

Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation¹

This standard is issued under the fixed designation D 6954; 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 guide provides a framework or road map to compare and rank the controlled laboratory rates of degradation and degree of physical property losses of polymers by thermal and photooxidation processes as well as the biodegradation and ecological impacts in defined applications and disposal environments after degradation. Disposal environments range from exposure in soil, landfill, and compost in which thermal oxidation may occur and land cover and agricultural use in which photooxidation may also occur.

1.2 In this guide, established ASTM International standards are used in three tiers for accelerating and measuring the loss in properties and molecular weight by both thermal and photooxidation processes and other abiotic processes (Tier 1), measuring biodegradation (Tier 2), and assessing ecological impact of the products from these processes (Tier 3).

1.3 The Tier 1 conditions selected for thermal oxidation and photooxidation accelerate the degradation likely to occur in a chosen application and disposal environment. The conditions should include a range of humidity or water concentrations based on the application and disposal environment in mind. The measured rate of degradation at typical oxidation temperatures is required to compare and rank the polymers being evaluated in that chosen application to reach a molecular weight that constitutes a demonstrable biodegradable residue (using ASTM International biometer tests for CO₂ evolution appropriate to the chosen environment). By way of example, accelerated oxidation data must be obtained at temperatures and humidity ranges typical in that chosen application and disposal environment, for example, in soil (20 to 30°C), landfill (20 to 35°C), and composting facilities (30 to 65°C). For applications in soils, local temperatures and humidity ranges

must be considered as they vary widely with geography. At least one temperature must be reasonably close to the end use or disposal temperature, but under no circumstances should this be more than 20°C away from the removed that temperature. It must also be established that the polymer does not undergo a phase change, such as glass transition temperature (T_g) within the temperature range of testing.

1.4 The residues resulting from the oxidations are then exposed to appropriate disposal or use environments in standard biometric test methods to measure the rate and degree of biodegradation (Tier 2).

1.5 The data generated under Tier 1 evaluation and the determined time for the biodegradation in the chosen environment (Tier 2) allow ranking relative to other polymers evaluated under similar environmental conditions with this guide. The degree and time for biodegradation should be consistent with ASTM International methods, and any residues from the intermediate oxidation stage and from biodegradation must be shown to be environmentally benign and not persistent (Tier 3).

NOTE 1—The intended use of this guide is for comparison and ranking of data to aid in the design and development and the reduction of environmental impacts of polymers that require no more than 24 months to oxidize and biodegrade in the intended use and disposal options and create no harmful or persistent residues under the appropriate disposal conditions (for example, two seasons of crop-growing conditions in soil).

1.6 It is cautioned that the results of any laboratory exposure in this guide cannot be directly extrapolated to actual disposal environments; confirmation to real world exposure is ultimately required as with all ASTM International standards.

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

NOTE 2—There is no ISO standard that is the equivalent of this standard guide. Note this changed all subsequent Note numbers.

¹ This guide is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.96 on Biodegradable Plastics and Biobased Products.

Current edition approved May 1, 2004. Published May 2004.

1.8 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 requirements prior to use.

2. Referenced Documents

2.1 ASTM Standards:²

- D 883 Terminology Relating to Plastics
- D 3826 Practice for Determining Degradation End Point in Degradable Polyethylene and Polypropylene Using a Tensile Test
- D 3987 Test Method for Shake Extraction of Solid Waste with Water
- D 5071 Practice for Exposure of Photodegradable Plastics in a Xenon Arc Apparatus
- D 5208 Practice for Fluorescent Ultraviolet (UV) Exposure of Photodegradable Plastics
- D 5272 Practice for Outdoor Exposure Testing of Photodegradable Plastics
- D 5338 Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions
- D 5510 Practice for Heat Aging of Oxidatively Degradable Plastics
- D 5526 Test Method for Determining Anaerobic Degradation of Plastic Materials Under Accelerated Landfill Conditions
- D 5951 Practice for Preparing Residual Solids Obtained after Biodegradability Standard Methods for Plastics in Solid Waste for Toxicity and Compost Quality Testing
- D 5988 Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials after Composting
- D 6002 Guide for Assessing the Compostability of Environmentally Degradable Plastics
- D 6400 Specification for Compostable Plastics
- E 1440 Guide for an Acute Toxicity Test with the Rotifer *Brachionus*

2.2 Other Standards:

- EPA TITLE 40 CFA 40CFR62, 40CFR50-189, 40CFR260-299, 40CFR300-399, 700-799, and 49CFR100-180³
- OECD Guideline 207 Earthworm, Acute Toxicity Tests⁴
- OECD Guideline 208 Terrestrial Plants, Growth Test⁴
- ORCA Guidelines for the Evaluation of Feedstock for Source Separated Biowaste Composting and Biogasification⁵

3. Terminology

3.1 Definitions:

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.

