

Effects of two different carbon black on the depletion of antioxidants in HDPE geosynthetics

W.K. Wong and Y.G. Hsuan

Drexel University, Department of Civil, Architectural and Environmental Engineering, Philadelphia, PA, USA

Keywords: Carbon Black, Antioxidants, Oxidation, High Density Polyethylene

ABSTRACT: Long term antioxidant (AO) depletion study was conducted on high density polyethylene (HDPE) blended with two different particle sizes of CB (75 and 27nm) in four concentrations (2, 3, 4 and 5%). All samples were incorporated with an antioxidant package consisted of 1000 ppm Irganox[®] 1010 and 1000 ppm Irgafos[®] 168. Test samples were prepared by compression molding. The oxidation process was carried out at 85°C in both forced air oven and water bath conditions. The amount of AO in the incubated samples was determined using the standard oxidative induction time (OIT) test. Results showed that the OIT value of non-incubated samples increased linearly with CB loading. Samples with CB particle size of 27 nm exhibited a higher initial OIT value compared with CB with 75 nm in all 3 loadings. Strong interactions between CB and AOs led to faster OIT decreasing rates in comparison to samples without CB. Furthermore, the OIT decreasing rates of water incubated samples were found to be independent to the CB types and loadings, and they are much faster than those incubated in the air condition. In the air environment, samples with high initial OIT value (i.e., high CB loadings) exhibited higher decreasing rate than samples with low CB loadings.

1 INTRODUCTION

Many studies have been focused on the impact of carbon black (CB) on the oxidation of polyolefins. Positive effects of adding CB as an ultraviolet (UV) protector and as a mild thermo-oxidation stabilizer were well documented (Watson, 1955, Hawkins et al., 1959-a, Pleshanovet et al., 1982, Pritchard, 1998). However, most of the commercial geosynthetic products contain not only CB, but also antioxidants (AO) for protecting polymer against oxidation. Due to the complex structure and surface chemistry of CB, interaction between CB and AO are still uncertain. Both synergetic and antagonistic effects were reported. Gilroy & Chan (1984) studied polyethylene (PE) consisted of various percentages of CB blended with four types of AO to demonstrate the retardation effect on the onset of the oxidation. Phease et al. (2000)

found that adding CB into both phenolic and phosphite type of AOs increased the oxidative induction time (OIT). On the other hand, Kovacs & Wolkober (1976) found that highly oxidized CB has antagonistic effects on amine type of AOs. Hawkins et al. (1959-b.) found that CB combined with certain types of phenol antioxidant or amines can greatly reduce the function of the AOs.

However, the interaction between CB and AO during the service duration has not been investigated. From our previous paper (Wong & Hsuan, 2009), rapid AO depletion was detected in samples with CB while a slow gradually depletion trend was observed for samples without CB in the air incubation condition. Also the effect of CB on the depletion of AO was found to be similar even the evaluated AO formulations were different. In this study, the effect of CB particle sizes and concentrations on the AO depletion was evaluated.

2 EXPERIMENT

2.1 Test Materials

A HDPE resin with density of 0.952 g/cm^3 was blended with two types of CB with particle size of 27 nm and 75 nm at 5 concentrations, 0%, 2%, 3%, 4%, and 5%. In addition to CB, 1000 ppm Irganox[®] 1010 and 1000 ppm Irgafos[®] 168 were added on each blend. Total of eight formulations were made using a laboratory single screw extruder. The extruded chips were compression molded according to ASTM D4703, A1 at a cooling rate of $15^\circ\text{C}/\text{min}$. The thickness of the plaques ranged from 1.8 mm (0.071 inch) to 2.1 mm (0.083 inch). Small samples with dimensions of 75 mm (3 inch) x 90 mm (3 ½ inch) were cut from the plaques for incubation.

2.2 Incubation Conditions

The thermo-oxidation process was accelerated using forced air oven and water bath at 85°C . Samples were hung in the oven with 1" spacing. For water incubation, samples were weighted to the bottom of the bath. Air was constantly purged into water to provide constant oxygen content as well as circulation.

