Designation: E2550 – 11

Standard Test Method for Thermal Stability by Thermogravimetry[1]

1. Scope

1.1 This test method covers the assessment of material thermal stability through the determination of the temperature at which the materials start to decompose or react and the extent of the mass change using thermogravimetry. The test method uses minimum quantities of material and is applicable over the temperature range from ambient to 800°C.

1.2 The absence of reaction or decomposition is used as an indication of thermal stability in this test method under the experimental conditions used.

1.3 This test method may be performed on solids or liquids, which do not sublime or vaporize in the temperature range of interest.

1.4 This test method shall not be used by itself to establish a safe operating or storage temperature. It may be used in conjunction with other test methods (for example, E487, E537 and E1981) as part of a hazard analysis of a material.

1.5 This test method is normally applicable to reaction or decomposition occurring in the range from room temperature to 800 °C. The temperature range may be extended depending on the instrumentation used.

1.6 This test method may be performed in an inert, a reactive or self-generated atmosphere.

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 There is no ISO standard equivalent to this test method.

1.9 *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. This standard may involve hazardous materials, operations, and equipment.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E473 Terminology Relating to Thermal Analysis and Rheology
E487 Test Method for Constant-Temperature Stability of Chemical Materials
E537 Test Method for The Thermal Stability of Chemicals by Differential Scanning Calorimetry
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E1142 Terminology Relating to Thermophysical Properties
E1445 Terminology Relating to Hazard Potential of Chemicals
E1582 Practice for Calibration of Temperature Scale for Thermogravimetry
E1981 Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry
E2040 Test Method for Mass Scale Calibration of Thermogravimetric Analyzers

3. Terminology

3.1 *Definitions:*

3.1.1 Specific technical terms used in this test method are defined in Terminologies E473, E1142 and E1445. These terms include thermogravimetry (TG), thermogravimetric analysis (TGA), thermal stability, onset temperature (T_o), derivative, and TG curve.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *DTG curve, n*—a plot of the first derivative of TG data with respect to temperature or time.

3.2.2 *mass change plateau, n*—a region of the TG curve with a relatively constant mass; it is accompanied by a minimum in the DTG curve for a mass loss, or a maximum for a mass gain.

4. Summary of Test Method

4.1 A sample of the material to be examined is placed in an inert container and then heated at a controlled rate of 1 to 20°C

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[1] This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Calorimetry and Mass Loss.

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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.

min^{-1} under a controlled atmosphere. The sample mass is recorded continuously as a function of time and temperature.

4.2 When the sample undergoes a reaction or thermal decomposition involving a mass change, that change is indicated by a departure from the initially established baseline of the mass record (see Fig. 1).

4.3 The onset temperature and mass changes are determined and reported.

5. Significance and Use

5.1 TG provides a rapid method for determining the thermal decomposition and reaction mass change of a material.

5.2 This test method is useful in detecting potentially hazardous reactions and in estimating the temperatures at which these reactions occur. This test method is recommended as a screening test for detecting the thermal hazards of an uncharacterized material or mixture (see Section 8).

5.3 Energetic materials, pharmaceuticals and polymers are examples of materials for which this test might be useful. This test is especially useful for materials having melting points that overlap with the onset of reaction or decomposition.

NOTE 1—In Differential Scanning Calorimetry (DSC), the melting endotherm may interfere with the determination of the onset temperature for reaction or decomposition.

5.4 This test is not suitable for materials that sublime or vaporize in the temperature range of interest. A sample with volatile impurities needs to be purified prior to the TGA testing. Alternatively, the sample can be tested as is, however, special caution is required during the data analysis. The mass loss due to the loss of impurity should not interfere with the determination of reaction or decomposition temperature.

5.5 The four significant criteria of this test method are: the detection of a sample mass change; the extent of the mass change; the approximate temperature at which the event occurs; the observance of effects due to the atmosphere.

6. Limitations

6.1 Many environmental factors affect the existence, magnitude and onset temperature of a particular reaction or decomposition. Some of these, including heating rate, instrumental sensitivity, and atmosphere reactivity, will affect the detectability of a reaction or decomposition using this procedure. Therefore, it is imperative that the results obtained from the application of this test method be viewed only as an indication of the thermal stability of a material.

6.2 This test method can only be used to detect reaction or decomposition that involves a mass change, such as a production of gaseous species or a mass gain in reactive atmosphere. This test method is not suitable for materials that sublime or vaporize in the temperature of interest.

