



Designation: D 3895 – 02

## Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry<sup>1</sup>

This standard is issued under the fixed designation D 3895; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope\*

1.1 This test method outlines a procedure for the determination of oxidative-induction time (OIT) of polymeric materials by differential scanning calorimetry (DSC). It is applicable to polyolefin resins that are in a fully stabilized/compounded form.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazards information is given in Section 8.

NOTE 1—This test method is similar to ISO 11357-6, but not identical. The temperature used by ISO is 210°C.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 4703 Practice for Compression Molding Thermoplastic Materials into Test Specimens, Plaques, or Sheets<sup>2</sup>

E 473 Terminology Relating to Thermal Analysis<sup>3</sup>

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method<sup>3</sup>

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers<sup>3</sup>

### 3. Terminology

3.1 Definitions—Definitions of terms applying to thermal analysis appear in Terminology E 473.

#### 3.2 Description of Term Specific to This Standard:

3.2.1 *oxidative induction time*—a relative measure of a material's resistance to oxidative decomposition; it is determined by the thermoanalytical measurement of the time

interval to onset of exothermic oxidation of a material at a specified temperature in an oxygen atmosphere.

#### 3.2.2 Abbreviations:

3.2.3 HDPE—high-density polyethylene.

3.2.4 LDPE—low-density polyethylene.

3.2.5 LLDPE—linear low-density polyethylene.

3.2.6 OIT—oxidative induction time.

### 4. Summary of Test Method

4.1 The sample to be tested and the reference material are heated at a constant rate in an inert gaseous environment (nitrogen). When the specified temperature has been reached, the atmosphere is changed to oxygen maintained at the same flow rate. The specimen is then held at constant temperature until the oxidative reaction is displayed on the thermal curve. The time interval from when the oxygen flow is first initiated to the oxidative reaction is referred to as the induction period.

4.1.1 The end of the induction period is signaled by an abrupt increase in the specimen's evolved heat or temperature and may be observed by a differential scanning calorimeter (DSC). The OIT is determined from the data recorded during the isothermal test.

4.2 The type of containment system used depends on the intended application use of the material being tested. Polyolefins used in the wire and cable industry typically require copper or aluminum pans, whereas polyolefins used in geomembrane and vapor-barrier film applications exclusively use aluminum pans.

4.3 Unless otherwise specified, the analysis temperature used in this test has been set arbitrarily at 200.0°C. For samples that have relatively low or high stabilization levels, a different temperature may be selected (typically between 180 and 220°C) to yield a thermal curve that can be interpreted and analyzed easily.

### 5. Significance and Use

5.1 The OIT is a qualitative assessment of the level (or degree) of stabilization of the material tested. This test can be used as a quality control measure to monitor the stabilization level in formulated resin as received from a supplier, prior to extrusion.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.30 on Thermal Properties (Section D 20.30.07).

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 08.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 14.02.

\*A Summary of Changes section appears at the end of this standard.

NOTE 2—The OIT measurement is an accelerated thermal-aging test and as such can be misleading. Caution should be exercised in data interpretation since oxidation reaction kinetics are a function of temperature and the inherent properties of the additives contained in the sample. For example, OIT results are often used to select optimum resin formulations. Volatile antioxidants may generate poor OIT results even though they may perform adequately at the intended use temperature of the finished product.

NOTE 3—There is no accepted sampling procedure, nor have any definitive relationships been established for comparing OIT values on field samples to those on unused products, hence the use of such values for determining life expectancy is uncertain and subjective.

## 6. Apparatus

6.1 *Differential Scanning Calorimeter*—As a minimum requirement, the thermal analysis equipment shall be capable of measuring heat flow of at least 10-mW full scale. The instrument recorder should be capable of displaying heat flow or temperature differential on the *Y*-axis and time on the *X*-axis. The time base must be accurate to  $\pm 1\%$  and be readable to 0.1 min.

NOTE 4—The OIT test is a function of a particular compound's stabilizer system and should not be used as a basis of comparison between formulations that might contain, different resins, stabilizers, or additive packages, or all of these.

6.2 *Gas-Selector Switch and Regulators*, for high-purity nitrogen and oxygen. The distance between the gas-switching point and the instrument cell should be kept small to minimize the switching volume.

6.3 *Analytical Balance*, 0.1-mg sensitivity.

6.4 *Bore-Hole Cutter*, 6.4-mm diameter.

6.5 *Specimen-Encapsulating Press*.

6.6 *Forceps, Scalpel, and Cutting Board*.