³ Available from United States Environmental Protection Association (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460.

⁴ Available from OECD, 2 rue Andre Pascal, F-75775 Paris Cedex 16, France.

⁵ Available from ORCA, Avenue E. Mounier 83, Box 1, Brussels, Belgium B-1200.

3.1.1 Definitions of most terms applicable to this guide appear in Terminology D 883 and Guide D 6002.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *environmental degradation of a plastic*, *n*—abiotic or biotic degradation process or both that occurs in a given environment and includes photodegradation, oxidation, hydrolysis, and biodegradation. Living organisms effect biotic degradation processes and abiotic degradation processes are nonbiological in nature.

3.2.1.1 *Discussion*—Term not defined in Terminology D 883.

3.2.2 *gels*, *n*—cross-linked polymer structures insoluble in solvents that do not break the primary or cross-linking bonds in the polymer. Cross-links created during oxobiodegradation of polymers are chemical bonds created by the degradation process, mostly carbon-carbon bonds, and thus extremely resistant to solvent degradation.⁶

3.2.3 *oxidation*, *n*—process promoted thermally or by irradiation in the presence of oxygen.

4. Summary of Guide

4.1 This guide may be used to compare and rank the rate and degree of thermal oxidative degradation of a plastic material relatively to a molecular weight range that can be established as biodegradable in a chosen environment. Subsequently, the biodegradation of these degraded polymers in diverse environments such as soil, compost, landfill, and water may be compared and ranked using standard biometric test methods and measuring carbon dioxide evolution.

NOTE 3—If composting is the designated disposal route, Specification D 6400 is the only ultimate and definitive applicable specification for measuring biodegradation or compostability. Oxidation followed by biodegradation under the conditions found in this guide does not confer the designation “compostable” or any connotation that the applications are acceptable for composting in a commercial or municipal composting facility.

4.2 This guide uses a tiered criteria-based approach to assess the consecutive oxidation and biodegradability of plastic products and ecological impacts in defined applications. This is shown schematically in Section 6. Each tier in this guide includes objectives and a summary that presents test methods, method principles, test duration, and interpretation of results.

4.3 The tiered approach is chosen in the laboratory for convenient separation of oxidative degradation, biodegradation, and ecological impact stages even though in the real world all three are likely to be concurrent rather than consecutive.

4.4 Tiered Methodology:

4.4.1 Tier 1 measures the rate and extent of molecular weight loss resulting from oxidation that is indicative of losses in physical properties from oxidation. Tier 1 requires either accelerated testing or long-term testing over a range of relative humidity or amount of moisture. Accelerated testing must be performed under conditions and temperatures that are acceptably typical of the specific application and disposal environments under consideration. Practices D 5208, D 5510, and

⁶ Vollmert, B., *Polymer Chemistry*, Springer-Verlag, New York, 1973, p. 27, also pp. 543–561.

D 5071 may be used to specify the oxidative conditions and Practice D 3826 may be used to define the point of embrittlement.

NOTE 4—For measuring the extent of disintegration/fragmentation, a sieve test is required. In this tier, the fragments are subjected to molecular weight analysis and a total mass balance is obtained in the process. Exposure temperatures may range from 20 to 70°C in the presence of air and specified moisture or water levels for selected periods of time. At least one temperature must be reasonably close to the end use or disposal temperature, but under no circumstances should this be more than 20°C away from that temperature. It must also be established that the polymer does not undergo a phase change, such as glass transition temperature (T_g) within the temperature range of testing. As an alternate degradation process, the test samples may be exposed to photooxidation in air as per Practices D 5208 or D 5071 and the mass change of the plastic recorded after exposure.

4.4.2 Tier 1 accelerated oxidation tests are not indicators of biodegradability and should not be used for the purpose of meeting the specifications as described in Specification D 6400 and claiming compostability or biodegradation during composting. (If oxidation is thought to be sufficiently rapid in Tier 1, suggesting that composting may be a disposal environment, then Specification D 6400 must be done and all the specifications in Section 6 (Detailed Requirements) must be met.