6.3 This test method may not be reliable for heterogeneous samples.

NOTE 2—For heterogeneous samples, it is recommended to perform replicate measurements to determine the variability of the results. If inconsistent results are obtained, the study should be carried out using larger-scale apparatus, such as accelerating rate calorimetry.

7. Apparatus

7.1 *Thermogravimetric Analyzer (TGA)*—The essential instrumentation required to provide the minimum thermogravimetric analytical capability for this practice includes:

7.1.1 A thermobalance composed of:

7.1.1.1 A furnace to provide uniform controlled heating of a specimen to a constant temperature or at a constant rate within the applicable temperature range of this test method.

7.1.1.2 A temperature sensor to provide an indication of the specimen/furnace temperature to ±0.1°C.

7.1.1.3 A continuously recording balance to measure the specimen mass with a minimum capacity of 10 mg and a sensitivity of ±10 µg.

NOTE 3—An apparatus with a larger capacity can also be used. The sensitivity must be at least ±0.1 mass %.

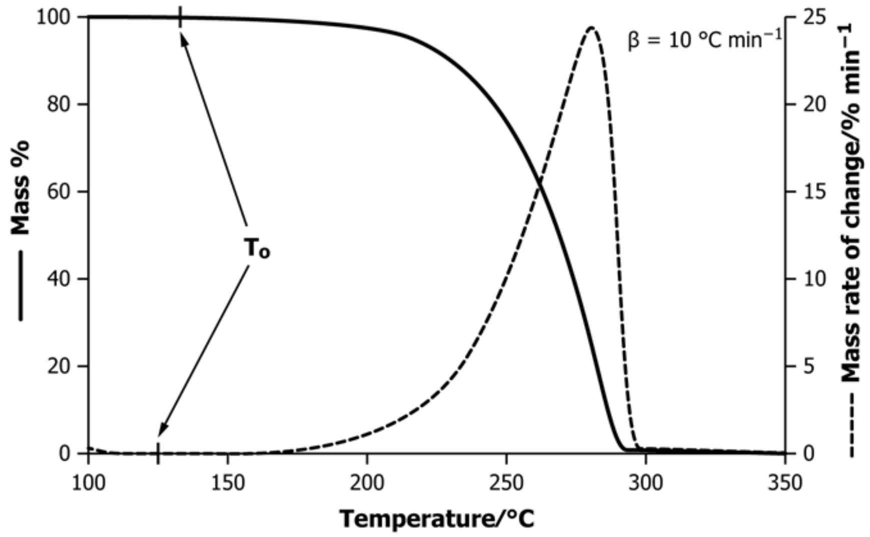

FIG. 1 Typical TG and DTG Curves

7.1.1.4 A means of maintaining the specimen/container under atmospheric control of an inert or reactive gas of 99.9+ % purity at a purge rate of 20 to 100 ±5 mL min^{-1}.

NOTE 4—Purge rate may vary depending on the instrument used. Excessive purge rates should be avoided as this may introduce interferences due to turbulence effects and temperature gradients.

NOTE 5—Experiments can also be performed in a self generated atmosphere. DSC sealed containers with a pinhole of 0.025 to 0.38 mm diameter have been shown to establish saturation of a gaseous self generated atmosphere.[3]

7.1.2 A temperature controller capable of executing a specific temperature program by operating the furnace between selected temperature limits at a rate of temperature change between 1 and 20°C min^{-1} to within ±0.1°C min^{-1}.

7.1.3 A recording device capable of recording and displaying on the Y-axis any fraction of the specimen mass signal (TGA curve) including the signal noise as a function of any fraction of the temperature (or time) signal on the X-axis including the signal noise.

7.1.4 Containers (pans, crucibles, etc.) that are inert to the specimen and that will remain gravimetrically stable within the temperature limits of this test method.

NOTE 6—For experiments in a self generated atmosphere, DSC sealed containers with pinhole of 0.025 to 0.38 mm diameter can be used.

7.2 Auxiliary equipment necessary or useful in conducting this test method includes:

7.2.1 A balance with a capacity of 100 mg or more to weigh specimens or containers, or both, to ±0.1 mg.

7.2.2 Device to encapsulate the specimen in DSC sealable containers for self-generated atmosphere studies.

8. Safety Precautions

8.1 The use of this test method as an initial test for material whose potential hazards are unknown requires that precautions be taken during the sample preparation and testing.

8.2 Larger specimens (>5 mg) should be used only after consideration is given to the potential for hazardous reaction(s). For energetic material or materials whose characteristics are unknown, it is safest to start with a specimen mass of no more than 1 mg and a lower heating rate (1 to 10°C min^{-1}).

