

Evaluation of Oxidation Induction Time as a Tool for Characterization of AO Content

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Statement of Purpose: The goal of this study is to assess the feasibility of employing the Oxidative Induction Time (OIT) for differentiating and quantifying the concentration of antioxidant-doped UHMWPE formulations.

Background: The procedure for the determination of OIT by Differential Scanning Calorimetry (DSC) has been described in ASTM D3895. OIT has been established as a qualitative tool for the assessment of the degree of stabilization in polymers, oils and bio-fuels [1]. It is rapidly becoming the method of choice for determining oxidative stability and to rank antioxidant activity because it is a much faster process than the conventional “accelerated” aging test [2].

Methods: Ultra high molecular weight polyethylene (UHMWPE) powder (GUR 1020 resin, Ticona) was mixed with the antioxidant Pentaerythritol tetrakis [3-(3, 5-di-tert-butyl-4-hydroxyphenyl) propionate], **PBHP**, to produce the following antioxidant stabilized UHMWPE formulations: 600, 750 & 900 ppm (w/w). 8-10 mg of each powder concentration was weighed using an analytical balance and open aluminum DSC pans. Each pan was then placed in the DSC along with an open, empty pan as reference. Each sample was analyzed using DSC Q1000 (TA Instruments -Waters LLC). Each sample was loaded one at a time to limit the exposure to the environment. The OIT program that was employed consisted of: ramp to 200°C @ 40°C/min under nitrogen (gas 1), isothermal hold for 5.00 min, mark time zero, select gas 2 (oxygen), isothermal hold for 90 min at 200°C, revert to nitrogen, mark end of cycle 1 and effect cool down to 40°C @ 20°C/min.

Results: The OIT values of three sample specimens at each concentration (600, 750 & 900 ppm) were determined in accordance with the method specified in ASTM D3895. Table 1 shows the average OIT (min), standard deviation, RSD (%) and regression analysis for linearity at each concentration. This method was repeated on multiple days. A linearity $R^2 \geq 0.995$ (Figure 1) was obtained on day 1, but this was not repeatably obtained (Figure 2) when measuring the same set of samples again on day 2. The deviation from linearity obtained on day 2 prompted a re-measurement of 600 ppm powder only on day 3. A paired t-test analysis confirmed that there was not a statistically significant difference in the OIT times between samples of the same concentrations (Table 2) when measured on multiple days. There was however, variability in the measured OIT values within each concentration (N=3) on the different days that is reflected in the standard deviation and %RSD values. The RSD values on day 1 for all three concentrations were $\leq 5\%$ resulting in an $R^2 \geq 0.995$. However, on day 2, the data was more scattered, with RSD values $> 5\%$ at all three concentrations resulting in R^2 well below 0.995. Consequently, poor correlation to linearity was noted.

Table 1. Variations in day to day measurements

	Day 1			Day 2			Day 3
	600	750	900	600	750	900	600
PPM	600	750	900	600	750	900	600
OIT (min)	25.87	33.76	40.07	27.63	31.88	40.83	27.64
Stdev	1.23	1.27	1.47	1.44	5.21	2.76	2.78
RSD	4.77	3.77	3.67	5.20	16.35	18.03	10.08
R^2	0.9959			0.9591			

Table 2. P-values for same concentrations on different days

Day 1 vs. Day 2				Day 1 vs. Day 3	
PPM	600	750	900	PPM	600
600	0.1833			600	0.9959
750		0.3259		750	
900			0.7011	900	

Figure 1. Linearity of response on day 1

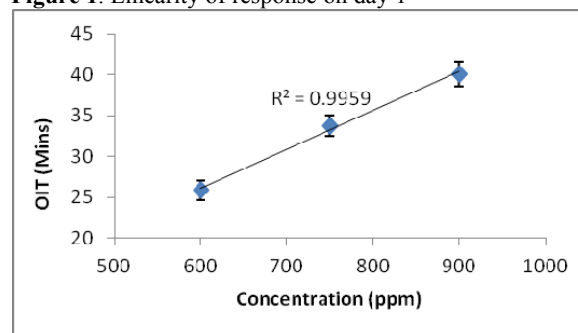
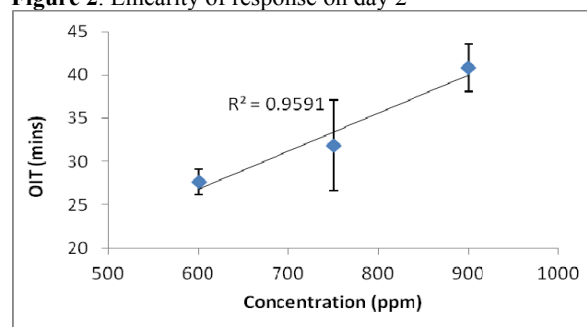


Figure 2. Linearity of response on day 2



Conclusions:

The data shows that good repeatability between samples of the same concentration on different days can be achieved but collectively it does not produce good linearity. While OIT appears to be a viable test method for differentiating AO concentrations qualitatively, its use to quantify concentrations appears to be limited without further optimization.

References:

- [1] Dunn, R.O., Fuel Process. Tech., **86**, 1071 – 1085, 2005
- [2] Braithwaite, G.J.C., et al., Trans. **56th** ORS, # 2294, 2010,