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Standard Test Method for
Assignment of the DSC Procedure for Determining T_g of a Polymer or an Elastomeric Compound[1]

This standard is issued under the fixed designation D7426; 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 the assignment of the glass transition temperatures (T_g) of materials using differential scanning calorimetry.

1.2 This test method is applicable to amorphous materials, including thermosets or semicrystaline materials containing amorphous regions, that are stable and do not undergo decomposition or sublimation in the glass transition region.

1.3 The normal operating temperature range is from –120 to 500°C. The temperature range may be extended, depending upon the instrumentation used.

1.4 Computer or electronic-based instruments, techniques, or data treatment equivalent to this test method may also be used.

NOTE 1—Users of this test method are expressly advised that all such instruments or techniques may not be equivalent. It is the responsibility of the user of this standard to determine the necessary equivalency prior to use.

1.5 ISO 11357–2 is equivalent to this test method.

1.6 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.7 *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]

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

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

E1142 Terminology Relating to Thermophysical Properties

2.2 *ISO Standard:*[3]

ISO 11357–2 Differential Scanning Calorimetry (DSC)-Part 2 Determination of Glass Transition Temperature

3. Terminology

3.1 *Definitions:*

3.1.1 The following terms are applicable to this test method and can be found in Terminology E473 and Terminology E1142: *differential scanning calorimetry (DSC)*, *differential thermal analysis (DTA)*, *glass transition*, *glass transition temperature* (T_g), and *specific heat capacity*.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 There are commonly used transition points associated with the glass transition region. (See Fig. 1.)

3.2.2 *extrapolated end temperature* (T_e), *°C, n*—the point of intersection of the tangent drawn at the point of greatest slope on the transition curve with the extrapolated baseline following the transition.

3.2.3 *extrapolated onset temperature* (T_f), *°C, n*—the point of intersection of the tangent drawn at the point of greatest slope on the transition curve with the extrapolated baseline prior to the transition.

3.2.4 *inflection temperature* (T_i), *°C, n*—the point on the thermal curve corresponding to the peak of the first derivative (with respect to time) of the parent thermal curve. This point corresponds to the inflection point of the parent thermal curve.

3.2.5 *midpoint temperature* (T_m), *°C, n*—the point on the thermal curve corresponding to ½ the heat flow difference between the extrapolated onset and extrapolated end.

3.2.5.1 *Discussion*—The inflection point temperature (T_i) is

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[1] This test method is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.10 on Physical Testing.

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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] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

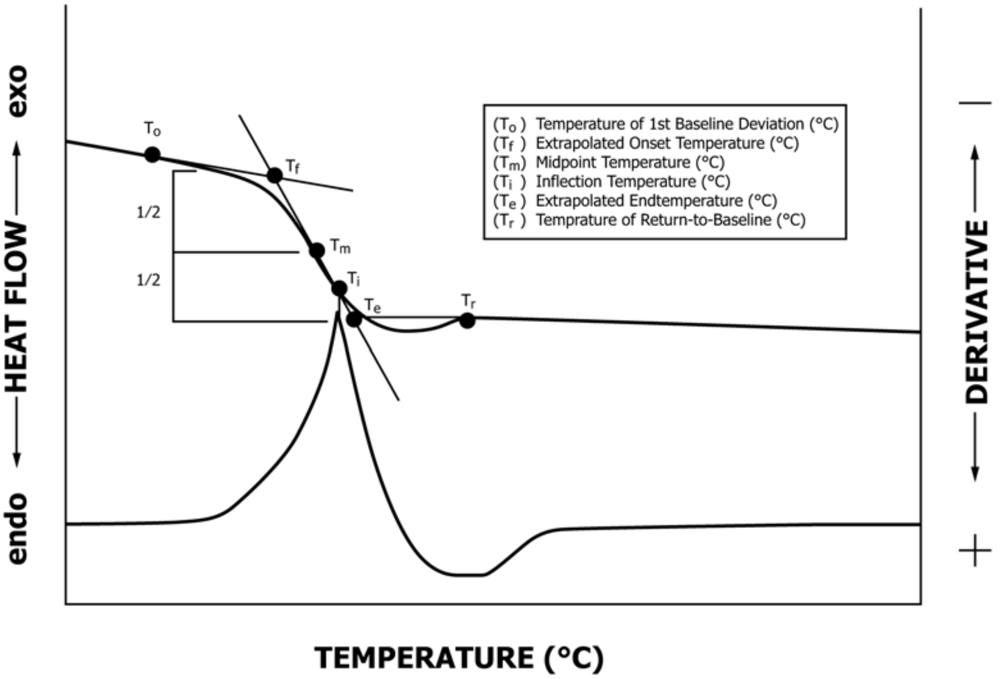

FIG. 1 Glass Transition Region Measured Temperatures

most easily determined from the first derivative curve and will be used as the glass transition temperature (see Fig. 1).

