Sensitive Measurement of Vitamin E Concentration using OIT

Heuer, E G; Stark, N; Braithwaite, G J C; McCormack, C A; Miller, B L; Gsell, R
+ Cambridge Polymer Group, 56 Roland Street, Suite 310, Boston, MA, 7 Zimmer GmbH, Sulzer-Allee 8 CH-8404 Winterthur, 7 Zimmer, Inc., 1800 West Center Street, Warsaw, IN 46580
gavin.braithwaite@campoly.com

Introduction: Vitamin E (VE) is increasingly being used to improve oxidative stability of highly crosslinked ultra-high molecular weight polyethylene (UHMWPE), a prominent orthopaedic implant material. A method for sensitively determining low concentrations of VE becomes crucial for confirming intended material properties including desired loading as a function of position. Here we describe a novel method for quantifying VE concentration using oxidation induction time (OIT) determined by differential scanning colorimetry. Current methods, such as Fourier transform infrared (FTIR) spectroscopy [1], can only quantify with repeatability and reproducibility levels of VE greater than 0.5 wt% (ASTM F2759) which is near the expected loading range for implanted UHMWPE (< 0.5 wt%). OIT is an ASTM method for measurement of oxidative stability and has a broad history of use with polyethylene, chiefly as an indicator of oxidative degradation and/or resistance [2-4]. We conducted OIT measurements on UHMWPE stabilized with varying concentrations of VE at three stages of processing. Comparison with initial VE wt% and processing conditions revealed an exponential relationship that could be used to determine the effective VE concentration of unknown samples using an OIT master curve.

Materials and Methods: GUR 1050 powder was blended with VE in the following wt%: 0.01, 0.02, 0.05, 0.10, 0.25, 0.28, and 0.38 with approximately ±0.02% uncertainty. Three sample sets were produced: un-irradiated powder, direct compression molded pucks, and direct compression molded pucks e-beam irradiated to 200 kGy. OIT analysis was performed on a Q1000 DSC (TA Instruments) according to ASTM D3895-98 [5]. Three specimens per sample from each set were tested. Powder samples were prepared by homogenization at 200 °C under nitrogen in the test pan for 10 minutes. Molded samples were prepared by using a 6 mm punch to cut circles from a microtomed 200 µm thick film. Analysis differed from that outlined in the standard. A method was developed equivalent to the Tangent method that was insensitive to misleading or atypical features present in the oxidative exotherm.

Results and Discussion: The determined OIT values for the tested samples were compared to the given VE wt% as shown in Figure 1. A strong logarithmic correlation was found for the powder (R² = 0.9914). The unirradiated consolidated samples appear to follow a similar trend.

Figure 1: Oxidation induction time as a function of nominal Vitamin E concentration for all samples tested. Error bars are one standard deviation for OIT and ±0.02 for VE concentration.

These data indicate a logarithmic relationship between OIT and VE concentration dependent upon processing conditions. During processing, some of the VE will presumably be used to protect the UHMWPE reducing the amount of VE available for further protection. OIT measurements should only reflect this reduced amount, termed effective VE concentration (EVC). For instance, since irradiation is known to generate many free-radicals, the EVC of the irradiated samples is considerably lower than the original given concentration. EVC can be determined by developing a correction for specific processing conditions. Using the minimally processed powder samples as the reference material, an exponential equation was calculated from measured OIT and given VE concentration. A theoretical VE concentration for each sample was then determined using this equation and measured OIT values. Since the theoretical concentration decreased with subsequent processing steps, a scaling factor was determined by dividing the calculated concentration by the given VE wt%. The EVC of each sample was then determined using the average scaling factor for each sample set and given VE concentration. The determined EVC as a function of measured OIT is presented in Figure 2. The resulting master curve holds for all samples with OIT values higher than 3 minutes regardless of processing conditions. OIT values of less than 3 minutes are believed to be near the resolution limit of the technique and these rapidly oxidizing samples do not behave in the same manner as the other samples.

Figure 2: Effective Vitamin E concentration as a function of oxidation induction time. Exponential fit for the unirradiated powder samples used for calculations is shown.

Conclusion: The OIT technique presented above provides a novel, sensitive method for determining the VE concentration in UHMWPE components. This method could be used for both QC and R&D purposes to evaluate effective VE levels after different processing conditions. The developed master curve implies that, for given processing conditions, OIT can be used to determine the effective VE concentration of a blended and processed UHMWPE component. In addition, this technique is sensitive enough to detect changes in the effective VE concentration after simple compression molding of components. Thus, 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: Materials providing by Zimmer, Inc. Funding was provided by Zimmer, Inc.