4.5 Gel Formation and Consequences During Oxidation Phase—Discussion:

4.5.1 Gel formation is a frequent side reaction of the oxidative degradation of polymers, especially polyolefins. Gels are cross-linked structures arising from the free radical nature of oxidative degradation. They are insoluble in nonreactive solvents, that is, solvents that do not break additional bonds. Normally, gels are not available to biodegradation. Some gels dissolve on further oxidative degradation and become available for ultimate biodegradation. However, the prooxidant (catalyst) may be excluded from the gel structure because of solubility changes in gel phase. In this case, the gel would become a nondegradable or very slowly degradable new fraction within the polymer. It is important to establish the extent of gel and its nature or permanence in the polymer residue and report these findings.

4.5.2 The purpose of Tier 2 is to estimate the biodegradability of all the fragmented products from Tier 1 under laboratory scale conditions appropriate to the application using current Test Methods D 5988 and D 5338. The entire material from the Tier 1 exposure is subjected to biodegradation testing. The percent biodegradation shall be calculated and reported as stated in the above referenced standards. The results from Tier 1 and Tier 2 shall be combined and used for comparison and ranking purposes between polymers of interest.

4.5.3 Tier 3 involves considerations of the ecological impacts in the final disposal medium such as soil, as in all biodegradation testing methods, which is basically a comparison of the test medium before and following oxidation and biodegradation.

5. Significance and Use

5.1 This guide is a sequential assembly of extant but unconnected standard tests and practices for the oxidation and biodegradation of plastics, which will permit the comparison

and ranking of the overall rate of environmental degradation of plastics that require thermal or photooxidation to initiate degradation. Each degradation stage is independently evaluated to allow a combined evaluation of a polymer's environmental performance under a controlled laboratory setting. This enables a laboratory assessment of its disposal performance in, soil, compost, landfill, and water and for use in agricultural products such as mulch film without detriment to that particular environment.

NOTE 5—For determining biodegradation rates under composting conditions, Specification D 6400 is to be used, including test methods and conditions as specified.

5.2 The correlation of results from this guide to actual disposal environments (for example, agricultural mulch films, composting, or landfill applications) has not been determined, and as such, the results should be used only for comparative and ranking purposes.

5.3 The results of laboratory exposure cannot be directly extrapolated to estimate absolute rate of deterioration by the environment because the acceleration factor is material dependent and can be significantly different for each material and for different formulations of the same material. However, exposure of a similar material of known outdoor performance, a control, at the same time as the test specimens allows comparison of the durability relative to that of the control under the test conditions.

6. Procedures

6.1 Test sample selected to be in the thickness of the application form.

6.2 The tier testing procedure is outlined schematically in Fig. 1.

6.3 In Tier 1, the test sample is exposed to several discrete temperatures (one being within 20°C of the end use temperature) within the range of 20 to 70°C in the presence of specified levels of air and specified moisture or water levels for defined periods of time using the procedure apparatus and following the calculations in Practice D 5510. The temperature ranges specified in Practice D 5510, paragraphs 8.3.1 and 8.3.4 are not germane to this guide and need not be followed. For thin films, the exposure period would be the time required for the film to reach 5 % or less elongation to break (Practice D 3826) and the fragmented film to reach a recorded average weight-average molecular weight (MW) of 5000 or less. The time at three different temperatures required (with the mentioned caveats) for molecular weight reduction should be established.

6.3.1 A sample from Tier 1 residue should be dissolved in an appropriate nonreactive solvent and the gel phase, if any, separated by filtration, the gel dried, and the amount of gel reported as weight fraction of total sample. This should be regarded as nondegradable fraction of polymer.

6.3.2 The gel may be subjected to further oxidative degradation and extent of subsequent reversion to soluble and degradable material reported.

6.3.3 The acceptable amount of gel will depend on the particular application and the maximum acceptable wt % gel written into specifications for the particular class of end uses.

