RECERTIFICATION OF THE POLYETHYLENE OXIDATION INDUCTION TIME REFERENCE MATERIAL

*Roger L. Blaine, Ph.D.
TA Instruments, Inc., 109 Lukens Drive, New Castle, DE 19720, USA
and
Alan T. Riga, Ph.D.
TechCon, Inc., 6325 Aldenham Drive, Cleveland, OH 44143, USA

*corresponding author

ABSTRACT

A commercial Oxidation Induction Time (OIT) reference material polyethylene film is retested six years after its original certification. Using ASTM International Standard E1858, the mean value, within laboratory repeatability and between laboratory reproducibility were unchanged at 29.3 min, 1.7 and 2.1 min, respectively. In addition the new results are reported on an interlaboratory test for Oxidation Onset Temperature (OOT) for the same material using Method A (oxygen purge gas) and C (air purge gas) of ASTM Standard E2009. The mean values are found to be 236.8 and 245.0 °C under oxygen and air, respectively. The within laboratory repeatability standard deviation is 1.1 and 0.68 °C, and the between laboratory reproducibility standard deviation is 1.3 and 1.4 °C, respectively, for oxygen and air.

INTRODUCTION

In 1996, a well-characterized polyethylene sample was proposed as a reference material for Oxidation Induction Time (OIT) determinations (*1*). Subsequently, this OIT Reference Material was commercialized by TA instruments, New Castle, DE, (part number 900319.901) and is in widespread use as a diagnostic and research tool for polyethylene performance and the OIT test method. The reference material was used in a number of interlaboratory test programs including those for ASTM standards E1858 and E2009 (*2,3*). The sample was also examined under a wide variety of conditions by Lecon Woo and co-workers at Baxter Healthcare (*4, 5, 6*).

In the original 1996 paper, it was suspicioned that the OIT value of the material was decreasing with time due to the reduction in the antioxidant package through slow "leaching" out. According to the estimates in the early work of Blaine and coworkers, the OIT value should have declined to about 25 minutes by 2002 if the earlier trend continued. This was predicted from a series of test programs conducted between 1991 and 1995, the data for which is presented in Figure 1. The decrease in OIT value was uncertain, however, as the trend could be attributable to normal experimental scatter.

In an attempt to stabilize the OIT value of the film in its preparation for commercialization, two sheets of the polyethylene film reference material were placed

into an envelope composed of the same polyethylene film. It was thought that the two inner sheets of film would then be protected from leaching by the sacrificial envelope of the same material. The envelope was then placed into a second darkened and opaque, brown polyethylene envelope to serve as a light shield and labeled container.

This present work was undertaken six years after the original certification in an attempt to determine the effectiveness of the stabilization process and to recertify the value for the OIT Reference Material.

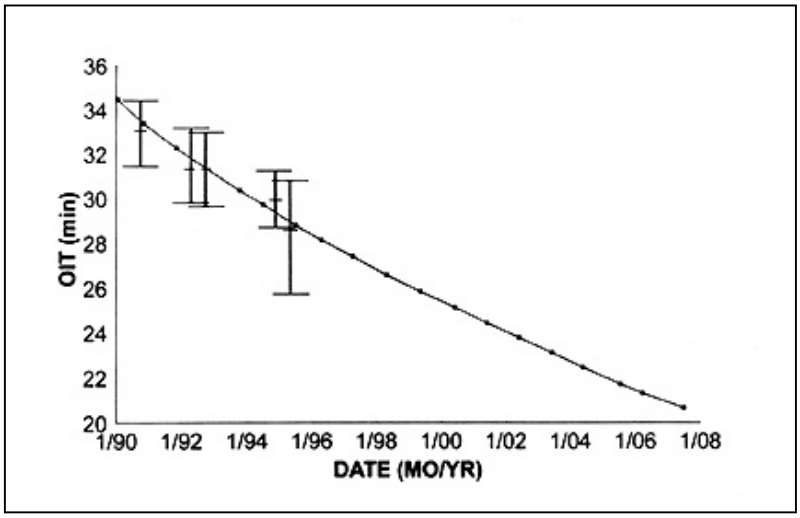

Figure 1 – Projected Decay of OIT with Time

EXPERIMENTAL

All work was carried out on model Q1000 and 2920 Differential Scanning Calorimeters provided by TA Instruments. All DSC's were equipped with auto samplers for precise sample placement. One each of the Q1000's was fitted with the Finned Air Cooling System (FACS), the Refrigerated Cooling System (RCS) and Liquid Nitrogen Cooling System (LNCS). All instruments were temperature calibrated with indium at a heating rate of 10 °C/min according the ASTM International Standard E967 (*7*). Temperature calibration was then re-performed at 1 °C/min to approximate the isothermal temperature condition as described in E1858.

5 mg pieces of the OIT reference materials were cut from the original film sheet using a 6.3 mm paper punch. These sample disks were then placed in open DSC plans previously cleaned in toluene and dichloromethane. OIT was determined using method E1858 where the specimen is loaded at ambient temperature and then heated at 20 °C/min to the isothermal test temperature in inert nitrogen. The sample is held at this test temperature for 5 minutes. The purge gas is then switched from nitrogen to oxygen at 50 mL/min and the elapsed time clock is set to zero. The time to the onset of oxidation is then measured and reported as OIT in minutes. The sample temperature is recorded 5 minutes into this method segment. All work was carried out at an isothermal test temperature of 200 °C with a minimum of 10 replicates from each laboratory resulting in 27 degrees of experimental freedom. The interlaboratory results are presented in Table 1.

