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Standard Test Methods for the Assignment of the Glass Transition Temperature by Modulated Temperature Differential Scanning Calorimetry[1]

This standard is issued under the fixed designation E2602; 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 These test methods describe the assignment of the glass transition temperature of materials using modulated temperature differential scanning calorimetry (MTDSC) over the temperature range from –120 to +600°C. The temperature range may be extended depending upon the instrumentation used.

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

1.3 There are no ISO equivalents to this standard.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E473 Terminology Relating to Thermal Analysis and Rheology

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

E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters

E1142 Terminology Relating to Thermophysical Properties

E1356 Test Method for Assignment of the Glass Transition Temperatures by Differential Scanning Calorimetry

E1545 Test Method for Assignment of the Glass Transition Temperature by Thermomechanical Analysis

E1640 Test Method for Assignment of the Glass Transition Temperature By Dynamic Mechanical Analysis

3. Terminology

3.1 *Definitions*—Specific technical terms found in these test methods are defined in Terminologies E473 and E1142 including *differential scanning calorimetry, glass transition, glass transition temperature, specific heat capacity*, and *thermal curve*.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *extrapolated end temperature (Te), n*—the point of intersection of the tangent drawn at the point of greatest slope (that is, the inflection point) in the transition region with the extrapolated baseline following the transition.

3.2.2 *extrapolated onset temperature (Tf), n*—the point of intersection of the tangent drawn at the point of greatest slope (that is, the inflection point) in the transition region with the extrapolated baseline prior to the transition.

3.2.3 *midpoint temperature (Tm), n*—the point on the thermal curve corresponding to the average of the extrapolated onset and extrapolated end temperatures.

3.2.4 *modulated, n*—a prefix indicating that a parameter changes in a periodic manner during the experiment.

3.2.5 *modulated heat flow, n*—the heat flow resulting from an applied modulated temperature program.

3.2.6 *modulated temperature differential scanning calorimetry (MTDSC), n*—a method of differential scanning calorimetry (DSC) that varies the temperature sinusoidally or with a periodic step-and-hold or pulse program to the test specimen over a traditional isothermal or temperature ramp program. Results from the experiment include reversing and nonreversing heat flow and specimen temperature.

3.2.7 *nonreversing heat flow, n*—the kinetic component of the total heat flow. That is, the portion of the heat flow that responds to temperature and not to the temperature rate of change.

3.2.8 *reversing heat flow, n*—the portion of the total heat flow that responds to the temperature rate of change.

3.2.9 *total heat flow, n*—the value of the modulated heat flow averaged over one modulation period or impulse.

[1] These test methods are 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.

3.2.9.1 *Discussion*—The total heat flow is equivalent to the heat flow signal of conventional differential scanning calorimetry.

3.2.9.2 *Discussion*—The total heat flow is equal to the sum of the reversing and nonreversing heat flows.

4. Summary of Test Method

4.1 The determination of the glass transition by differential scanning calorimetry using Test Method E1356 is difficult when kinetic events such as the cure exotherm of a thermoset resin occur at or near the glass transition. In MTDSC, the total heat flow signal is separated into reversing and nonreversing components. The heat capacity change that indicates the glass transition appears in the reversing heat flow signal, while kinetic events (for example, curing, enthalpy of recovery, etc.) appear in the nonreversing heat flow signal. The separation of these two signals permits the determination of the enthalpy of reaction and the assignment of the glass transition in a single experiment.

4.1.1 This MTDSC method involves the continuous monitoring of the reversing and nonreversing heat flow into or out of a test specimen as it is heated at a controlled rate through the glass transition region.

5. Significance and Use

5.1 Materials undergo an increase in molecular mobility at the glass transition seen as a sigmoidal step increase in the heat capacity. This mobility increase may lead to kinetic events such as enthalpic recovery, chemical reaction or crystallization at temperatures near the glass transition. The heat flow associated with the kinetic events may interfere with the determination of the glass transition.

5.2 The glass transition is observed in differential scanning calorimetry as a sigmoidal or step change in specific heat capacity.

5.3 MTDSC provides a test method for the separation of the heat flow due to heat capacity and that associated with kinetic events making it possible to determine the glass transition in the presence of interfering kinetic event.

