C.). At 75°C water, coupons have also reached Stage B as MI retained value decreased to 80%, and at 65°C, coupons have not yet reached Stage B and C after 1000 days.

Since the critical OIT value for P-1 and P-2 was found to be approximately 3 minutes, which was used to predict the lifetime of AOs in these two pipes. The activation energy and corresponding predicted AO lifetime at 23°C in different incubation environments are shown in Table 5. The activation energy values for the AO depletion mechanism are relatively similar in all three incubation conditions, ranging from 61 to 72 kJ/mol.

Table 5 – Activation energy and predicted AO lifetime at 23°C

Pipe	Air		Water		Water/Air	
	Activation Energy (kJ/mol)	Lifetime (year)	Activation Energy (kJ/mol)	Lifetime (year)	Activation Energy (kJ/mol)	Lifetime (year)
P-1	61	150	1st – 67 2nd – 70	187	NA	NA
P-2	72	448	67	86	67	101
NA = not available						

10. Conclusions

- The antioxidant in P-1 exhibited strong leaching and/or hydrolysis phenomenon in water and water/air cycle condition during early stage of the incubation. The decrease of OIT with time was modeled by the second order reaction.
- The leaching and/or hydrolysis phenomenon of AO was less pronounced in P-2 in water and water/air cycle environment, particularly at 75 and 65°C. The decrease in OIT with time was expressed by the first order reaction.
- The depletion of antioxidants in the water/air cycle environment took place predominately during the water incubation.
- The MI decreased gradually and consistently with incubation time, indicating a cross-linking in polymer. In contrast, large variability was detected in the tensile break elongation among different incubation periods. The cause for the variability of tensile break elongation is still being evaluated.

- The boundaries of separating Stage A, B, and C were defined based on the MI retained values and they are at 90%, 80% and 50%, respectively. The average OIT value at the end of Stage A was found to be 3.0 minutes for P-1and P-2 in water incubation.
- The predicted lifetimes of AOs (Stage A) for P-1 and P-2 were determined based on the 3-minute OIT value. The AO lifetimes of P-1 in air and water environments are very similar, 150 vs. 187 years. In contrast, the AO lifetimes of P-2 is longer in air than in water, 448 vs. 86.
- The lifetime of the pipe corresponds to the summation of Stage A, B, and C, and thus the lifetime of the pipe is expected to be much longer than 100 year service life.

11. Recommendation to Modify Current Interim Specification on Oxidation Resistance

This study demonstrates the importance of AO in corrugated HDPE pipe. The pipe properties remain essentially unchanged as long as AO present in the pipe. To ensure there is sufficient amount of AO in the corrugated HDPE pipes, the interim specification requires three junction specimens to be incubated at 80^{o}C water bath under stress of 250 psi for 265-day; the average OIT retained value should be greater or equal to 3 min. (The alternative condition is at 85^{o}C water for 187-day). The incubation duration defined in the interim specification is based on the activation energy value of 75 kJ/mol, which is slightly higher than the activation energy range for the AO depletion mechanism in air and water incubation environment.

The test results of this study however show that tensile breaking elongation and MI values of P-2 began to decrease when OIT value approached to 3 minutes at 85^{o}C in water. On the other hand, P-1 water coupons showed essentially no changes in MI even thought OIT is slightly shorter than 3 minutes. Therefore, only requiring the OIT retained value may not be sufficient to ensure the oxidation status of the pipe. Additional tests, such as tensile breaking elongation and/or MI, would complement the OIT test and assure the oxidation status of the polymer. However, the large variation of the tensile breaking elongation observed in this study suggests that this property is not a suitable parameter to be used for product qualification. In comparison, MI is a straight forward test with less variability. In this research report, the Stage A is defined by a MI retained value of 90% which is consistent with the standard deviation of the MI test for a single laboratory, according to ASTM D 1238 (see Table 6). However, the variability among different labs is much higher and is included in the consideration of specification recommendation.

Table 6 – Precision values for two HDPE resins included in Table 4 of ASTM D1238

Material	Condition	Average	S_r	S_R	I_r	I_R
		(g/10 min)				
HDPE-1	190/2.16	0.27	0.008 (3%)	0.022 (8%)	0.023 (9%)	0.063 (23%)
HDPE-2	190/2.16	0.40	0.012 (3%)	0.038 (10%)	0.035 (9%)	0.108 (27%)

S_r = within-lab standard deviation of the average
S_R = between-labs standard deviation of the average
I_r = 2.83 S_r, and
I_R = 2.83 S_R.

The modified requirements for OR is three pipe junction specimens to be incubated at 80°C water bath under 250 psi for 265-day; the average OIT value should be greater or equal to 3 min, and the MI value should be within ± 20% of the original unaged value.