



Standard Test Method for Oxidative Induction Time of Polyolefin Geosynthetics by High-Pressure Differential Scanning Calorimetry¹

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1. Scope

1.1 This test method covers a procedure for the determination of the oxidative induction time (OIT) of polyolefin geosynthetics using high pressure 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 This test method measures the oxidative induction time associated with a given test specimen at a specified temperature and pressure.

1.4 This is an accelerated test for highly stabilized materials. It is applicable only to material whose OIT values under 3.4 MPa of oxygen is greater than 30 min at 150°C.

1.5 The values stated in SI units are to be regarded as the standard. The values stated in parentheses are provided for information only.

1.6 *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 precautionary statements are given in Section 8.

2. Referenced Documents

2.1 ASTM Standards:

- D 3417 Test Method for Heats of Fusion and Crystallization of Polymers by Thermal Analysis²
- D 3895 Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry²
- D 4439 Terminology for Geosynthetics³
- D 4491 Test Methods for Water Permeability of Geotextiles by Permittivity³
- D 4565 Test Methods for Physical and Environmental Performance Properties of Insulations and Jackets for Telecommunications Wire and Cable⁴

¹ This test method is under the jurisdiction of ASTM Committee D-35 on Geosynthetics and is the direct responsibility of Subcommittee D35.02 on Endurance Properties.

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² Annual Book of ASTM Standards, Vol 08.02.

³ Annual Book of ASTM Standards, Vol 04.09.

⁴ Annual Book of ASTM Standards, Vol 10.02.

D 4703 Practice for Compression Molding Thermoplastic Materials into Test Specimens, Plaques, or Sheets⁵

E 473 Terminology Relating to Thermal Analysis⁶

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers⁶

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁶

G 88 Guide for Designing Systems for Oxygen Service⁶

3. Terminology

3.1 Definitions:

3.1.1 *differential scanning calorimetry (DSC), n*—a technique in which the difference in heat flow inputs into a substance and a reference material is measured as a function of temperature or time, while the substance and reference material are subjected to a controlled-temperature program. (See Terminology E 473.)

3.1.2 *geomembrane, n*—an essentially impermeable geosynthetic composed of one or more synthetic sheets. (See Terminology D 4439.)

3.1.2.1 *Discussion*—In this test method, essentially impermeable means that no measurable liquid flows through a geosynthetic when tested in accordance with Test Method D 4491.

3.1.3 *geosynthetic, n*—a planar product manufactured from polymeric material used with soil, rock, earth, or other geotechnical engineering-related material as an integral part of a man-made project, structure, or system. (See Terminology D 4439.)

3.1.4 *high-pressure differential scanning calorimetry (HP-DSC), n*—differential scanning calorimetry in which the substance and reference material are exposed to a controlled superambient atmosphere.

3.1.5 *index test, n*—a test procedure that may be used to establish an order for a set of specimens with respect to the property of interest.

3.1.6 *oxidative induction time (OIT), n*—the elapsed time between first exposure to an oxidizing gas and the onset to oxidation of a material under isothermal conditions.

3.1.6.1 *Discussion*—Oxidative induction time is an index

⁵ Annual Book of ASTM Standards, Vol 08.03.

⁶ Annual Book of ASTM Standards, Vol 14.02.

test parameter dependent upon a wide range of experimental conditions including temperature, pressure of oxygen, purge gas flow rate, and the presence or absence of catalysts.

4. Summary of Test Method

4.1 The specimen to be tested and the corresponding reference material are heated from room temperature at a constant rate in a non-purging, high-pressure oxygen environment at a defined pressure. When the specified temperature has been reached, the specimen is then held at that temperature until the oxidative reaction is displayed on the thermal curve. The OIT is the time interval from the start of the temperature program test to the onset of the oxidative reaction.

4.2 In this procedure, an elevated pressure of oxygen is used to accelerate the reaction and to reduce analysis time.

4.3 Unless otherwise specified, the temperature used in this test method shall be 150°C, and the chamber pressure is to be maintained at 3.4 MPa (500 psi) using a constant volume test condition.

5. Significance and Use

5.1 The oxidative induction time is a characteristic of a compounded polyolefin product that is dependent not only on the type and amount of additives present, but also on the type of resin. In well-behaved systems, this test method can be used as a quality control measure to monitor the stabilization in geosynthetics as received from a supplier.

5.2 When this test method is used to compare different geomembrane formulations containing different antioxidant packages, then those results shall be considered valid only at the temperature of test.

5.3 This test method is intended as an geosynthetic test. Use of the OIT value to estimate the lifetime of the geomembrane from which the test specimen is taken is not addressed nor shall it be used for this purpose.