NOTE 6—As a general guide, less than 5 % wt gel would seem

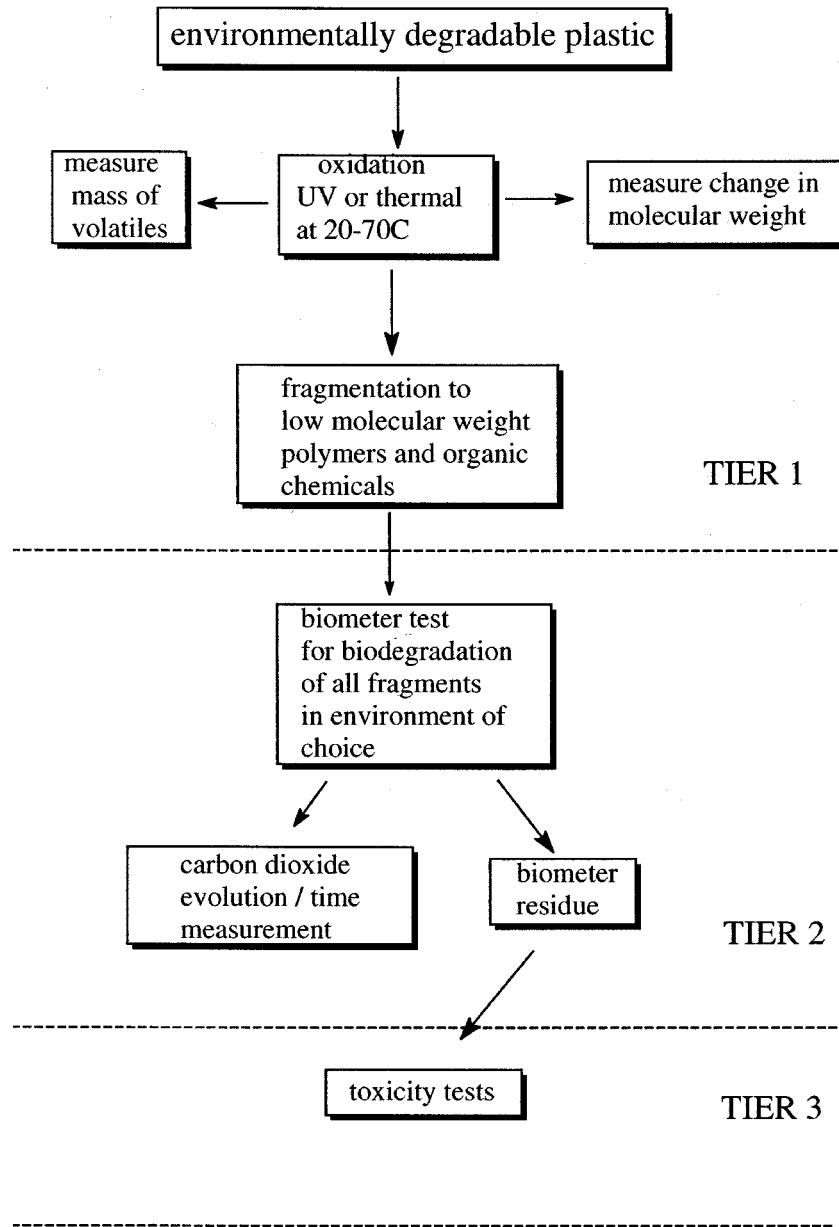


FIG. 1 Flow Schematic of the Guide

acceptable (an amount chosen without scientific basis). Clearly, very large amounts of gel, say 30 % or more, would prevent the system from reaching 60 % CO_2 evolution. However, intermediate amounts, for example, a residue with 20 % gel, could exhibit an overall 60 % by generating in excess of 80 % CO_2 from the linear fragments and the gel fraction showing no CO_2 evolution.

6.4 In Tier 1, the loss in weight of the sample is measured. The molecular weight and polydispersity index or tensile elongation (Practice D 3826) of the samples before and after the exposure should be determined and recorded, along with % gel.

6.5 All of the fragment residues from Tier 1 should be collected and subjected to Tier 2 testing for rate and degree of biodegradation in the chosen use or disposal environment.

6.6 In Tier 2, after the test samples are exposed to the abiotic degradation process described in Tier 1, the entire test material should be subjected to biodegradation tests as per ASTM International test methods for appropriate environments, Test Methods D 5988, D 5338, and D 5526. The time profile of carbon dioxide evolution is recorded and the time to reach the appropriate thresholds are noted.