Table 1 – Interlaboratory Oxidation Induction Time Test Results

Lab. (no.)	Mean (min)	Std. Dev. (min)
1	30.2	1.2
2	28.1	1.6
3	30.9	2.2
4	28.1	1.6
mean	29.3	
repeatability		1.7
reproducibility		2.1

RESULTS AND DISCUSSION

The results from the four laboratories were statistically treated using ASTM Method E691 (*8*). The mean value was 29.3 minutes with a within laboratory repeatability standard deviation of the ± 1.7 minutes and a between laboratory reproducibility standard deviation of ± 2.1 minutes. These values are compared to the 1995 test date in Table 2. The mean values are different by about 3 % but this is not considered significant based upon the precision of the measurement as evaluated by the Student's T-test. A comparison of the results shows that the repeatability and reproducibility standard deviations are within the statistical limits at the 95 % confidence limit according to the statistical F-test.

Thus the steps taken to stabilize the condition of the OIT material appear successful and the material may be regarded as unchanged over the 5-year period since the original work.

Table 2 – Oxidation Induction Time Comparative Test Results

	1995	2001
Mode	31.2	30.3
Median	30.2	29.3
Mean	30.0 ± 1.2	29.3 ± 1.7

OXIDATION ONSET TEMPERTURE (OOT)

A second set of measurements was made on the OIT Reference Materials – that of the Oxidation Onset Temperature (OOT). While the Oxidation Induction Time test is an isothermal time-to-event test, the test for Oxidation Onset Temperature test is a dynamic heating rate test. According to ASTM International Standard E2009, the test specimen is heated from ambient temperature at 10 °C/min in an oxidizing atmosphere. The (extrapolated onset) temperature at which the test specimen begins to oxidize is taken as the OOT value. Differences in OOT value may be used to rank-order dramatic

changes (such as different antioxidant packages) while the companion isothermal OIT test may be used to evaluate the more subtle lot-to-lot variations of a particular formulation.

EXPERIMENTAL

Two interlaboratory test (ILT) programs were carried out in 2001 to obtain within laboratory repeatability and between laboratory reproducibility for the determination of E2009 Oxidation Onset Temperature. One study used oxygen as a reactive purge gas (Method A) and the other used air (Method C). The Oxidation Induction Time Reference Material was used as the test specimen in these studies. The results of these ILTs add to the list of reference values for this material.

In the first study seven laboratories, using four instrument models from a single instrument manufacturer (TA Instruments), determined the OOT value in oxygen in hextuplicate using E2009 Method A. In the second study six laboratories using four instrument models from a single manufacturer, determined the OOT value in air in heptuplicate using E2009 Method C. The mean value, repeatability and reproducibility standard deviation for OOT for the OIT Reference Material are presented in Table 3 with 25 and 30 degrees of experimental freedom for oxygen and air purge gases, respectively.

Table 3 – Oxidation Onset Temperature Test Results

Oxidant	Mean	Std. Dev. (°C)	
	(°C)	Repeatability	Reproducibility
Oxygen	236.8	1.1	1.3
Air	245.0	0.68	1.4

CONCLUSIONS

The Oxidation Induction Time Reference material available from TA Instruments is stable over the six-year period since its original certification. Thus the experimental value originally provided and added to in the interim should be considered valid. Additionally, Oxidation Onset Temperature values in oxygen and air are added to the certificate for the material.

REFERENCES

1. R. L. Blaine and M. B. Harris, “A Proposed Reference Material for Oxidative Induction Time by Differential Scanning Calorimetry”, *Oxidative Behavior of Materials by Thermal Analytical Techniques*, A. T. Riga and G. H. Patterson (Eds.), Special Technical Publication 1326, American Society for Testing and materials, West Conshohocken, PA, **1997**, pp. 193-204.
2. E1858, “Method for Determining Oxidation Induction Time of Hydrocarbons by Differential Scanning Calorimetry”, American Society for Testing and Materials, West Conshohocken, PA

3. E2009, “Oxidation Onset Temperature of Hydrocarbon by Differential Scanning Calorimetry”, American Society for Testing and Materials, West Conshohocken, PA.
4. S. Y. Ding, M. T. K. Ling, A. R. Khare, L. Woo, “Durability of a Reference Material Over Diverse Conditions”, *Thermochimica Acta*, **2000**, 357-358, pp. 147-153.
5. L. Woo, Y. S. Yank, M. T. K. Ling, C. Qin, A Khare, “Flow, Pressure, Temperature Dependence of Oxidation Induction Time Measurements on a Heat Flow DSC”, *Proc. 56th Ann. Tech. Conf, Soc. Plast. Eng.,* **1998**, 2, pp. 1986-1990.
6. L. Woo, A. R. Khare, C. L. Sandford, M. T. K Ling, S. Y. Ding, “Relevance of High Temperature Oxidative Stability Testing to Long Term Polymer Durability”, *Journal of Thermal Analysis and Calorimetry*, **2001**, 64, pp. 539-548.
7. E967, “Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers”, American Society for Testing and Materials, West Conshohocken, PA.
8. E691, “Conducting an Interlaboratory Study to Determine the Precision of a Test Method”, American Society for Testing and Materials, West Conshohocken, PA.

KEYWORDS

differential scanning calorimeter, polyolefins, oxidative stability, thermoplastic polymers