3.2.6 Two additional transition points are sometimes identified and are defined as follows:

3.2.7 *temperature of first deviation (T_o), °C, n*—the point of first detectable deviation from the extrapolated baseline prior to the transition.

3.2.8 *temperature of return to baseline (T_r), °C, n*—the point of last deviation from the extrapolated baseline beyond the transition.

4. Summary of Test Method

4.1 This test method involves continuously monitoring the difference in heat flow, or temperature between, a reference material and a test material when they are heated or cooled at a controlled rate through the glass transition region of the test material and analyzing the resultant thermal curve to provide the glass transition temperature.

5. Significance and Use

5.1 Differential scanning calorimetry provides a rapid test method for determining changes in specific heat capacity in a homogeneous material or domain. The glass transition is manifested as a step change in specific heat capacity. For amorphous and semi-crystalline materials the determination of the glass transition temperature may lead to important information about their thermal history, processing conditions, stability of phases, and progress of chemical reactions.

5.2 This test method is useful for research, quality control, and specification acceptance.

6. Interferences

6.1 A change in heating rates and cooling rates can affect the results. The presence of impurities will affect the transition, particularly if an impurity tends to plasticize or form solid solutions, or is miscible in the post-transition phase. If domain size has an effect upon the detected transition temperature, the specimens to be compared should be of the same domain size.

6.2 In some cases the specimen may react with air during the temperature program causing an incorrect transition to be measured. Whenever this effect may be present, the test shall be run under either vacuum or an inert gas atmosphere. Since some materials degrade near the glass transition region, care must be taken to distinguish between degradation and glass transition.

6.3 Since milligram quantities of sample are used, it is essential to ensure that specimens are homogeneous and representative, so that appropriate sampling techniques are used.

7. Apparatus

7.1 *Differential Scanning Calorimeter*—The essential instrumentation required to provide the minimum differential scanning calorimetric capability for this method includes a test chamber composed of a furnace(s) to provide uniform controlled heating (cooling) of a specimen and reference to a constant temperature or at a constant rate over the temperature range from –120 to 500°C, a temperature sensor to provide an indication of the specimen temperature to ±0.1°C, differential sensors to detect heat flow difference between the specimen and reference with a sensitivity of ±50 μW, a means of sustaining a test chamber environment of a purge gas of 10 to 100 mL/min within 4 mL/min, and a temperature controller capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits at a rate of temperature change of up to 10°C/min constant to ±0.5°C/min.

7.2 *Recording Device,* capable of recording and displaying any fraction of the heat flow signal (including noise) on the Y-axis and any fraction of the temperature signal (including noise) on the X-axis.

7.3 *Containers (pans, crucibles, vials, etc.),* inert to the specimen and reference materials and of suitable structural shape and integrity to contain the specimen and references.

7.4 *Inert Reference Material,* with a heat capacity approximately equivalent to that of the specimen may be used, for ease of interpretation. The inert reference material may often be an empty specimen capsule or tube.

7.5 *Nitrogen,* or other inert purge gas supply, of purity equal to or greater than 99.9 %.

7.6 *Analytical Balance,* with a capacity greater than 100 mg, capable of weighing to the nearest 0.1 mg.

8. Specimen Preparation

8.1 *Powders or Granules*—Avoid grinding if a preliminary thermal cycle as outlined in 10.2 is not performed. Grinding, microtoming, or similar techniques for size reduction often introduce thermal effects because of friction or orientation, or both, and thereby change the thermal history of the specimen.

8.2 *Molded Parts or Pellets*—Cut the samples with a microtome, razor blade, paper punch, or cork borer (size No. 2 or 3) to appropriate size in thickness or diameter, and length that will approximate the desired mass in the subsequent procedure.

8.3 *Films or Sheets*—For films thicker than 40 µm, see 8.2. For thinner films, cut slivers to fit in the specimen tubes or punch disks, if circular specimen pans are used.

8.4 Report any mechanical or thermal pretreatment.

9. Calibration

9.1 Using the same heating rate, purge gas, and flow rate as that to be used for analyzing the specimen, calibrate the temperature axis of the instrument following the procedure given in Test Method E967.

10. Procedure

10.1 Use a specimen mass appropriate for the material to be tested. In most cases a 10 to 40 mg mass is satisfactory. An amount of reference material with a heat capacity closely matched to that of the specimen may be used. An empty specimen pan may also be adequate.