8.3 When particle size reduction by grinding is necessary, the user of the test method shall presume that the material is sensitive to stimuli such as friction and electrostatic discharge. Accordingly, appropriate tests shall be conducted on those materials prior to grinding. Use of suitable protective equipment is always recommended when preparing materials of unknown hazard. If a Material Safety Data Sheet is available, it shall be acquired and studied prior to handling unknown materials.

8.4 Toxic or corrosive effluents, or both, may be released when heating the material and could be harmful to the personnel or the apparatus. Use of an exhaust system to remove such effluents is highly recommended.

9. Sampling

9.1 Samples shall be representative of the material being studied including particle size and purity.

9.2 In the absence of other information, the samples are assumed to be analyzed as received. If a treatment, such as drying, is applied to the sample prior to analysis, this treatment and any resulting mass change must be noted in the report.

9.3 The selection of specimen mass depends upon the magnitude of hazard associated with the material, the sensitivity of the instrument, the heating rate and the specimen homogeneity. This test method should be carried out on as small of a quantity of material as possible, while specimens are still large enough to be representative of the material and to exhibit adequate signals. Typical specimen mass is between 1 and 10 mg.

NOTE 7—The particle size of the specimen should be considered, since thicker specimens may show transition broadening due to the thermal conductivity lag into the specimen cores.

10. Preparation of Apparatus

10.1 Prepare the TGA using any procedures described in the manufacturer's operations manual.

10.2 Place the temperature sensor in the proper position in accordance with the manufacturer's operations manual.

NOTE 8—Care must be taken to ensure that the specimen container is not in contact in any way with the sensor, unless the TGA was designed with the temperature sensor fixed to the crucible holder. It is also important that the temperature sensor is not moved after temperature calibration has been carried out.

10.3 Maintain a constant flow of purge gas for the furnace in the range from 20 to 100 mL min^{-1} throughout the experiment.

11. Calibration

11.1 Calibrate the mass signal using Practice E2040 or instrument manufacturer's guidelines and record details.

11.2 Calibrate the furnace temperature in accordance with Practice E1582 using the same heating rate, purge gas, flow rate and temperature sensor position to be used for subsequent specimens tests.

12. Recommended Condition of Tests

12.1 *Specimen Mass*—5 mg of specimen is generally considered adequate. Decrease the specimen mass to 1 mg if the characteristics of materials are unknown.

NOTE 9—For energetic material, it is recommended to use a specimen mass of no more than 1.0 mg.

12.2 *Heating Rate*—A rate of 10 to 20°C min^{-1} is considered normal.

NOTE 10—The onset temperature is affected by heating rate. Therefore, only results obtained at the same heating rate shall be compared.

NOTE 11—A lower heating rate (1 to 10°C min^{-1}) should be used when a complex change of mass is encountered.

NOTE 12—For energetic material, it is recommended to use a lower heating rate (1 to 10°C min^{-1}). For primary explosives, it is suggested to start with a heating rate of no more than 3°C min^{-1}.

12.3 *Temperature Range*—The temperature typically ranges from room temperature to 600°C.

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[3] Kwok, Q., and Seyler, R.J., *Journal of Thermal Analysis and Calorimetry*, Vol 83, No. 1, 2006, p. 117.

13. Procedure

13.1 Tare an empty and clean specimen container.

13.2 Weigh the specimen with a mass within 10 mass % of the target size into the tared container.

NOTE 13—Powder and granular samples should be distributed evenly over the sample container to maximize the exposed surface.

13.3 Place the specimen and container into the TGA at ambient temperature.

13.4 Heat the specimen at a constant rate of 10°C min^{-1} and record the TG curve. Continue heating until a constant mass is obtained or the temperature is well above the useful temperature range of the material tested.

NOTE 14—Other heating rates may be used but shall be reported.

13.5 Once the experiment is complete, cool the instrument to room temperature, remove, and clean or replace the specimen container.

13.6 Display the TG and DTG curves.

13.7 Using the TG curve, construct a baseline from the initial mass extrapolated upward in temperature.

13.8 For any reaction(s) observed, determine the onset temperature by selecting a point on the TG curve where a deflection is first observed from the established baseline prior to the thermal event.

NOTE 15—The TG curve should be zoomed to a scale of 1 to 2 mass % for the onset temperature selection (see Fig. 2).

NOTE 16—The onset temperature can also be determined from the DTG curve where a deflection from the DTG established baseline is first observed. However, only results obtained from the same method should be compared.

13.9 Calculate the mass change for reaction(s) or decomposition(s) by subtracting the sample mass at the onset temperature by the mass on the mass change plateau immediately after the thermal event.