6.6.1 For products consisting of a single polymer (homopolymers or random copolymers), 60 % of the organic carbon must be converted to carbon dioxide before ending the test, and the gel content generated in Tier 1 must be no higher than 10 %.

NOTE 7—Testing may be continued to determine better the length of time the materials will take to biodegrade.

6.6.2 For products consisting of more than one polymer (block copolymers, segmented copolymers, blends, or addition of low molecular weight additives), 90 % of the organic carbon must be converted to carbon dioxide, before ending the test.

6.6.3 Alternately, a 90 % CO₂ evolution end point can be used to demonstrate that excessive amounts of gel have not been formed.

6.7 Tier 3 is endpoint specific in that it is focused on postdegradation analysis after completion of Tier 2 testing.

6.8 Standard methods for determining the biodegradation of plastics simulating solid waste treatment systems have been developed. In addition to the rate and degree of biodegradation, the impact of the biologically decomposed plastics on the quality of the compost, soil, and water is important, in particular with regard to any toxicity that the residual plastics may exhibit in the final end product, soil, or water. Therefore, the effects of residual plastics on toxicity need to be measured as well as the impact on the soil quality to evaluate the safety of biological aerobic or anaerobic degradation.

6.9 Test Method D 5951 provides a guide for preparing residual solids from tests simulating conditions of solid material degradation for subsequent toxicity following biodegradation or compost testing. A summary of that preparation follows:

6.9.1 After biodegradation in the chosen environment, remove residual solids and mix the contents of each replicate vessel carefully. Continue mixing until the contents are mixed thoroughly. The resulting homogeneous mixture should have a uniform moisture content and appearance. Repeat the same procedure for positive reference and blank replicates.

6.9.2 Three subsamples are taken from the homogeneous mixture on which the dry solids are determined in accordance with APHA method 2540E.⁷

6.9.3 The rest of the mixture is dried at a temperature of 20 to 45°C until a dry solids content of 65 ± 2 % is reached. The dry solids content is determined after drying.

6.9.4 The dried mixtures can be stored for a maximum of four weeks at 4°C. The mixtures should be opened on a weekly basis to prevent slow accumulation of acids in the mixtures as a result of anaerobic conditions.

6.9.5 For the terrestrial toxicity tests and the determination of further biodegradation of the plastic materials in the soil, the final dried mixture at 65 % dry solids is used as is. For the aquatic toxicity tests, an extraction is performed in accordance with Test Method D 3987.

6.9.6 Several methods have been developed for the determination of toxicological effects. A distinction can be made

between aquatic toxicity tests and terrestrial toxicity tests. The following terrestrial and aquatic ecotoxicity tests are suggested for obtaining evidence regarding product effects on plant and animal life. In addition, compliance with respective national, state, and local regulatory requirements is also required. Soil or aquatic test material must be evaluated before and following oxobio-degradation testing in Tier 2; heavy metals or other substances of concern must be determined directly on test material before degradation in order to verify that their concentration is within acceptable limits based on the Environmental Protection Agency (EPA) toxic materials list listed in 40CFR62, 40CFR150-189, 40CFR260-299, 40CFR300-399, 700-799, or 49CFR100-180. Finally, the soil or aquatic test material must be evaluated before and following oxobio-degradation testing for greater than two units of pH or greater than 30 % shift in the ability of the soil to hold and percolate water.

6.9.7 Aquatic toxicity test with *Rotifer brachionus* in accordance with Guide E 1440. The test duration is one day.

6.9.8 *Plant Germination*—The potential effect of materials on plant germination may be assessed with the cress seed test. This step may be especially valuable for screening processing additives used at 1 % or less in the plastic. Soils from the above soil biodegradation testing may be evaluated at the beginning and end of the test to establish the potential effect of microbial degradation products. In the cress test, soil is extracted with water and filtered. The supernatant is used for the germination test. Various dilutions of the supernatant are prepared, and aliquots are added to petri dishes lined with filter paper. Cress seeds are placed on the wet paper and left to germinate in the dark over four days at room temperature. The percentage of germinated seeds is determined after four days and compared to a water control. Soils containing test materials should not be significantly different from the blank soil at 95 % confidence interval.

6.9.9 *Plant Growth Test as Described by OECD Guideline 208*—This procedure determines phytotoxicity by mixing the compost containing the material with soil. The plant emergence survival and growth is evaluated. Three plant species are generally tested. The test duration is approximately one month. The results from the biodegraded test soil material are compared to a soil control.