2.3 Test Method

The amount of AOs in the samples was measured by the standard oxidative induction time (OIT) test according to the ASTM D3895 procedure using a differential scanning calorimeter (DSC) at a heating rate of $10^\circ\text{C}/\text{min}$ to 200°C . Test specimen was cut across the thickness of the incubated samples and weighed to $3.5 \pm 1 \text{ mg}$.

3 RESULTS

3.1 Effects on the Initial OIT Value

In this paper, the OIT value of non-incubated samples is designated as "initial OIT". The initial OIT value increases with the loading for both CB types, as shown in Figure 1. Similar results were also observed by other researchers. Phease et al. (2000) found increasing initial OIT with CB loading on two different ratios of Irganox[®] 1010 and Irgafos[®] 168, 1:1 and 2:1. Pleshanov et al. (1982) showed

that the onset of oxidation was delayed linearly with increasing CB loading.

However, the linear relationship does not extend to 0% CB. The extrapolated OIT value at 0% of 27 nm and 75 nm CB are 69.9 and 39.3 minute, respectively, whereas the OIT value of 0% CB sample was measured to be 58.7 minute. Such discrepancy suggests that CB interacts with AOs differently at concentrations below 2%.

The particle size of CB also affects the initial OIT value. Samples contained 27 nm CB exhibited higher OIT than 75 nm at the same loading. CB with smaller particle size has higher specific surface area; the number of hydroxide groups that are attached to the surface of CB would subsequently increase. The hydroxide groups function as antioxidant and thus can lead to higher OIT value.

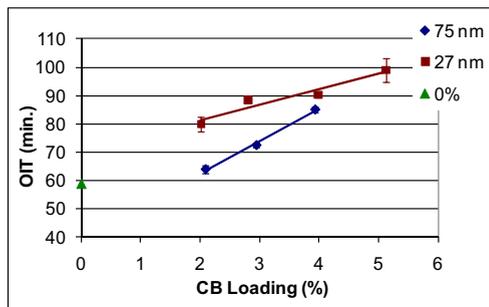
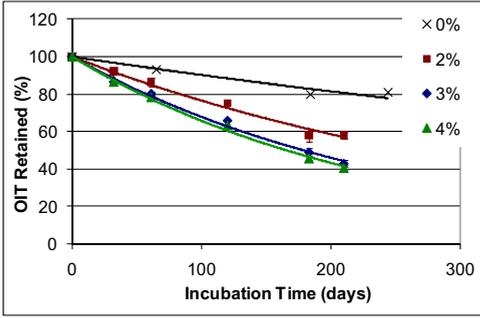


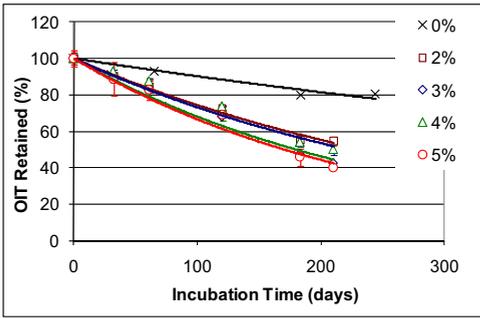
Figure 1: CB effects on the initial OIT values

3.2 Interaction in Oven Incubation

Figure 2 showed plots of normalized OIT versus time for oven incubated samples. Compared with sample with 0% CB, the interaction between CB and AO can be observed in all CB samples. The OIT retained value decreases exponentially with incubation time, indicating that the AO depletion followed the first order reaction.



(a) CB75 nm particle sizes



(b) CB 27 nm particle sizes

Figure 2: AO depletion at 85°C Oven

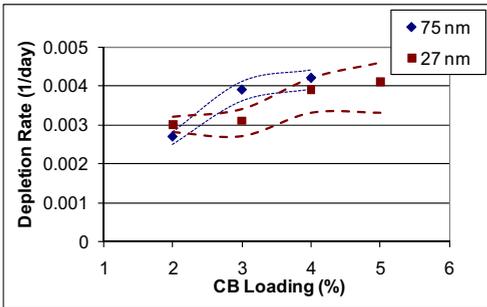


Figure 3: Depletion rates verse CB loading

Contrary to the effects on the initial OIT value, samples with lower CB loading exhibit slower depletion rate than samples with higher CB loading for both particle sizes. Figure 3 shows a graph by plotting depletion rate against CB loading. (The dotted lines represent 95% confident level.) Results showed the 75 nm particle size have a lower variability than 27 nm samples. This effect could be explained by the fact that CB with smaller par-

ticles size is more difficult to be evenly dispersed within the sample than large particles. In addition, the AO depletion rate does not increase linearly with loading for both CB sizes. The depletion rate seems leveling off as CB loading exceeded 3%.