5.4 These test methods are useful in research and development, quality assurance and control and specification acceptance.

5.5 Other methods for assigning the glass transition temperature include differential scanning calorimetry (Test Method E1356), thermomechanical analysis (Test Method E1545) and dynamic mechanical analysis (Test Method E1640).

6. Apparatus

6.1 The instrumentation required to provide the capability for these test methods includes a MTDSC composed of:

6.1.1 A *differential scanning calorimeter (DSC) test chamber* of (*1*) a *furnace or furnaces* to provide uniform controlled heating or cooling of a specimen and reference to a constant temperature or at a constant rate within the range from –120 to +600°C, (*2*) a temperature sensor to provide an indication of the specimen temperature readable to ±0.01°C, (*3*) a differential sensor to detect a heat flow difference between specimen and reference equivalent to 1 µW and (*4*) a means of sustaining a test chamber environment of inert nitrogen (or other low conductivity) purge gas at a rate of 20 to 60 mL/min constant to within ±10 %.

NOTE 1—The temperature range of interest depends upon the temperature of the glass transition. The apparatus need only address the temperature region from 50°C below to 50°C above the anticipated glass transition temperature.

6.1.2 A *temperature controller*, capable of executing a specific temperature program by (*1*) operating the furnace between selected temperature limits at a rate of temperature change of 7 ± 0.1°C/min, (*2*) holding at an isothermal temperature within the temperature range of –120 to +600°C within ±0.1°C, and (*3*) for Test Method A, varying temperature sinusoidally with an amplitude of ±0.9 to 1.1°C and a period of 50 to 71 s (frequency of 14 to 20 mHz) or applying a ±0.5°C pulse at intervals between 15 and 30 s.

6.1.3 A *calculating device*, capable of transforming the experimentally determined modulated temperature and modulated specimen heat flow signals into the required continuous output forms of reversing and nonreversing heat flow and average test temperature to the required accuracy and precision.

6.1.4 A *data collection device*, to provide a means of acquiring, storing and displaying measured or calculated signals or both. The minimum output signals required for MTDSC are heat flow, reversing heat flow, nonreversing heat flow, elapsed time and average specimen temperature signals.

6.2 A *coolant system* to provide cooling at rates of at least 2°C/min.

6.3 *Inert nitrogen* or other low conductivity purge gas flowing at a rate of 20 to 60 mL/min constant to within ±10 %.

NOTE 2—Helium, a commonly used purge gas with high thermal conductivity, may result in reduced temperature range, precision and accuracy. Follow the manufacturers recommendation when using helium.

6.4 A *balance* with a range of at least 200 mg to weigh specimens or containers, or both to ±0.01 mg.

6.5 A *Sapphire disk calibration material*, 10 to 30 mg for heat capacity calibration.

6.6 *Indium metal* of >99.99 % purity for temperature and enthalpy calibration.

6.7 *Containers* (pans, crucibles, etc.) that are inert to the specimen and are of suitable structural shape and integrity to contain the specimen in accordance with the specific requirements of these test methods.

6.8 A means, tool or device to close, encapsulate or seal the container of choice.

7. Calibration and Standardization

7.1 Calibrate the temperature signal from the MTDSC apparatus in accordance with Practice E967 using an indium reference material and a heating rate of 5°C/min (see Note 3 and Note 5).

7.2 Calibrate the total heat flow signal from the MTDSC apparatus in accordance with Practice E968 using an indium reference material.

7.3 Calibrate the apparatus for modulated temperature derived signals (such as reversing heat flow, nonreversing heat flow, etc.) with the instructions provided by the manufacturer as described in the operations manual using the sapphire calibration material (6.4) and 5°C/min heating rate, ±1°C amplitude and 60 s period (16.5 mHz frequency) or ±1.0°C temperature impulse with 15 to 30 s duration.

NOTE 3—The calibration shall be performed using the same heating rate, and temperature modulation conditions to be used for the test specimen.

8. Procedure

TEST METHOD A SINUSOIDAL TEMPERATURE

8.1 Into a tared container weigh to within ±0.01 mg, 5 to 20 mg of the test specimen. Seal a lid on the sample container.

