Designation: D8117 – 17

Standard Test Method for
Oxidative Induction Time of Polyolefin Geosynthetics by Differential Scanning Calorimetry[1]

This standard is issued under the fixed designation D8117; 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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers a procedure for the determination of the oxidative induction time (OIT) of polyolefin geosynthetics using differential scanning calorimetry.

1.2 The focus of the test is on geomembranes, but geogrids, geonets, geotextiles, and other polyolefin-related geosynthetics are also suitable for such evaluation.

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

NOTE 1—This standard and ISO 11357-6 2013 address the same subject matter, but differ in technical content.

1.4 *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.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4439 Terminology for Geosynthetics

D4703 Practice for Compression Molding Thermoplastic Materials into Test Specimens, Plaques, or Sheets

E473 Terminology Relating to Thermal Analysis and Rheology

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms applying to thermal analysis, refer to Terminology E473.

3.1.2 For definitions of terms related to geosynthetics, refer to Terminology D4439.

3.2 *Definitions of Terms 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.

3.3 *Abbreviations:*

3.3.1 *HDPE*—high-density polyethylene.

3.3.2 *LDPE*—low-density polyethylene.

3.3.3 *LLDPE*—linear low-density polyethylene.

3.3.4 *OIT*—oxidative induction time.

4. Summary of Test Method

4.1 The sample to be tested is 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 OIT is determined from the data recorded during the isothermal period. 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 will be recorded as an exothermic event by a differential scanning calorimeter (DSC).

4.2 The test is conducted in open aluminum pans.

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 has the

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[1] This test method is under the jurisdiction of ASTM Committee D35 on Geosynthetics and is the direct responsibility of Subcommittee D35.02 on Endurance Properties.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

potential to be used as a quality control measure to monitor the stabilization level in formulated resin as received from a supplier, prior to extrusion.

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 shall 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 ±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, 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 shall be such that the time required to transition to an oxygen environment is less than 1 min. At a flow rate of 50 mL/min, this equates to a maximum switching volume of less than 50 mL.

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 *Electronic Mass Flow Controller, Rotometer (Calibrated), or Soap-Film Flowmeter,* for gas flow calibration.

6.8 *Specimen Holders*—Degreased aluminum pans (6.0- to 7.0-mm diameter, 1.5-mm height).

NOTE 5—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 Platens.*

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

6.11 *Polyethylene Terephthalate Film (PET) or Polytetrafluoroethylene (PTFE)-Coated Cloth,* for sample-plaque preparation.

6.12 *Thickness Gauge.*

6.13 *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 vigorously accelerates combustion. 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 Compression mold the sample into sheet format (thickness of 250 ± 15 µm) prior to analysis 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 6—If the sample requires homogenization prior to analysis, one of the procedures given in Appendix X1, Appendix X2, or Appendix X3 is recommended. Poor sample uniformity will adversely affect test precision.

NOTE 7—If the sample contains a layer or layers of polymers other than polyolefins, the polyolefin may be tested separately from the entire cross-section. A recommended procedure is given in Appendix X4.

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

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

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

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

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

9.1.6 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 8—If controlled cooling is not necessary, the option to prepare the test sample using Practice D4703, Annex A1 (Procedure C), is acceptable.

10. Procedure

10.1 *Instrument 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. Calibrate the instrument at least once per month or before use if longer than one month.

10.1.1 Place 5 ± 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 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 9—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 (see Practice E967) 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.

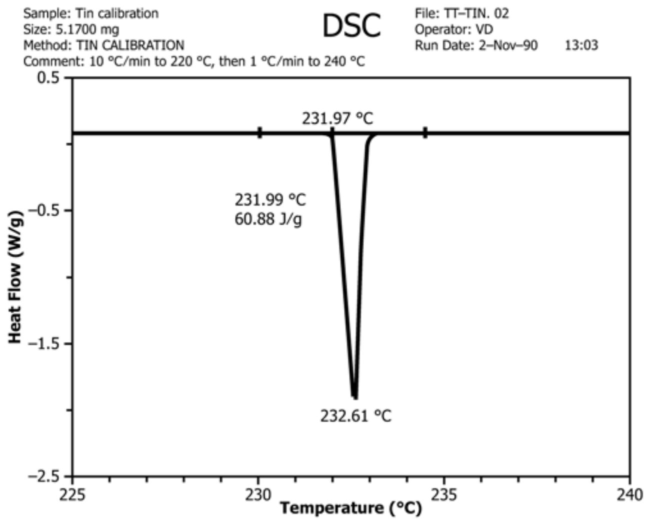


FIG. 1 Indium and Tin Melting Thermal Curves

NOTE 10—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 pre-purge 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, 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 the maximum exotherm has been reached to allow a complete examination of the entire exotherm. (See Figs. 2 and 3). At the tester's discretion, it is acceptable to terminate the test at a predetermined heat flow change provided that data are available to support the alternative. It is also acceptable to terminate the test 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 is 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 are 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. Expand the *x*-axis 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 is, at times, difficult if the exothermic peak has a leading edge. It is possible that exothermic peaks with leading edges occur if the oxidation reaction is slow.

