

# Using Oxidative Induction Time to Determine Antioxidant Concentration in UHMWPE

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- Highly crosslinked polyethylene (UHMWPE) has been seen to oxidize *in vivo* in some situations
- Vitamin E (VE) and other antioxidants increasingly being used to improve oxidative stability
- Currently there is no sensitive technique for measuring VE concentration post-production
  - Current methods (FTIR) [1] routinely  $\sim$  0.2 wt%, although more complex procedures possibly down to 0.038 wt% [2]
  - Near expected loading range of < 0.5 wt%
- Oxidation Induction Time (OIT) is an ASTM method that measures oxidative stability in polymers [3] with a broad history of use with polyethylene [3-5]

## Materials

- Three sets
  - un-processed powder
  - direct compression molded (DCM) pucks
  - DCM pucks irradiated to crosslink (10 MeV e-beam)
- GUR 1050 powder (Ticona) solvent blended with VE (DSM)
  - 0.01, 0.02, 0.05, 0.10, 0.25, 0.28, 0.38 (wt/wt)  $\pm$  0.0012 wt%
  - determined using Accelerated Solvent Extractor (ASE, Dionix, Inc.)

## Methods

- OIT (ASTM D3895-98 [6]) Q1000 DSC (TA Instruments)
  - Triplicate
  - Powder homogenized in DSC prior to testing (200 °C, N<sub>2</sub>, 10 mins)
  - Molded samples cut from 200  $\mu$ m film using a 6 mm diameter punch
- Vitamin E Index (VEI) [1] determined using FTIR
  - BioRad FTS3000 FTIR bench and UMA500 microscope
  - average of 10 positions
- Comparison between the techniques shown in Figure 1

## Results

- OIT and VEI values for all materials shown in Figure 1
- OIT compared to nominal VE concentration in Figure 2
  - A simple power-law relationship exists between OIT and VE concentration dependent upon processing conditions
  - Power-law fit was applied to the powder samples using Excel goal-seek (Microsoft) of the form  $VE = a \cdot OIT^b + c$
  - Unirradiated consolidated samples qualitatively similar trend, with slightly lower OIT
  - Irradiated consolidated samples indicated a significantly lower OIT

## Discussion

- During processing, VE is expected to be partially consumed, reducing the amount of VE available for further protection
- OIT measurements should only reflect this reduced amount, termed here the effective VE concentration (EVC)
  - Determined using the empirically obtained power law fit
  - The ratio VE/EVC can be used as a measure of relative consumed VE (see Figure 3)
  - Powder samples VE/EVC=1 (never more than 5.4% deviation), - indicates that the power-law is a good model
  - Consolidated sample VE/EVC $\sim$ 1.15-1.30 consistent with slight loss of VE activity at high temperature and pressure
  - Irradiated samples VE/EVC $\gg$ 10, consistent with a marked drop in effective stabilizer due to high radiation dose
- Calculations appear to hold for OIT > 5 minutes (near technique resolution), regardless of processing conditions
  - Power-law fit predicts that an OIT of 5 minutes is equivalent to 0.0004% concentration.