5.3.1 The OIT measurement is an accelerated thermal aging test and, as such, interpretation of resulting data may be misleading if done by an inexperienced operator. Caution should be exercised in data interpretation since oxidation reaction kinetics are a function of temperature and the properties of the additives contained in the geosynthetic sample. For example, OIT values are often used to select optimum resin formulations. Certain antioxidants, however, may generate poor OIT results even though they may be adequate at their intended use temperature and vice versa.

5.4 This test method can be used for other purposes such as manufacturing control and research and development.

5.5 Oxidation induction time is strongly dependent upon test temperature and the partial pressure of oxygen. The higher the test temperature or the oxygen partial pressure, or both, the shorter the oxidation induction time.

5.5.1 The use of high test temperature, however, may have deleterious effects. The first of these is the potential volatilization of additive packages used to stabilize the test materials. The second is the potential for the influence of chemical mechanisms which are not significant at end-use operation conditions.

5.5.2 This test method uses high oxygen pressure to accelerate the test period while making use of lower test tempera-

tures to protect additive packages.

5.6 The results from this test method may or may not correlate with those obtained by other OIT measurements such as Test Method D 3895 or Test Methods D 4565.

6. Apparatus

6.1 *Differential Scanning Calorimeter*—Thermal analysis equipment capable of heating rates up to $20 \pm 1^\circ\text{C}/\text{min}$ and of automatically recording the differential heat flow between the test sample and a reference sample is necessary. The equipment must be capable of measuring sample temperature to $\pm 1^\circ\text{C}$ while maintaining a set temperature to $\pm 0.5^\circ\text{C}$.

NOTE 1—Modern computer-based instrumentation equipped with “iso-track” modes provide adequate specimen temperature control.

6.2 *Data Presentation Device*—A printer, plotter, recorder, or other recording output device capable of displaying heat flow on the Y-axis versus time on the X-axis as output signals from differential scanning calorimeters in 6.1.

6.3 *High-Pressure DSC Cell*—A unit capable of maintaining pressure up to 3.4 MPa (500 psig). The system shall be equipped with a pressure gage to monitor the internal pressure of the cell to permit manual release of pressure to maintain desired level.

NOTE 2—The gage shall be accurate to 2 % at 3.4 MPa (500 psig).

NOTE 3—All pressures in this test method are indicated relative to atmosphere pressure—that is, they are “gage” pressures.

6.4 *High-Pressure Oxygen Cylinder Regulator*—A pressure regulator capable of regulating a pressure up to 5.5 MPa (800 psi). The outlet of the cylinder is to be linked to the high-pressure cell using a *clean* stainless steel tube.

6.5 *Analytical Balance*, 0.1-mg sensitivity.

6.6 *Specimen Holders*, degreased aluminum pans, 6.0 to 7.0-mm diameter.

6.7 *Core Hole Borer*, cork borer or arch punch producing 6.3-mm (0.25-in.) disks.

7. Reagents and Materials

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

7.2 *Hexane or Acetone*, for cleaning specimen pans and stainless steel tubing, see 8.2 and 8.3.

7.3 *Indium (99.999 % Purity)*, for calibration purposes, see 9.1.

7.4 *Oxygen*, purity >99.5 % for the test atmosphere.

8. Precautions

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 stainless steel tube connecting the high-pressure cell to the oxygen cylinder must be thoroughly cleaned by hexane (or acetone) and then dried before being connected to the cell.

8.3 All specimen holders should be cleaned by washing with hexane (or acetone) and then drying before being used in the test.

8.4 The use of pressurized oxygen requires appropriate and careful handling procedures. The user of this test method shall

be familiar with the precautions described in Guide G 88.

9. Sampling

9.1 Using a bore hole cutter, cork borer, or punch, cut several 6.3-mm (0.25-in.) round specimen from the geosynthetic test sample.

9.2 Compression mold these assembled parts into a uniform plaque to a thickness of 0.25 mm (10 mil) (see Practice D 4703).

NOTE 4—The temperature at which molding takes place may be at or above the test temperature of this test method. Prolonged exposure to air at these temperatures may induce a negative bias into OIT measurement. Molding should be performed at as low a temperature and as quickly as possible to minimize this bias.

9.3 Cut test specimens from the plaque using a 6.3-mm (0.25-in.) bore hole cutter or punch.

10. Calibration

10.1 Using Test Method E 967, temperature calibrate the differential scanning calorimeter using indium metal and a heating rate of 1°C/min from 145 to 165°C.

10.1.1 Perform the calibration step at least once a month or whenever changes have occurred in the experimental setup.

11. Procedure

NOTE 5—Procedures for preparing the test specimen may be different for different polyolefin geosynthetic products, for example, geomembranes, geonets, geogrids, or geotextiles.

11.1 Prepare a specimen with a mass of 5 ± 1 mg.

11.2 Place the weighed specimen into the cleaned specimen pan.

11.3 Place the specimen and reference pans into the cell.

NOTE 6—Open pans are used in this test method.