NOTE 11—The oxidation may not occur as a smooth transition and multiple steps or slopes may be produced. When this occurs, resampling and retesting is recommended. Use of one of the homogenization methods mentioned in the appendixes of this standard may be used to obtain a homogeneous specimen and a single exothermic peak.

NOTE 12—If multiple slopes result from the oxidation process, OIT needs to be defined to accurately reflect the oxidation of the polymer. It is up to the user to determine which slope best represents the material property for an application. It must be noted in the report if the tangent line is not drawn from the first steep slope.

NOTE 13—If the selection of the appropriate baseline is not obvious using the tangent method, try the offset method. Draw a second baseline parallel to the first baseline at a distance of 0.05 W ⁄g above the first baseline. The intersection of this second line with the exotherm signal is defined as the onset of oxidation. The time from this intersection to zero time is the OIT.

NOTE 14—Other gas flow rates or specimen weights, or both, may be used if shown to be equivalent.

11. Report

11.1 Report the following information:

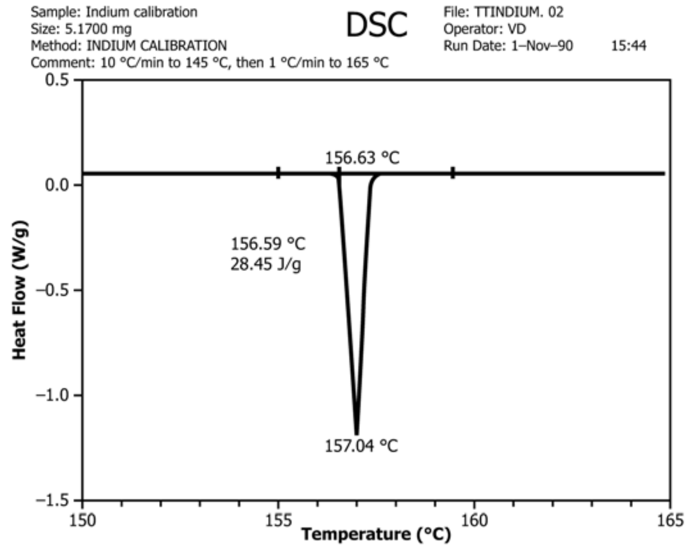
11.1.1 Identification of the sample,

11.1.2 Type of sample pan,

11.1.3 Test temperature used,

11.1.4 Measurement technique used (that is, tangent method or offset method, OIT not determined from the first steep slope), and

11.1.5 Average OIT in minutes (three significant digits).



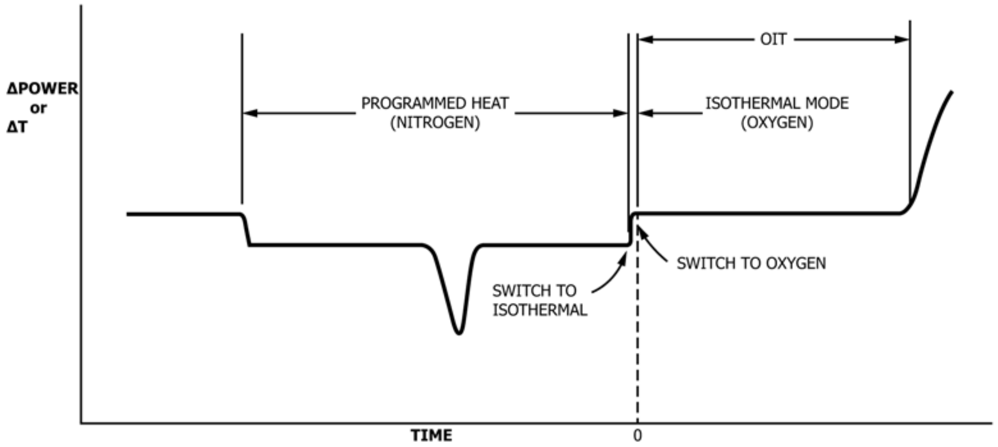


FIG. 2 Evaluation of OIT from Recorded Time-Based Thermal Curve

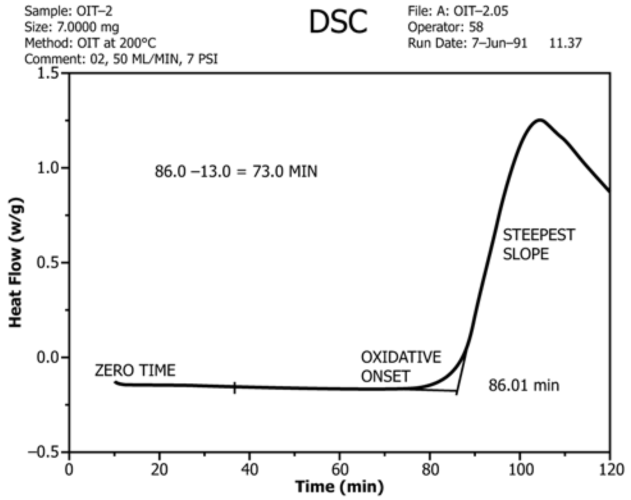


FIG. 3 Determination of OIT

12. Precision and Bias[3]

12.1 The data in Table 1 is based on a round robin conducted in 1991 in accordance with Practice E691, involving four polyethylene materials tested by eleven laboratories. The test materials were obtained from three laboratories. The OIT of each sample was determined in duplicate on two separate days (that is, a total of four OIT determinations). Of the 14 laboratories that participated in the round-robin exercise, eleven laboratories used heat flux-type instruments and three laboratories used power compensation-type instruments.