6.7 *Rotometer (Calibrated) or Soap-Film Flowmeter*, for gas-flow calibration.

6.8 *Specimen Holders*—Degreased aluminum or oxidized-copper pans (6.0 to 7.0-mm diameter, 1.5-mm height). Use the appropriate pan type for the material being tested.

NOTE 5—Aluminum lids are required for temperature calibration.

NOTE 6—Both types of pans are commercially available. Alternatively, the copper pans can be fabricated manually. Details on copper pan preparation and oxidation as well as instructions for aluminum pan conditioning (degreasing) are given in Annex A2-Annex A4.

NOTE 7—The material composition of the specimen holder can influence the OIT test result significantly (that is, including any associated catalytic effects).

6.9 *Compression-Molding Device with Heated Platen*s.

6.10 *Spacer Plates, Shim Stock, Caul Plates, etc.*

6.11 *Mylar<sup>4</sup> (Polyester Film) or Teflon<sup>4</sup> (Polytetrafluoroethylene) Coated Cloth*, for sample-plaque preparation.

6.12 *Thickness Gage*.

6.13 *Laboratory Gas Burner*, for copper-pan oxidation.

6.14 *Boiling Flask*, with condenser and heating mantle.

6.15 *Forced-Air Oven*.

## 7. Reagents and Materials

7.1 All chemical reagents used in this procedure shall be analytical grade unless otherwise specified.

7.2 *Oxygen*—Ultra-high-purity grade (extra dry).

7.3 *Nitrogen*—Ultra-high-purity grade (extra dry).

7.4 *Aluminum Pan Degreasing Solvent*.

7.5 *Indium* (99.999 % purity).

7.6 *Tin* (99.999 % purity).

## 8. Hazards

8.1 Oxygen is a strong oxidizer that accelerates combustion vigorously. Keep oil and grease away from equipment using or containing oxygen.

8.2 The use of pressurized gas requires safe and proper handling.

## 9. Sampling

9.1 The following sample preparation procedures are recommended: the test sample is compression molded into sheet format (thickness of  $250 \pm 15 \mu\text{m}$ ) prior to analysis to yield consistent sample morphology and weight. Specimen disks (6.4-mm diameter) cut from the sheet will have a weight of approximately 5 to 10 mg, depending on sample density.

NOTE 8—If the sample requires homogenization prior to analysis, the melt compounding procedure given in Appendix X1 is recommended. Poor sample uniformity will affect test precision adversely.

9.1.1 Meter out the required mass of the sample and place the material in the center of the appropriately sized spacer between two sheets of Mylar<sup>4</sup> or Teflon<sup>4</sup> coated cloth and two caul plates.

9.1.2 Place the assembly into the compression-molding device. The preheat and pressing temperature should be 160°C for polyethylene and 190°C for polypropylene.

9.1.3 Heat the sample with appropriate pressure and time settings to obtain a plaque with uniform thickness.

9.1.4 Remove the plaque assembly and place it between two thick steel plates (heat sink) and cool the plaque to ambient temperature. Alternatively, the plaque can be quenched in ice water.

9.1.5 Determine the average thickness of the sheet to ensure that it is within the allowable tolerances.

9.1.6 Use the bore-hole cutter to punch out a disk from the plaque and record the specimen weight.

9.1.7 Place the specimen disk into the appropriate pan type. Use an identical empty pan as the reference. (Do not crimp or seal the pans.)

NOTE 9—The test sample may also be prepared using Practice D 4703, Annex 1 (Procedure C), with the exception that controlled cooling is not necessary.

## 10. Procedure

10.1 *Instrumental Calibration*—This procedure uses a two-point calibration step. Indium and tin are used as the calibrants since their respective melting points encompass the specified analysis temperature range (180 to 220°C). Calibrate the instrument in accordance with the manufacturer's instructions using the following procedure. The calibration step should be performed at least once per month.

10.1.1 Place  $5 \pm 0.5$  mg of indium/tin into an aluminum sample pan. Place an aluminum cover over the pan, and seal using the encapsulating press. Prepare an empty sealed pan to

<sup>4</sup> Mylar and Teflon are registered trademarks of DuPont.

be used as the reference. Place the specimen and reference pans into their respective locations in the instrument cell.

10.1.2 Turn on the nitrogen-gas flow at a rate of 50 mL/min (with an absolute pressure of 140 kPa).

10.1.3 Use the following melting profiles:

*Indium:* = ambient to 145°C at 10°C/min, 145 to 165°C at 1°C/min

*Tin:* = ambient to 220°C at 10°C/min, 220 to 240°C at 1°C/min

NOTE 10—The specified heating rates are for calibration use only.