11.4 Secure the top plate of the test chamber and tighten the cell system.

11.5 Operate and test under constant volume conditions according to the following procedure:

11.5.1 Close the pressure release valve and the inlet valve of the cell. Only the outlet valve is opened.

11.5.2 Adjust the pressure of the cylinder regulator to deliver 3.4-MPa (500-psi) test pressure. Other pressures may be used with the agreement of all parties concerned but must be reported. (See Note 8.)

11.5.3 Slowly open the inlet valve of the cell and allow oxygen to purge the cell for 2 min.

NOTE 7—Rapid pressurization may cause a temperature increase due to adiabatic compression (see Guide G 88). The user shall observe the temperature of the test specimen and adjust the pressurization rate so that a temperature rise of no more than 5°C is observed.

11.5.4 After 2 min, close the outlet valve, allow the cell to reach full pressure, then turn off the inlet valve. Also turn off the oxygen supplied from the cylinder.

11.6 Commence programmed heating of the specimen from ambient temperature to 150°C at a rate of 20°C/min. Zero time is taken at the initiation of the temperature program. Then hold the temperature isothermally at 150°C until the oxidative exothermic peak is detected. At the same time, the thermal

curve of the entire test is being recorded. Other test temperatures may be used, with the agreement of all parties concerned, but must be reported.

NOTE 8—150°C is the temperature typically used for polyethylene-based material and 170°C for polypropylene-based materials. If a temperature other than 150°C is selected, this OIT value must be greater than 30 min.

NOTE 9—The test temperature must be above the melting temperature of the polymer. The melting of the specimen may be observed as an endothermic response in the temperature program portion of the thermal curve (see Fig. 1).

NOTE 10—A slight gain in pressure at the beginning of the test is anticipated as the temperature of the cell increases. Decrease the pressure back to 3.4 MPa (500 psi) by slightly opening the pressure release valve.

NOTE 11—The time to onset of oxidation may be more than 900 min. For a first-time specimen, the isothermal time period of 1000 min is suggested.

11.7 Record the sample temperature 5 min after isothermal conditions have been reached.

NOTE 12—This value must be $150 \pm 0.5^\circ\text{C}$ for the test to be valid.

11.8 Terminate the test after the oxidative exothermic peak has passed through its maximum value.

11.9 After the test is completed, *slowly* release the pressure by gradually opening the pressure release valve.

NOTE 13—It usually takes 30 to 60 s to completely release the pressure.

11.10 Clean the instrument cell by thermal desorption after every three to four tests to remove any accumulated organic matter so as to ensure safe operation.

NOTE 14—The DSC cell should be cleaned by holding the cell at a temperature of 400°C for 3 min under air or oxygen atmosphere.

12. Analysis Response

12.1 Plot the data with the heat flow signal on the y-axis, versus time on the x-axis.

12.2 Determine the value for OIT in the following manner:

12.2.1 Plot data with a y-axis sensitivity sufficient to show the full oxidative exotherm. A full-scale sensitivity of 5 W/g is usually adequate.

12.2.2 Extend the horizontal baseline generated prior to the onset to oxidation.

NOTE 15—For the oxidation exotherm containing a small shoulder peak at the beginning of oxidation, a sigmoidal baseline may be more appropriate than the straight baseline.

12.2.3 Draw a tangent at the inflection point of the exothermic peak and extend this tangent to intersect with the baseline.

12.2.4 The time at the intersection, measured from the initiation of the temperature program from ambient temperature is the onset of oxidative degradation and is taken as the OIT value.

12.2.5 Measure the OIT as shown in Fig. 1.

12.3 Report individual values and their mean for duplicate determinations as OIT.

13. Report

13.1 Report the following information,

13.1.1 Identification of the specimen,

NOTE 16—This test method is not valid for OIT values less than 30 min.