8.2 Beginning at a temperature at least 50°C below the anticipated glass transition temperature, initiate the temperature modulation at an amplitude of ±1°C and a period of 60 s. Record the total, reversing and nonreversing heat flow signals with a data collection rate of 1 s/point or faster.

NOTE 4—Other temperature ranges, amplitudes and periods may be used but shall be reported.

8.3 Initiate an underlying heating rate of 5°C/min to an end temperature approximately 50°C higher than the end of the glass transition.

NOTE 5—Other heating rates may be used but shall be reported.

NOTE 6—Other temperature ranges, amplitudes and periods may be used but shall be reported.

8.4 Prepare a plot of reversing heat flow on the ordinate (Y-axis) versus average sample temperature on the abscissa (X-axis). The glass transition is indicated by a sigmoidal step change in the reversing heat flow signal such as that shown in Fig. 1.

8.5 Construct a tangent to the baseline before the glass transition, extrapolating it to higher temperatures. Construct a tangent to the baseline after the glass transition, extrapolating it to lower temperatures. Construct a tangent at the point of maximum slope (that is, the inflection point) in the midst of the glass transition until it intersects with the two baseline constructions. The intersection points with the baseline before and after the glass transition are identified as *Tf* and *Te*, respectively.

8.6 The midpoint transition temperature (*Tm*) is determined as the midpoint between *Tf* and *Te*, that is, $Tm = (Tf + Te) / 2$.

8.7 Report the glass transition temperature (*Tg*) to be that of the midpoint temperature (*Tm*).

NOTE 7—Other temperatures between *Tf* and *Te* may be used but shall be reported.

TEST METHOD B STEP TEMPERATURE

8.8 Into a tared container weigh 5 to 20 mg of the test specimen to within ±0.01 mg. Seal a lid on the sample container.

8.9 Beginning at a temperature at least 50°C below the anticipated glass transition temperature, start a program of temperature increments of 1°C with a heating rate of 5°C/min (see Note 8) and isothermal holding for 1 minute with the advancement condition of stability < 5 µW over 6 s to a temperature that is approximately 50°C above the anticipated glass transition temperature.

NOTE 8—Other temperature increments, heating rates, isothermal holding periods and advancement condition may be used but shall be reported.

NOTE 9—The temperature increments shall be sufficiently small that at least five full steps occur across the glass transition

8.10 Prepare a plot of specific heat capacity on the ordinate (Y-axis) versus average sample temperature on the abscissa

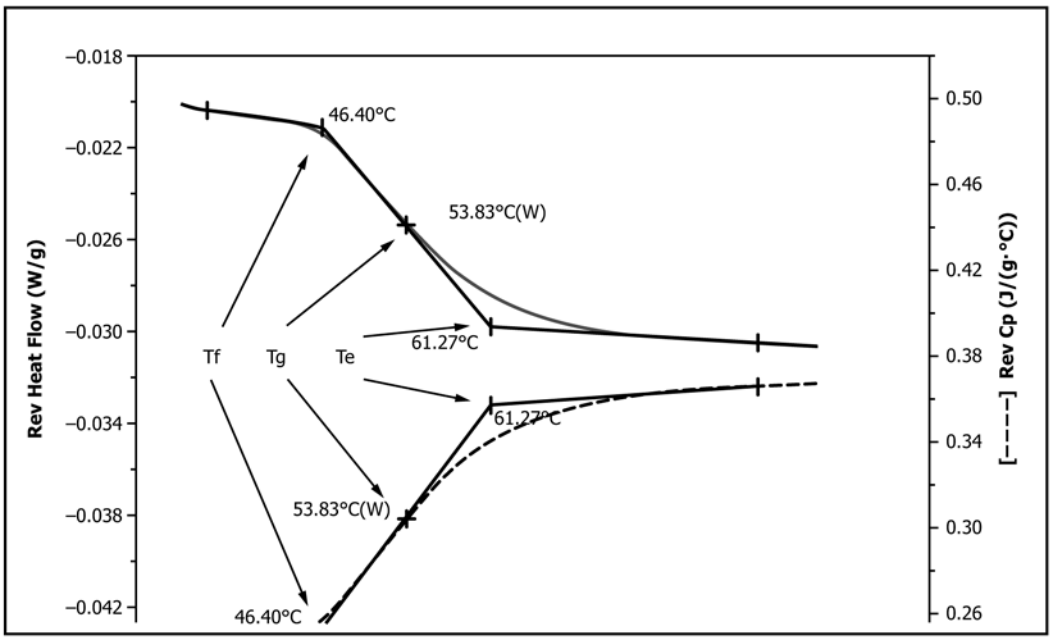

FIG. 1 Reversing Heat Flow and Specific Heat Capacity in the Region of the Glass Transition

(X-axis). The glass transition is indicated by a sigmoidal step change in the specific heat capacity signal as shown in Fig. 1.