6.9.10 *Earthworm Test in Accordance with OECD Guideline 207*—This procedure determines possible toxicity by mixing the biodegraded material with a specified soil. The earthworm weight change and survival are measured. The results from test soil containing material are compared to soil controls.

7. Report

7.1 The reporting section must clearly and objectively include the proposed real world applications and disposal environments for which the plastic is being developed with indicated exposure and lifetime expectancies.

7.2 *Tier 1*—The report must identify the following:

7.2.1 Resin grade plus the commercial name of the formulation additive or percent of catalyst concentrations.

NOTE 8—Identification of test samples needs to be sufficient to inform

⁷ Method 2540E in *Standard Methods for the Examination of Water and Wastewater*, 19th edition, American Public Health Association, 800 I St., NW, Washington, DC 20001.

readers of the commercial identification of the formulation and of the additives and their availability in the marketplace.

7.2.2 The proposed disposal medium or media for the plastic must be indicated with anticipated life expectancy noted.

7.2.3 The exposure conditions such as temperature, time, moisture, and oxygen concentrations need to be reported.

7.2.4 The exposure conditions and time of exposure (kJ/m²·nm at 340 nm) to radiation, if used, must be recorded.

7.2.5 Molecular weight and polydispersity index, tensile elongation, and percentage of gels of the samples before and after the indicated time for abiotic test exposure should be reported.

7.2.6 Complete mass balances are to be reported.

7.3 *Tier 2*—The report must state the following:

7.3.1 Extent of biodegradation (carbon dioxide evolution profile to plateau as per standards) and expressed as a percentage of total theoretical carbon balance.

7.3.2 Percentage of gel or other nondegradable fractions.

7.3.3 Volatiles produced by the oxidation process.

7.3.4 Temperature and moisture conditions.

7.3.5 Additions of inoculants and moisture and their timing and any additional mixing procedures.

7.4 Resulting data from Tier 1 combined with data from Tier 2 for comparison and ranking of polymers under test.

7.5 *Tier 3*—The report shall include the following:

7.5.1 Detailed description of preparation of material for testing.

7.5.2 Specific testing performed as described in 6.9 with particular emphasis on any deleterious effects of the soil or aquatic additive.

7.5.3 Regulated metal concentrations, pH, and ability to hold and percolate water before and following oxobiodegradation testing.

8. Keywords

8.1 biodegradation; ecotoxicity; environmental degradation; oxidation; photooxidation; thermal

BIBLIOGRAPHY

- (1) Arnaud, R., Dabin, P., Lemaire, J., Al-Malaika, S., Chohan, S., et al, "Photodegradation and Biodegradation of Commercial Photodegradable Polyethylenes," *Polym. Degrad. Stab.*, Vol 46, 1994, pp. 211-224.
- (2) Chiellini, E., Corti, A., and Swift, G., "Biodegradation of Thermally-Oxidized Fragmented LDPE Samples," *Polym. Degrad. Stab.*, Vol 81, 2003, pp. 341-351.
- (3) Grassie, N. and Scott, G., *Polymer Degradation and Stabilization*, Cambridge University Press, Cambridge, 1985.
- (4) Jakubowicz, I., "Evaluation of Degradability of Biodegradable Polyethylene," *Polym. Degrad. Stab.*, Vol 80, 2003, pp. 39-43.
- (5) Schuurmann, G. and Market, B., *Ecotoxicology—Ecological Fundamentals, Chemical Exposure, and Biological Effects*, ISBN 0-471-17644-3, John Wiley and Sons, New York, 1998.
- (6) Scott, G., "Abiotic Control of Polymer Biodegradation," *Trends in Polymer Science*, Vol 5, 1997, pp. 361-368.
- (7) Scott, G., *Atmospheric Oxidation and Antioxidants*, Elsevier, Amsterdam, 1965.
- (8) Scott, G. and Gilead, D., Eds., *Degradable Polymers: Principles and Applications*, 1st Edition, Chapman and Hall, London, 1995.
- (9) Scott, G., Ed., *Degradable Polymers: Principles and Applications*, 2nd Edition, Kluwer Academic Publishers, Dordrecht, 2002.
- (10) Stevens, E., *Green Plastics: An Introduction to the New Science of Biodegradable Plastics*, Princeton University Press, Princeton, NJ, November 2001.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).