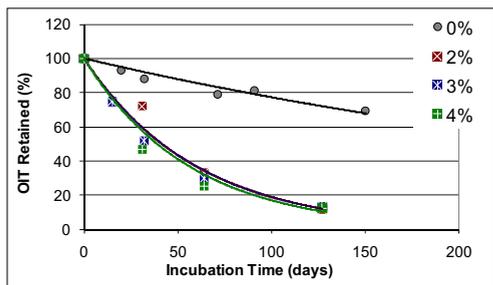
Therefore, the high initial OIT value caused by the high CB content did not necessary lead to a long AO lifetime. Comparing the OIT value at 0 and 210 days of incubation, samples with lower CB content retained a higher OIT value, see Table 2. It seems that 27 nm CB at loadings of 2 to 3% provide the best performance in terms of OIT retention in the oven incubation condition.

Table 2. Comparing OIT at 0 and 210 days

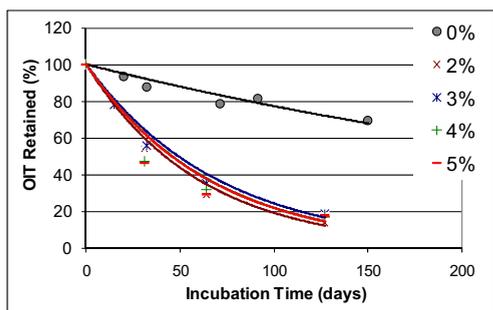
Blend (75nm)	Initial (min.)	210 days (min.)	Blend (27nm)	Initial (min.)	210 days (min.)
2%	63.8	37.1	2%	79.8	43.6
3%	72.4	31.1	3%	88.4	44.5
4%	85.0	34.6	4%	90.3	38.6
			5%	99.0	39.6

3.3 Effects on Water Incubation Samples

Rapid depletion of AO was found in water incubated samples, as shown in Figure 4. After 127 days of incubation, OIT dropped to less than 20% retained for all samples. There was no significant difference in depletion rate in both sets of samples. The OIT value decreased to 7-11 minutes for 75 nm; 11-17 minutes for 27nm. Even though CB could adsorb AO onto its surface, it could not prevent the rapid AO loss. However, sample with CB of 27 nm particle and 5% loading has the highest OIT retained value after 127 days of incubation, contradicting the OIT depletion behavior in the oven incubation.



(a) CB 75 nm particle sizes



(b) CB 27 nm particle sizes

Figure 4: AO depletion at 85°C water

4 DISSCUSION

Figure 5 showed the AO depletion in air and water incubation of samples with 2% CB with 27nm. The difference in the AO depletion rates is clearly revealed. The significantly higher depletion rate in the water incubated sample indicates that the AO depletion was not limited to free radical reactions; other mechanisms such as hydrolysis and/or physical leaching likely contributed to the loss. It is well known that phosphites are susceptible to hydrolysis (Haider & Karlsson, 2002, Rotschova et al,1991).

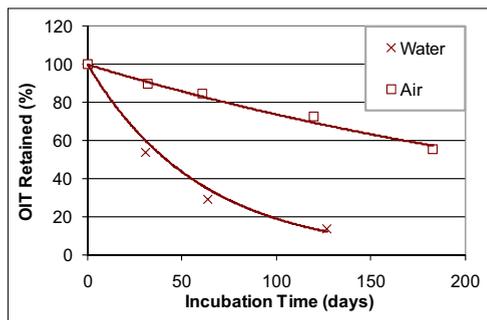


Figure 5: AO depletion of 2% in water and air

By comparing samples with and without CB, interaction between CB and AO is more revealing in air incubation condition. The surface chemistry of CB is believed to be one of the major factors for such interaction. Hydroxide groups found on the CB surface can react with free radicals and delay the oxidation. However, other oxygen compounds such as quinone (oxygen with double bond) can react with the AOs rather than free radical, resulting in consuming AO (Kovacs & Wolkober, 1976). In this study, following assumptions are proposed to explain the test results:

- AOs tend to attract onto CB surface by the hydrogen bonds. The increase of initial OIT value may be due to the high mobility of AO at 200°C of the OIT testing temperature. The AO could detach from the CB surface, allowing AO and CB to react with free radicals separately. In result, a high initial OIT value was obtained.
- During the oven incubation, AOs depleted by reacting with free radicals as well as quinine type of oxygen compounds on the CB surface, resulting a greater reduction of OIT. Furthermore, a higher concentration of CB contains more quinone that leads to a higher depletion rates.
- Effectiveness of CB function as a mild AO was depended on the ratio of phenolic and quinone types of functional groups

5 CONCLUSION

Based on the above study, the following conclusions can be drawn:

- A linear relationship was found between initial OIT and CB loading.
- Initial OIT can be increased by reducing CB particle sizes.
- Higher concentrations of CB exhibit higher depletion rates in air incubation samples, and thus counter the benefit of high initial OIT
- Significant higher depletion rates were observed for the water incubation samples compared with the air samples. The depletion rates are not affected by the CB loading and particle sizes.
- In this study, combinations of small particle sizes and low CB loading results in higher OIT after 210 days of oven incubation.

Phase, T. L., Billingham, N. C., and Bigger, S. W. (2000). "The effect of carbon black on the oxidative induction time of medium-density polyethylene." *Polymer*, 41(26), 9123-9130.

Pleshanov, V. P., Berlyant, S. M., and Burukhina, G. A. (1982). "Study of kinetics of inhibition of thermo-oxidation of polyethylene by carbon black." *Polymer Science U.S.S.R.*, 24(6), 1462-1468

Rotschova, J., and Pospisil, J. (1992). "Influence of the Carbon Black Chezacarb EC on Polyolefin Thermo-oxidation: A Model Study with Cyclohexene Doped with Chain-Breaking Antioxidant." *Die Angewandte Makromolekulare Chemie*, 194 201.

Watson, W. F. (1955). "Combination of Rubber and Carbon Black on Cold Milling." *Ind. Eng. Chem.*, 47(6), 1281-1286.

Wong, W.K. and Hsuan, Y.G. (2009) "Carbon Black and Antioxidant Effect in High Density Polyethylene" *Geosynthetics 2009*, Salt Lake City, Utah

ACKNOWLEDGEMENTS

The project is funded by the Florida Department of Transportation. Carbon black used in this study was provided by Modern Dispersions Inc. Appreciation is given to GSI for using their facility. Miss W-K Wong is supported by the Geosynthetic Institute (GSI) Fellowship.

REFERENCE

Gilroy, H. M., and Chan, M. G. (1984). "Effect of Pigments on the Aging Characteristics of Polyolefins." *Polymer Science and Technology*, 26 273.

Haider, N., and Karlsson, S. (2002). "Loss and transformation products of the aromatic antioxidants in MDPE film under long-term exposure to biotic and abiotic conditions." *J Appl Polym Sci*, 85(5), 974-988.

Hawkins, W.L., Matreyek, W., and Winslow, F.H. (1959) (a.) "The morphology of Semicrystalline Polymers. Part I. The effect of Temperature on the Oxidation of Polyolefins." *Journal of Polymer Science*, 41(138), 1-11

Hawkins, W. L., Hansen, R. H., Matreyek, W., and Winslow, F. H. (1959) (b.) "The effect of carbon black on thermal antioxidants for polyethylene." *J Appl Polym Sci*, 1(1), 37-42.

Kovacs, E., and Wolkober, Z. (1976). "The Effect Of The Chemical and Physical Properties Of Carbon Black On The Thermal And Photooxidation Of Polyethylene." *Journal of Polymer Science, Symposium No. 57* 171.

Pritchard, G. (1998) *Plastics Additives - An A-Z Reference*. p.633