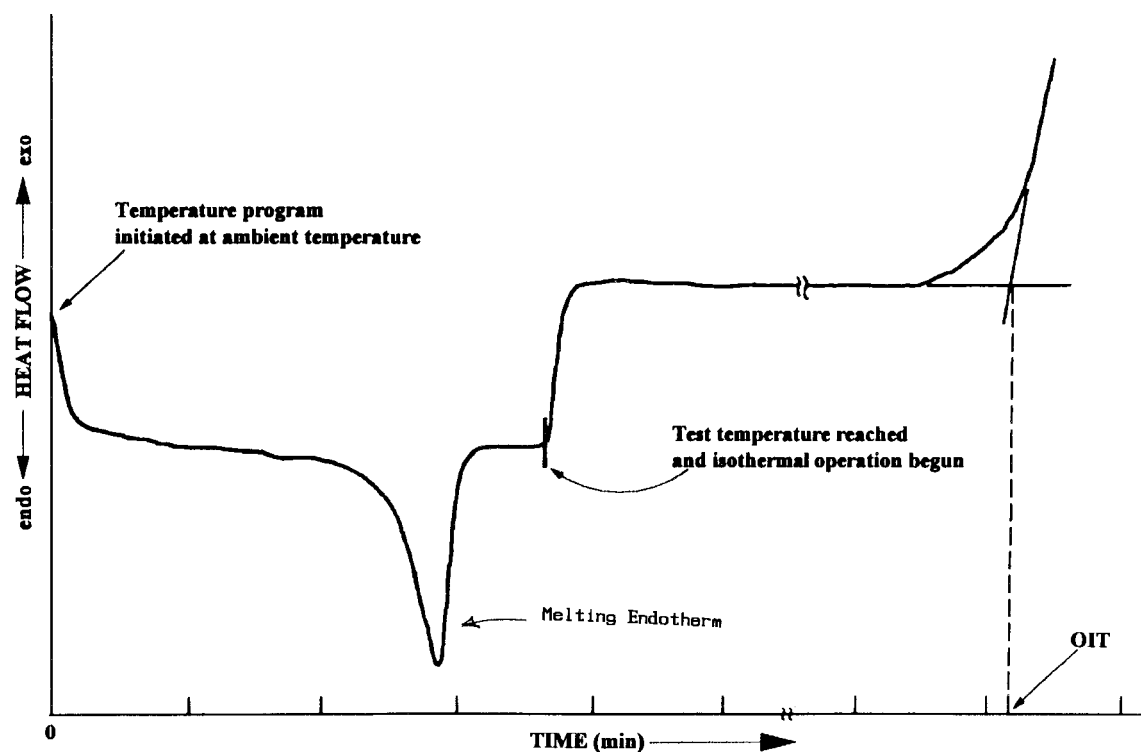


FIG. 1 Testing Temperature Curve

Should OIT values of less than 30 min be obtained, Test Method D 3895 is recommended.

- 13.1.2 Mass and configuration of the test specimen,
- 13.1.3 Method of conditioning the test specimen if different from that specified herein,
- 13.1.4 The mean value of duplicate OIT determinations,
- 13.1.5 The recorded temperature of the isothermal portion of the thermal curve, and
- 13.1.6 The recorded pressure of oxygen during the isothermal portion of the thermal curve.

14. Precision and Bias

14.1 An interlaboratory study using this test method was conducted in 1995-1996 using two polyethylene samples that were not geosynthetic materials. Following temperature calibration with indium, each of six laboratories tested the two test specimens with four replications. Instruments from a single manufacturer was employed. The results were treated by Practice E 691.⁷

NOTE 17—The instruments supplied by TA Instruments,⁸ were used in this interlaboratory test. While attempts were made to include apparatus from other suppliers, only laboratories with equipment supplied by this vendor were willing to participate in the interlaboratory study. Other vendors may supply apparatus suitable for use in this test method. Their use is permitted provided performance is shown to be consistent with the repeatability and reproducibility described in this section.

14.2 Precision:

14.2.1 For polyethylene, two values, each the mean of duplicate determinations, should be considered suspect if they differ by more than:

$$r = 95 \% \text{ repeatability limit (within laboratory) } = 6.5 \%$$

$$R = 95 \% \text{ reproducibility limit (between laboratories) } = 25 \%$$

14.2.2 The respective standard deviations among test results, related to the above values by the factor of 2.8 are:

$$S_r = \text{repeatability standard deviation} = 2.3 \%$$

$$S_R = \text{reproducibility standard deviation} = 9.1 \%$$

14.3 Bias—The OIT measurement is an index test for which no standard reference materials are available.

14.3.1 A polyethylene sample, characterized with this standard performed at 150°C and 3.4 MPa (500 psig) oxygen pressure, yielded a mean OIT value of 231 min with a repeatability standard deviation of 5.7 min (2.5 %) and a reproducibility standard deviation of 18 min (7.6 %).

14.3.2 The same polyethylene sample was also tested in 1993 by section 17 of Test Method D 4565 performed at 200°C and 10 kPa (15 psia) oxygen pressure, conditions different than those used in this test method. In that test, the mean was 31.4 min, with a repeatability standard deviation of 1.6 min (5.1 %) and a reproducibility standard deviation of 3.1 min (9.8 %).⁹

⁷ Supporting data have been filed at ASTM Headquarters. Request RR:D35-1003.

⁸ TA Instruments, 109 Lukens Drive, New Castle, DE 19720.

⁹ Supporting data have been filed at ASTM Headquarters. Request RR:D09-1034.

15. Keywords

15.1 differential scanning calorimetry; geogrid; geomembrane; geonets; geopipes; geosynthetics; geotextiles; oxidation; polyethylene; polyolefins; polypropylene

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