NOTE 17—Replicate experiments are recommended, particularly for a heterogeneous sample. Calculate the means and standard deviations for the onset temperature and mass change from replicates.

14. Report

14.1 The report shall include the following:

14.1.1 Description of the sample and any sample preparation or pretreatment, or both.

14.1.2 Initial specimen mass.

14.1.3 Description of apparatus including manufacturer and model.

14.1.4 Instrument calibration details.

14.1.5 Material of container.

14.1.6 Test conditions including atmosphere, flow rate, heating rate and temperature range.

14.1.7 The onset temperature and mass change of all reactions observed.

NOTE 18—If replicates were performed, the report should include the number of tests, the mean values and the standard deviations of the onset temperature and mass change.

14.1.8 When a test is repeated using a different atmosphere or a different heating rate, note any significant changes in the TG curves resulting from the different experiment conditions.

14.1.9 The specific dated version of this test method used.

15. Precision and Bias

15.1 The precision and bias of this standard method were determined in an interlaboratory test (ILT) in 2008. Thirteen laboratories using thermogravimetric analyzers from six manufacturers and ten instrument models participated in the ILT. The TG onset temperature, TG mass change and DTG onset temperature for the thermal stability of polyethylene terephtalate (PET) were determined. Each laboratory reported the onset temperatures and mass changes in quintuplicate. The statistical analysis was conducted in accordance with Practice E691.

15.2 *Precision:*

15.2.1 Within laboratory variability may be described using the repeatability value (r) obtained by multiplying the repeatability standard deviation by 2.8. The repeatability value estimates the 95 % confidence limit. That is, two within laboratory

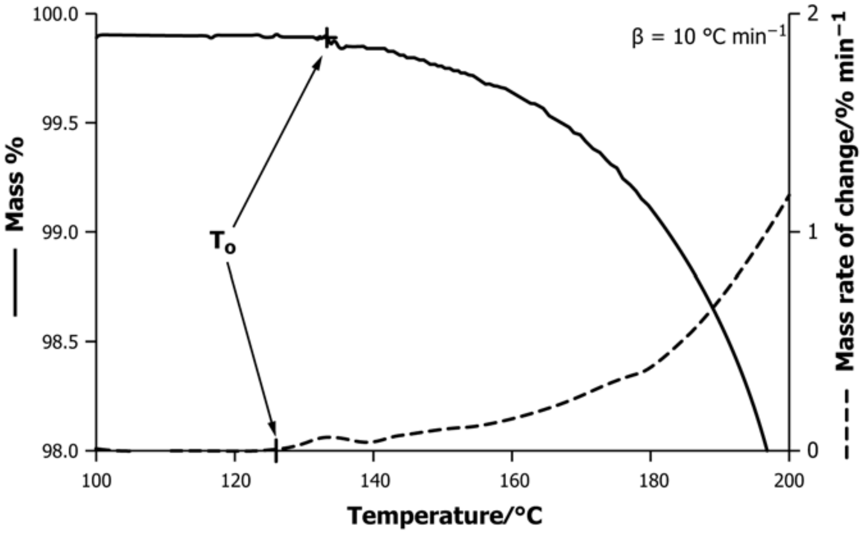

FIG. 2 Zoomed TG and DTG Curves for T_0 Determination

results should be considered suspect if they differ by more than the repeatability value (r).

15.2.2 The repeatability standard deviation for TG onset temperature is 6°C.

15.2.3 The repeatability standard deviation for TG mass change is 0.6 %.

15.2.4 The repeatability standard deviation for DTG onset temperature is 5°C.

15.3 Between laboratory variability may be estimated using the reproducibility value (R) obtained by multiplying the reproducibility standard deviation by 2.8. The reproducibility value estimates the 95 % confidence limit. That is, two between laboratory results should be considered suspect if they differ by more than the reproducibility value (R).

15.3.1 The reproducibility standard deviation for TG onset temperature is 54°C.

15.3.2 The reproducibility standard deviation for TG mass change is 2.3 %.

15.3.3 The reproducibility standard deviation for DTG onset temperature is 18°C.

15.4 *Bias:*

15.4.1 Bias is the difference between a test result and an accepted reference value. There is no accepted reference value for the thermal stability for PET. Therefore no bias information can be provided.

15.4.2 The mean values of TG onset temperature, TG mass change and DTG onset temperature for the thermal stability for PET at a heat rate of 10°C min^{-1} were observed to be 304°C, –87.0 % and 335°C, respectively.

16. Keywords

16.1 thermal analysis; thermal decomposition; thermal stability; thermogravimetric analysis; thermogravimetry

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