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# Interaction of antioxidants with carbon black in polyethylene using oxidative induction time methods

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ABSTRACT

Carbon black (CB) is added to the geosynthetics for ultraviolet protection. However, CB can interact with antioxidant (AO) in the geosynthetics, and their interaction has been documented to be synergistic and/or antagonistic towards the oxidation reaction. In this paper, two oxidative induction time (OIT) methods, a standard (Std) OIT test and a high pressure (HP) OIT test, were used to evaluate the interaction of CB with two types of antioxidants during the oven aging. Test samples made from high density polyethylene (HDPE) blended with different amounts of Irganox®1010 (I-1010) and Irgafos®168 (I-168) together with 0 or 2.5wt.% of carbon black were studied. The sample were incubated in a forced air oven at 85 °C to accelerate the oxidation reactions. After 1000 days, Std-OIT values of samples with 500 ppm and 1000 ppm I-1010 exhibited only 10% drop from their initial values from 19.42 min and 34.01 min to 17.53 and 31.0 min respectively. In comparison, a continuous decrease of Std-OIT value was observed for samples contained both I-1010 and I-168; a 40% drop was measured after 1000 days, corresponding to 16.4 and 26.8 min reduction. For samples contained 2.5% CB and I-1010, an exponentially decrease of Std-OIT and HP-OIT with aging time was obtained. However, adding I-168 to those samples did not change the OIT decreasing trends, indicating that the interaction of CB with I-168 is negligible. The test data further verify that the effectiveness of the OIT test is strongly correlated to the functional temperature range of the AO. The Std-OIT test with testing temperature of 200 °C can detect both I-1010 and I-168, while the 150 °C testing temperature of the HP-OIT test can only detect the I-1010.

## 1. Introduction

Geosynthetics made from HDPE are commonly incorporated 2–3% of carbon black (CB) for ultraviolet (UV) protection together with approximately 0.1–0.3% of antioxidant (AO) to ensure oxidation resistance of the products during their service time. When adding CB (channel black or furnace black) to pristine HDPE without AO, it has been found to delay the onset of oxidation in polyethylene. The function of suppressing thermal oxidation is related to the amount of oxygen containing group on CB surface (Hawkins et al., 1959a, b; Pleshanov et al., 1982). On the other hand, the degradation mechanism of different types of AOs on protecting polyolefin products under various environmental conditions, such as multiple heating cycles of extrusion, radiation, and thermo-oxidation, were well studied (Epacher et al., 1999a, b; Pock et al., 2004; Moore et al., 1988; Moss and Zweifel, 1989; Drake et al., 1990; Mallégol et al., 2001).

Even though AO and CB can protect polymer from oxidation degradation individually, when combined, both synergistic and antagonistic effects were found. By increasing CB loading or reducing the particle size of CB, it can enhance the OIT value of AO stabilized PE (Phease et al., 2000; Wong and Hsuan, 2012). On the other hand, Hawkins et al. (1959a) and Kovacs and Wolkober (1976) measured the oxygen absorption rate and found that CB combined with certain types of hindered phenol or secondary amines can greatly reduce the AOs' effectiveness in PE. The acidic nature of CB due to the high oxygen content, can hinder the performance of AO. They explained that the quinone active sites on the CB surface are stronger acceptors than the free radicals, resulting in AO reacting with the quinone instead of free radicals. Pena et al. (2001a, b) used flow micro-calorimetry to measure the heat of adsorption/desorption of primary and secondary AOs when blended with four types of CB. They found that the AO adsorption and desorption activities were not only dependent upon the particle size of CB but

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also influenced by oxygen groups content, neighboring surface functional groups, CB surface structure, and porosity.

In past decade, oxidation resistance of HDPE has been intensely studied, and oxidative induction time (OIT) test has been used in many of the studies to assess the remaining AO in samples with and without carbon black. Subjecting AO stabilized PE samples in aerobic and anaerobic environments at elevated temperatures, Lundback et al. (2006) used the OIT test to monitor the AO loss as well as to study AO diffusion through the thickness of the sample. Nagy et al. (2003), investigated the effectiveness of the AOs in polyethylene and the resistant of AOs to the hydrolysis. Thomas and Ancelet (1993) studied 14 HDPE geomembranes with different weight percentages of three types of AOs (Irganox®I-1010, Tinuvin®622, Irgaphos®I-168). Samples with and without CB were also evaluated. They found that the standard (Std)-OIT test cannot detect Tinuvin®622 (a HALS stabilizer) in samples without CB, while a significant higher HP-OIT value was measured. Furthermore, the service life of AOs in HDPE containing 2–3% CB have been investigated by many research teams (Smith et al., 1992; Viebke and Gedde, 1997, 1998; Hsuan and Koerner, 1998; Rowe and Rimal, 2008; Muller and Jacob, 2003; Wong and Hsuan 2009). All of these studies provide valuable findings and insights of the performance AO in PE products with and without CB. However the interaction between CB and AO during aging of HDPE products is not well studied and understand.