8.11 Construct a tangent to the baseline before the glass transition, extrapolating to higher temperatures. Construct a tangent to the baseline after the glass transition, extrapolating it to lower temperatures. Construct a tangent at the point of maximum slope (that is, the inflection point) in the midst of the glass transition until it intersects with the two baseline constructions. The intersections points with the baseline before and after the glass transition are identified as *Tf* and *Te*, respectively.

8.12 The midpoint transition temperature (*Tm*) is determined as the midpoint between *Tf* and *Te*, that is, *Tm = (Tf + Te) / 2*.

8.13 Report the glass transition temperature (*Tg*) to be that of the midpoint temperature (*Tm*).

NOTE 10—Other temperatures between *Tf* and *Te* may be used but shall be reported.

TEST METHOD C TEMPERATURE PULSE

8.14 Into a tared container weigh to within ±0.01 mg, 5 to 20 mg of the test specimen. Seal a lid on the sample container.

8.15 Beginning at a temperature at least 50°C below the anticipated glass transition temperature, initiate an pulse of ±0.5°C and a duration of 15 to 30 s. Record the total, reversing and nonreversing heat flow signals with a data collection rate of 1 s/point or faster.

NOTE 11—— Other temperature ranges, pulse amplitudes and durations may be used but shall be reported.

8.16 Initiate an underlying heating rate of 5°C/min to an end temperature approximately 50°C higher than the end of the glass transition.

NOTE 12—Other heating rates may be used but shall be reported.

NOTE 13—The heating rate selected should be sufficiently low to permit at least 5 full temperature pulses across the glass transition between the onset and end-point temperatures (see Test Method E1356).

8.17 Prepare a plot of reversing heat flow on the ordinate (Y-axis) versus average sample temperature on the abscissa (X-axis). The glass transition is indicated by a sigmoidal step change in the reversing heat flow signal such as that shown in Fig. 1.

8.18 Construct a tangent to the baseline before the glass transition, extrapolating it to higher temperatures. Construct a tangent to the baseline after the glass transition, extrapolating it to lower temperatures. Construct a tangent at the point of maximum slope (that is, the inflection point) in the midst of the glass transition until it intersects with the two baseline constructions. The intersection points with the baseline before and after the glass transition are identified as *Tf* and *Te*, respectively.

8.19 The midpoint transition temperature (*Tm*) is determined as the midpoint between *Tf* and *Te*, that is, *Tm* = (*Tf* + *Te*) / 2.

8.20 Report the glass transition temperature (*Tg*) to be that of the midpoint temperature (*Tm*).

NOTE 14—Other temperatures between *Tf* and *Te* may be used but shall be reported.

9. Report

9.1 Report the following information:

9.1.1 A complete identification and description of the material tested.

9.1.2 Description of the MTDSC apparatus used in the test.

9.1.3 Experimental conditions, including underlying heating rate and temperature modulation conditions.

9.1.4 The glass transition temperature (*Tg*).

9.1.5 The specific dated version of this test method and the Test Method (for example, A, B, or C) used.

9.1.6 The date and operator of the test.

10. Precision and Bias

10.1 The precision of these test methods will be determined in a interlaboratory test scheduled for 2010 to 2011. Anyone wishing to participate in this test should contact the E37 Staff Manager at ASTM International Headquarters.

10.2 For Test Method A, the within laboratory repeatability standard deviation for the assignment of the glass transition determined in a single laboratory was found to be 0.27 and 0.53°C at underlying heating rate of 2 and 5°C/min, respectively.

11. Keywords

11.1 cure; degree of cure; differential scanning calorimetry; glass transition temperature; modulated temperature differential scanning calorimetry; thermal analysis