10.2 Perform two cycles of heating and controlled or not controlled cooling between the two cycles. The first cycle often is useful to provide thermal history information, the second cycle provides information on the material with previous thermal history erased.

NOTE 2—Two cycles are not needed for elastomers, since the T_g is below ambient temperature.

NOTE 3—Other, preferably inert, gases may be used, and other heating and cooling rates may be used, but must be reported.

10.3 Hold temperature until the instrument is at equilibrium.

10.4 Program cool at a rate of 10°C/min to –100°C.

10.5 Hold temperature until the instrument is at equilibrium.

10.6 Repeat heating at same rate as in 10.4, and record the heating curve until all desired transitions have been completed. Other heating rates may be used but must be reported.

10.7 Determine temperature Ti_{Tii}, (see Fig. 1),

where:

T_i = inflection temperature, °C,
T_f = extrapolated onset temperature, °C, and
T_m = midpoint temperature, °C.

10.8 Increasing the heating rate produces greater baseline shifts thereby improving detectability. In the case of DSC the signal is directly proportional to the heating rate in heat capacity measurements.

NOTE 4—The glass transition takes place over a temperature range and is known to be affected by time dependent phenomena, such as the rate of heating (cooling). For these reasons, the establishment of a single number for the glass transition needs some explanation. Either T_f or T_m or T_i may be selected to represent the temperature range over which the glass transition takes place. The particular temperature chosen must be agreed on by all parties concerned. In selecting which value should be taken as, the reader may wish to consider the following:

(1) T_m was found to have higher precision than T_f (see 12.3).

(2) The measurement of T_f is often easier for those who construct the respective tangents by hand.

(3) T_m (preferred) or T_i is more likely to agree with the measurement of T_g by other techniques since it is constructed closer to the middle of the temperature range over which the glass transition occurs.

(4) T_f may be taken to more closely represent the onset of the temperature range over which the glass transition occurs. Any comparison of glass transition temperatures should contain a statement of how the test was run and how the value was obtained.

11. Report

11.1 Report the following information:

11.1.1 A complete identification and description of the material tested.

11.1.2 Description of instrument used for the test.

11.1.3 The scan rate in °C/min.

11.1.4 Identification of the specimen environment by pressure, gas flow rate, purity, and composition, including moisture, if applicable.

11.1.5 Results of the transition measurements using temperature parameters (T_i) cited in Fig. 1. T_i (used as T_g) is preferred.

11.1.6 Any side reactions (for example, crosslinking, thermal degradation, oxidation) shall also be reported and the reaction identified, if possible.

TABLE 1 T_g, Glass Transition Temperature (Δ°C): Distributor-Prepared Samples

Material	Average $\bar{x}$	Standard Deviation	Repeatability Limit (*r*)	Reproducibility Limit (*R*)
CR	–66.123	1.975	2.484	5.975
FKM	–16.221	2.349	1.246	6.675
HNBR	–41.437	2.096	1.918	6.124
ECO	–63.252	2.115	1.893	6.168
	AVERAGE		1.885	6.236

TABLE 2 T_g, Glass Transition Temperature (Δ°C): Lab-Prepared Samples

Material	Average $\bar{x}$	Standard Deviation	Repeatability Limit (r)	Reproducibility Limit (R)
CR	–65.879	1.466	2.307	4.612
FKM	–15.975	2.126	1.280	6.068
HNBR	–43.183	1.967	2.542	5.975
ECO	–62.905	2.063	1.711	5.984
	AVERAGE		1.960	5.660

12. Precision and Bias[4]

12.1 The precision of this test method is based on an interlaboratory study conducted in 2006. The testing was performed using the methods described in Practices E177 and E691. Twelve laboratories received 4 different polymers in 2 different states of preparation: fully prepared and weighed by the distributor (Table 1); and specimens that were to be prepped and weighed at the individual laboratories (Table 2). Each "test result" was an individual determination. Participating laboratories tested 6 replicate samples for both the prepared and unprepared specimens of each material.

12.1.1 *Repeatability*—Two test 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.

12.1.1.1 The average repeatability limit calculated from the materials in this study is 1.9225.

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

12.1.2.1 The average reproducibility limit calculated from the materials in this study is 5.948.

12.1.3 Any judgment in accordance with these two statements would have an approximate 95 % probability of being correct.

12.2 *Bias*—At the time of the study, no accepted reference material suitable for determining the bias for this test method was utilized, therefore no statement on bias is being made.

12.3 The precision statement was determined through statistical examination of 552 results, from 12 laboratories, on 4 materials.

13. Keywords

13.1 differential scanning calorimetry (DSC); differential thermal analysis (DTA); glass transition; specific heat capacity

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D11-1097.