10.1.4 Adjust the temperature-calibration software (or potentiometer) to set the melting point at 156.63 and 231.97°C<sup>5</sup> for indium and tin, respectively. The melting point of the calibrant is defined as the intercept of the extended baseline and the extended tangent to the first slope of the endotherm (that is, the onset). See Fig. 1.

NOTE 11—An inadequate melting thermal curve is occasionally obtained due to poor surface contact of the calibrant material to the pan surface. If this occurs, repeat the calibration step. (After one melting/crystallization cycle the calibrant material should coat the bottom of the pan evenly.)

### 10.2 Instrument Operation:

10.2.1 Load the specimen and reference pans into the cell.

10.2.2 Allow 5 min for a nitrogen prepurge prior to beginning the heating cycle to eliminate any residual oxygen. Commence programmed heating of the specimen (under nitrogen flow of 50 ± 5 mL/min) from ambient temperature to 200°C (set point) at a rate of 20°C/min.

10.2.3 When the set temperature has been reached, discontinue programmed heating and equilibrate the sample for 5 min at the set temperature. Turn on the recorder. If the instrument being used does not have an isothermal temperature-control-

mode feature, follow the alternate procedure outlined in Annex A1 or alternatively ensure accurate temperature control by monitoring and adjusting continually, as required.

10.2.4 Once the equilibrium time has expired, change the gas to oxygen at a flow rate of 50 ± mL/min. (Record this event.) This changeover point to oxygen flow is considered the zero time of the experiment.

10.2.5 Continue isothermal operation until at least 2 min have elapsed after the steepest point of the exotherm has been displayed (see Fig. 2). At the tester's discretion, the test may be terminated if time requirements stated in the product's specification have been met.

10.2.6 Upon completion of the test, switch the gas selector back to nitrogen and cool the instrument to ambient temperature. If additional testing is being conducted, cooling the instrument cell below 60 to 70°C should be sufficient to avoid any premature thermal oxidation of the sample.

10.2.7 Test frequency is established by the user. As a minimum requirement, samples should be tested in duplicate with the mean value reported.

10.2.8 Clean the DSC cell of contamination by heating to 500°C for 5 min in air (or oxygen) prior to conducting measurements and between the testing of different formulations.

10.3 Thermal Curve Analysis—The data is plotted with the heat-flow signal normalized to sample mass (that is, W/g) on the y-axis, versus time on the x-axis. The x-axis should be expanded as much as possible to facilitate analysis.

10.3.1 Extend the recorded baseline beyond the oxidative reactive exotherm. Extrapolate the steepest linear slope of this exotherm to intercept the extended baseline (see Fig. 3).

10.3.2 The OIT is measured to within ±0.1 min from zero time to the intercept point.

10.3.3 The tangent method used to measure the oxidation time is the preferred method, but the selection of the appropriate tangent to the exotherm sloped line may be difficult if the exothermic peak has a leading edge. Exothermic peaks with leading edges may occur if the oxidation reaction is slow.

<sup>5</sup> See Practice E 967.

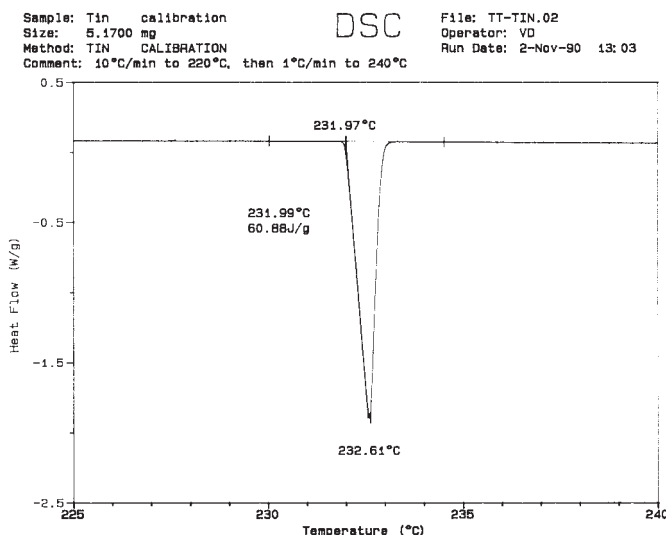


FIG. 1 Indium and Tin Melting Thermal Curves