TABLE 1 Precision and Repeatability – Oxidative Induction Time (min) of Polyethylenes

Material	Average	S_r	S_R	r	R
LDPE	24.0	2.8	4.3	8.0	12.2
LDPE	83.4	9.2	17.4	25.7	48.8
LLDPE	120	7.8	14.6	21.9	40.8
HDPE	163	8.3	21.7	23.2	60.9

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1178. Contact ASTM Customer Service at service@astm.org.

NOTE 15—The precision and bias data for other polyolefins may differ from the polyethylene material data shown in Table 1.

NOTE 16—The sample preparation steps for each test material (that is, sheet compression molding) were performed by one laboratory. Each participating laboratory received a set of specimen disks die cut from each of the molded sheets and samples of indium and tin required for instrument calibration. Each participating laboratory furnished its own specimen holders.

12.2 The following explanations of *r* and *R* (12.3 – 12.3.3) are only intended to present a meaningful way of considering the approximate precision of this test method. Do not apply the data in Table 1 rigorously to acceptance or rejection of material, as those data are specific to the round robin, and not representative of other lots, conditions, materials, or laboratories. Users of this test method are encouraged to apply the principles outlined in Practice E691 to generate data specific to their laboratory and materials, or between specific laboratories. The principles of 12.3 – 12.3.3 would then be valid for such data.

12.3 *Concept of* r *and* R—If S_r and S_R have been calculated from a large enough body of data, and for test results that were averages from testing four specimens, the following applies:

12.3.1 *Repeatability*—Two results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material. "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

12.3.2 *Reproducibility*—Two test results obtained by different laboratories shall be judged not equivalent if they differ by more than the "*R*" value for that material. "*R*" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

12.3.3 Any judgment in accordance with 12.3.1 or 12.3.2 would have an approximate 95 % (0.95) probability of being correct.

12.4 *Bias*—There are no recognized standards by which to estimate the bias of this test method.

13. Keywords

13.1 differential scanning calorimetry; oxidative induction time; polyolefins

APPENDIXES

(Nonmandatory Information)

X1. SAMPLE HOMOGENIZATION USING A TORQUE RHEOMETER

X1.1 If desired, the test sample may be homogenized prior to OIT analysis to minimize local variations of stabilizer concentration. A torque rheometer equipped with a mixing head is suitable for such purposes.

X1.2 Each sample should be blended at 60 r/min for 10 min, using a chamber temperature of 150 to 160 °C for polyethylene resins and 180 to 190 °C for polypropylene resins. The mixing chamber should be purged with nitrogen to suppress polymer and additive degradation.

X1.3 After a mixing time of 10 min, quench-cool the samples in liquid nitrogen or ice water. After sufficient cooling, compression mold the required amount of material into sheet format.

X2. SAMPLE HOMOGENIZATION USING A CRYOGENIC GRINDER

X2.1 If desired, the test sample may be homogenized prior to OIT analysis to minimize local variations of stabilizer concentration. A cryogenic grinder may be used to prepare a more homogeneous sample.

X2.2 Follow the instructions and safety precautions recommended by the manufacturer of the grinder.

X2.3 Be sure to cut the sample into small enough pieces, pre-cool long enough, and grind long enough to create a mixture of fine particles with no residual larger chunks.

X2.4 Let the sample warm to room temperature prior to exposure to the air to prevent condensation on the sample prior to compression molding the material into a sheet.

X3. SAMPLE HOMOGENIZATION USING A TWO-ROLL MILL

X3.1 If desired, the test sample may be homogenized prior to OIT analysis to minimize local variations of stabilizer concentration. A small, lab two-roll mill may be used to prepare a homogeneous sample.

X3.2 Small pieces of the sample are placed on a hot, two-roll mill that is turning. Conditions are dependent on the specific material and equipment being used, and so are outside the scope of this appendix.

X3.3 Conditions should be selected that can melt and mix the sample within 90 s. A nitrogen blanket (flow of nitrogen gas onto the sample) can help reduce oxidation but is not required.

X3.4 After the sample is well mixed, quench-cool the samples in liquid nitrogen or ice water. After sufficient cooling, compression mold the required amount of material into sheet format.

X4. SAMPLING INDIVIDUAL LAYERS FOR ANALYSIS

X4.1 If desired, an individual layer may be separated from the sample as a whole and analyzed for OIT separately. One method to do that is to cut multiple thin sections or thick microtomes followed by using a sharp instrument to remove or separate a particular layer. After an adequate amount of material is separated, it may be made into a plaque directly or may be homogenized using one of the procedures in the appendixes.

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