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# Recertification of the polyethylene oxidation induction time reference material

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**Abstract**

A commercial oxidation induction time (OIT) reference material polyethylene film is retested 6 years after its original certification. Using ASTM International Standard E 1858, the mean value, within laboratory repeatability and between laboratory reproducibility are unchanged at 29.3, 1.7 and 2.1 min, respectively. In addition, the new results are reported on an interlaboratory test (ILT) for oxidation onset temperature (OOT) for the same material using Method A (oxygen purge gas) and Method C (air purge gas) of ASTM Standard E 2009. 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.

*Keywords:* Polyethylene; Oxidation induction time; Stability; Lifetime

## 1. 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 ILT programs including those for ASTM standards E 1858 and E 2009 [2,3]. The sample was also examined under a wide variety of conditions by Woo and co-workers at Baxter Healthcare [4–6].

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 Harris [1], the OIT value should have declined to about 25 min 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 Fig. 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

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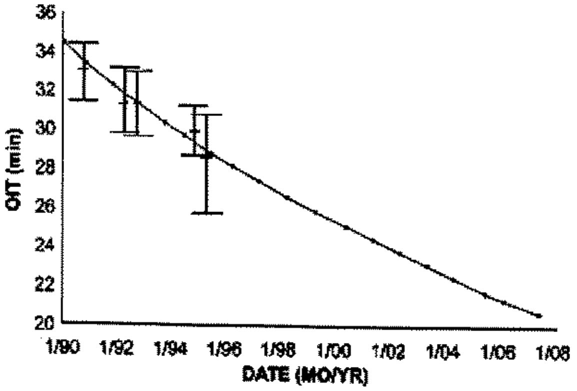

Fig. 1. Projected decay of OIT with time (reprinted with permission of the copyright holder).

Table 1
Interlaboratory OIT test results

| Laboratory (no.) | Mean (min) | S.D. (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 |

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 6 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.

## 2. Experimental

All work was carried out on model Q1000 and 2920 differential scanning calorimeters (DSCs) provided by TA Instruments. All DSCs 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 to the ASTM International Standard E 967 [7]. Temperature calibration was then re-performed at 1 °C/min to approximate the isothermal temperature condition as described in E 1858.

OIT reference materials of 5 mg pieces 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 E 1858 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 min. The purge gas is then switched from nitrogen to oxygen at 50 ml/min and the elapsed time clock is set to 0. The time to the onset of oxidation is then measured and reported as OIT in minutes. The sample temperature is recorded 5 min 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° of experimental freedom. The interlaboratory results are presented in Table 1.

## 3. Results and discussion

The results from the four laboratories were statistically treated using ASTM Method E 691 [8]. The mean value was 29.3 min with a within laboratory repeatability standard deviation of the ±1.7 min and a between laboratory reproducibility standard deviation of ±2.1 min. 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

Table 2
OIT comparative test results

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

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.

## 4. Oxidation onset temperature (OOT)

A second set of measurements was made on the OIT reference materials that of the OOT. While the OIT test is an isothermal time-to-event test, the test for OOT test is a dynamic heating rate test. According to ASTM International Standard E 2009, 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.

## 5. Experimental

Two ILT programs were carried out in 2001 to obtain within laboratory repeatability and between laboratory reproducibility for the determination of E 2009 OOT. One study used oxygen as a reactive purge gas (Method A) and the other used air (Method C). The OIT reference material was used as the test specimen in these studies. The ILT participants are listed in Table 3. (The author wishes to express his thanks to the participants for their efforts.) The results of these ILTs add to the list of reference values for this material.

Table 3
ILT participants

| Contributor | Affiliation | Location |
|---|---|---|
| Ricardo Collins | Lubrizol Corp. | Wickliffe, OH |
| Shouvik Roy | Univ. of Toledo | Toledo, OH |
| Alan Riga | Cleveland State Univ. | Cleveland, OH |
| Roger Blaine | TA Instruments | New Castle, DE |

In the first study, seven laboratories using four instrument heat flux DSC models (TA Instruments models 2010, 2920, Q100 and Q1000) determined the OOT value in oxygen in hextuplicate using E 2009 Method A. In the second study, six laboratories using four instrument models (TA Instruments models 910, 2920, Q100 and Q1000) determined the OOT value in air in heptuplicate using E 2009 Method C. The mean value, repeatability and reproducibility standard deviation for OOT for the OIT reference material are presented in Table 4 with 25 and 30° of experimental freedom for oxygen and air purge gases, respectively.

Table 4
OOT test results

| Oxidant | Mean (°C) | S.D. (°C) | |
|---|---|---|---|
| | | Repeatability | Reproducibility |
| Oxygen | 236.8 | 1.1 | 1.3 |
| Air | 245.0 | 0.68 | 1.4 |

## 6. Conclusions

The OIT reference material available from TA Instruments is stable over the 6-year-period since its original certification. Thus the experimental value originally provided and added to in the interim should be considered valid. Additionally, values for OOT in oxygen and air are added to the certificate for the material. Retesting and recertification of this material is planned in another 5 years.

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