This paper focuses on two objectives: i) study the effects of CB on AO during oven aging through ten AO/CB formulations. ii) Evaluate the long term oxidation of the two commonly used AO, Irganox®I-1010 (I-1010) and Irgaphos®I-168 (I-168). To understand the depletion mechanism of the two AOs, both Std and HP-OIT methods were utilized to measure the remaining AO in samples aged in a forced air oven at 85 °C. Furthermore, the effectiveness of the two OIT methods in detecting these two AOs was also evaluated. A long aging period (1200 days) was implemented to cultivate the complete depletion of one or both AO in the samples.

## 2. Test material

A total of ten HDPE samples with different amounts of AO and CB were prepared for this study. The neat HDPE resin used has a density of 0.953 g/cm$^3$ and melt index of 0.16 g/10 min. The HDPE resin was blended with Irganox®1010 (I-1010) and Irgafos®168 (I-168) with four concentration combinations. I-1010 is a type of hindered phenol serving as processing stabilizer as well as antioxidant during the product's service life. I-168 is a phosphite based AO and is function as a processing stabilizer. Carbon black (CB), 65 nm particle size, at 2.5 wt% was added to half of the AO blended samples. Also two referenced samples without AO, one neat HDPE resin and one with 2.5wt% CB, were prepared. The ten formulations are shown in Table 1.

**Table 1**
Antioxidant formulations of blended samples.

| Sample | Antioxidant | | Carbon black |
|---|---|---|---|
| | I-1010 (ppm) | I-168 (ppm) | (wt.%) |
| PE0 | 0 | 0 | 0 |
| PE0-C | 0 | 0 | 2.5 |
| PE1 | 500 | 0 | 0 |
| PE1-C | 500 | 0 | 2.5 |
| PE2 | 500 | 1000 | 0 |
| PE2-C | 500 | 1000 | 2.5 |
| PE3 | 1000 | 0 | 0 |
| PE3-C | 1000 | 0 | 2.5 |
| PE4 | 1000 | 1000 | 0 |
| PE4-C | 1000 | 1000 | 2.5 |

All samples were first extruded into pellets using the laboratory scale single screw extruder. Materials without CB were prepared by first dry blending HDPE resin fluff with an appropriate amount of AOs and then extruded into pellets. For material with carbon black, pellets were prepared by mixing the PE fluff, AOs, and CB powder (grinded from the CB master batch which consisted of 50 wt.% CB and 50 wt.% linear low density PE) and then extruded into pellets. The pellets were compression molded into plaques according to ASTM D4703, A1 at a cooling rate of 15 °C/min. The thickness of the plaques ranged from 1.8 mm to 2.1 mm. Each plaque was then cut into 75 mm × 90 mm test samples for oven incubation.

## 3. Incubation and OIT test methods

### 3.1. Oven incubation

All test samples were incubated in a forced air oven (THELCO Laboratory Oven, Model 70M) at 85 °C to accelerate the AO depletion. Samples were hung on the stainless strain racks inside the oven with 1 inch spacing. Samples were retrieved at different time intervals to assess the remaining AO using OIT tests.

### 3.2. Standard OIT (Std-OIT) test

The Std-OIT test was performed using the TA instrument Q20 Differential Scanning Calorimeter (DSC). The Std-OIT test was carried out according to the procedure described in ASTM D3895. A thin strip of the specimen was cut across the thickness of the sample and weighted to 3.5 ± 1 mg.

### 3.3. High Pressure OIT (HP-OIT) test

The HP-OIT test was performed using TA instrument 2920 Differential Scanning Calorimeter equipped with a high pressure cell. The test was carried out according to the procedure described in ASTM D5995, using the constant volume procedure. A thin strip of specimen was cut across the thickness of the sample and weighed to 3.5 ± 1 mg.

### 3.4. High Performance Liquid Chromatography (HPLC)

Prior to the HPLC analysis, Soxhlet extraction procedure was performed to obtain the remaining AO in the sample. Sample were grinded to 100-mesh particle size (100 μm) and extracted using cyclohexane, according to the procedure described in ASTM D6082. The extraction solutions were filtered through 0.45 mm PTFE filters before the analysis. AGILENT series 1100 HPLC with a UV-detector was used for HPLC analysis. The antioxidant concentration was then analyzed using reversed-phase HPLC, with acetonitrile/water (95/5) as the mobile phase and a Waters Symmetry C18 column (150 cm length). An injection volume of 10 ml and a flow rate of 0.5 ml min were used. The concentration of antioxidant was determined from the absorption at 280 nm.

## 4. Results

### 4.1. Initial OIT value

As the compound (HDPE and AOs) is going through the extrusion and then compression molded into a plaque, the high processing temperature and shear action during the extrusion can induce free radical reactions and consume part of the AOs even in an oxygen deficient environment (Kriston et al., 2009, Moss and