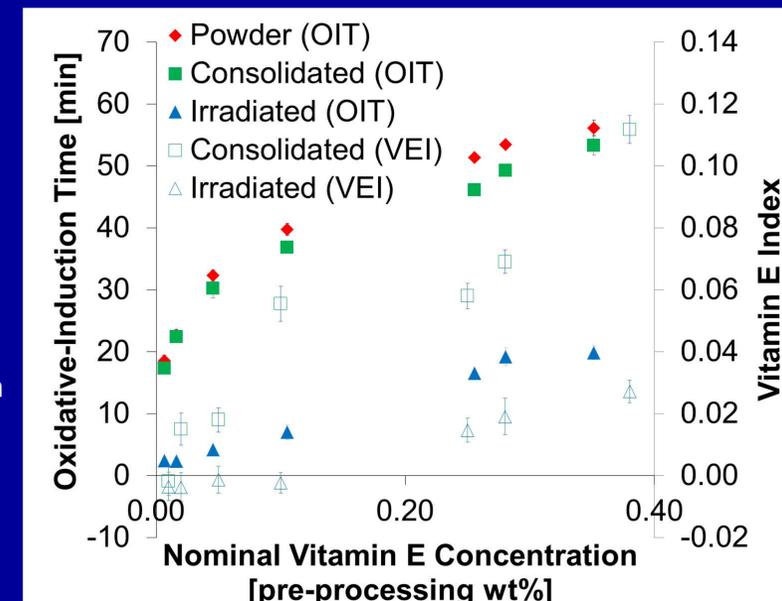


Figure 1: OIT and VEI v Nominal VE Conc. Error bars 1  $\sigma$ . Solid symbols are OIT, hollow symbols are VEI.

## Conclusions

- OIT provides a novel, sensitive method for determining VE concentration in UHMWPE components
- Suitable for QC and R&D to evaluate effective VE levels after processing
- Provides a provisional detection limit of < 0.001 wt%
- The technique could be used to investigate the influence of processing on effective VE concentration
- We are currently extending this research with a round-robin study to validate intra- and inter-lab repeatability
- Suggested future work includes determining the applicability of this method to other antioxidants

## Acknowledgements

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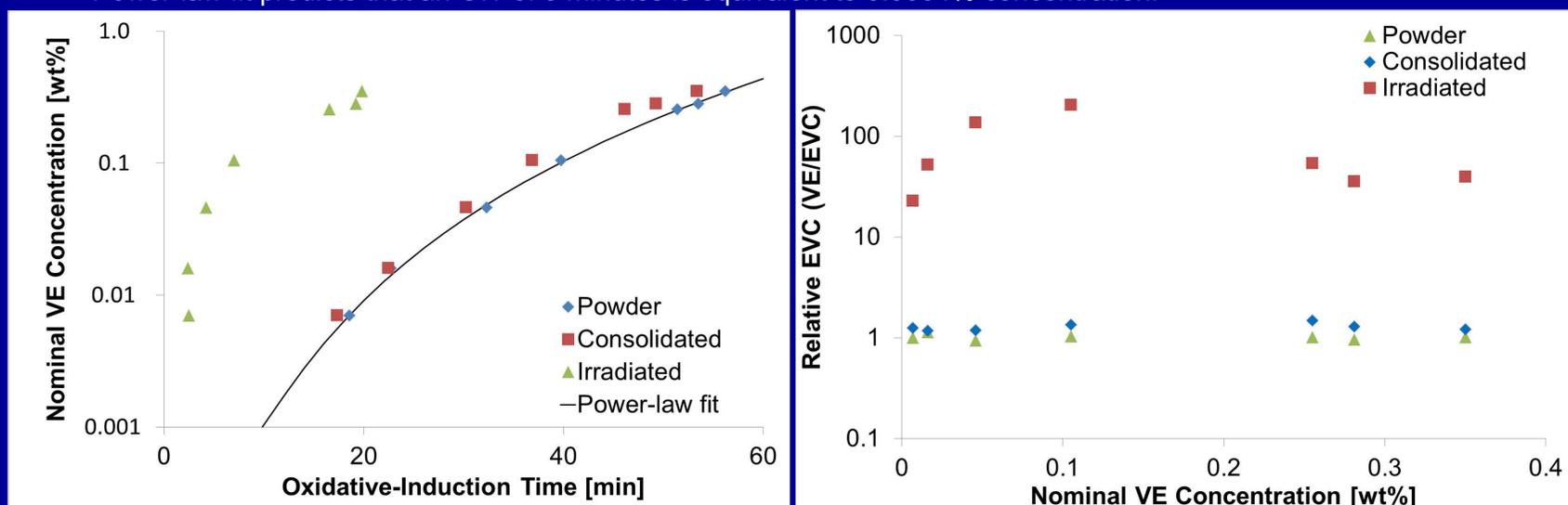
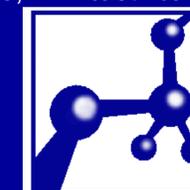


Figure 2: OIT value in minutes v Nominal Vitamin E concentration after three different processing steps. Error bars are 1  $\sigma$ .

Figure 3: Relative EVC (the ratio of the Nominal VE concentration to the EVC) versus nominal VE concentration.



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