Designation: D 3418 – 99

Standard Test Method for Transition Temperatures of Polymers By Differential Scanning Calorimetry[1]

This standard is issued under the fixed designation D 3418; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope *

1.1 This test method covers determination of transition temperatures of polymers (Note 1) by differential scanning calorimetry.

NOTE 1—First-order transition temperatures or melting points of semicrystalline polymers may also be determined or approximated by the procedures found in Test Methods D 789.

NOTE 2—This test method may be used in conjunction with Test Methods D 3417 or E 793 to simultaneously determine the enthalpies of melting and crystallization.

1.2 This test method is applicable to polymers in granular form (below 60 mesh preferred, avoiding grinding if possible) or to any fabricated shape from which appropriate specimens can be cut.

1.3 The normal operating temperature range is from the cryogenic region to 600°C. With special equipment, the temperature range can be extended.

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

1.5 *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.*

NOTE 3—This standard is similar but not equivalent to ISO 11357-1 and ISO 11357-2. The ISO procedures provide additional information not supplied by this test method.

2. Referenced Documents

2.1 *ASTM Standards:*

D 789 Test Methods for Determination of Relative Viscosity, Melting Point, and Moisture Content of Polyamide (PA)[2]
D 3417 Test Method for Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry
E 473 Terminology Relating to Thermal Analysis[3]
E 563 Practice for Preparation and Use of Freezing Point Reference Baths[4]
E 793 Test Method for Heats of Fusion and Crystallization by Differential Scanning Calorimetry[3]
E 794 Test Method for Melting and Crystallization Temperature by Thermal Analysis[3]
E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers[3]
E 1142 Terminology Relating to Thermophysical Properties[3]
E 1356 Test Method for Glass Transition Temperatures by Differential Scanning Calorimetry or Differential Thermal Analysis[3]
E 1953 Practice for Description of Thermal Analysis Apparatus[3]

2.2 *ISO Standards:*[5]

11357-1 Plastics—Differential Scanning Calorimetry (DSC)—Part 1: General Principles
11357-2 Plastics—Differential Scanning Calorimetry (DSC)—Part 2: Determination of Glass Transition Temperature

3. Terminology

3.1 Specialized terms used in this test method are defined in Terminologies E 473 and E 1142.

4. Summary of Test Method

4.1 This test method consists of heating or cooling the test material at a controlled rate in a specified purge gas at a controlled flow rate and continuously monitoring with a suitable sensing device the difference in temperature or the difference in heat input between a reference material and a test material due to energy changes in the material. A transition is

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[1] This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.30 on Thermal Properties (Section D20.30.07).

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[2] *Annual Book of ASTM Standards*, Vol 08.01.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 14.03.

[5] Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

***A Summary of Changes section appears at the end of this standard.**

marked by absorption or release of energy by the specimen resulting in a corresponding endothermic or exothermic peak or baseline shift in the heating or cooling curve.

5. Significance and Use

5.1 Thermal analysis provides a rapid method for measuring transitions due to morphological or chemical changes, or both, in a polymer as it is heated/cooled through a specified temperature range. Change in specific heat capacity, heat flow (in conjunction with Test Method D 3417), and temperature values can be determined for these polymer transitions. Differential scanning calorimetry can be used to assist in identifying specific polymers, polymer alloys, and certain polymer additives, which exhibit thermal transitions. Chemical reactions that cause or affect certain transitions can be measured with the aid of this technique; such reactions include oxidation, the curing of thermosetting resins, and thermal decomposition.

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

6. Interferences

6.1 An increase or decrease in heating rate from those specified can alter the results. The presence of impurities will affect the calculated transition temperature, particularly if an impurity tends to form solid solutions, or to be miscible in the melt phase. Since particle size has an effect upon detected transition temperatures, the specimens to be compared should be approximately the same particle size **(1-5)**.[6]

6.2 In some cases the specimens may react with air during the temperature cycle, causing an incorrect transition temperature to be measured. Where it has been shown that this effect is present, provision shall be made for running the test under vacuum or an inert gas blanket. Since some materials degrade near the melting region, care must be used to distinguish between degradation and transition.

6.3 Since milligram quantities of a specimen are used, it is essential to ensure that specimens are homogeneous and representative.

6.4 Toxic or corrosive effluents, or both, can be released when heating the material, and could be harmful to the personnel or to the apparatus.

7. Apparatus

7.1 *Differential Scanning Calorimeter (DSC)*—The essential instrumentation required to provide the minimum differential scanning calorimetric capability for this test method includes:

7.1.1 *DSC Test Chamber*—This chamber is composed of the following:

7.1.1.1 *Furnace(s)*, to provide uniform controlled heating (cooling) of a specimen and reference to a constant temperature or at a constant rate within the applicable cryogenic to 600°C temperature range of this test method.

7.1.1.2 *Temperature Sensor*, to provide an indication of the specimen temperature to ±10 mK (0.01°C).

7.1.1.3 *Differential Sensor*, to detect heat flow difference between the specimen and reference equivalent to 1 mW.

7.1.1.4 *Means of Sustaining a Test Chamber Environment* of inert purge gas at a purge flow rate of 10 to 50 ± 5 mL/min.

NOTE 4—Typically, 99+ % pure nitrogen, argon or helium are employed when oxidation in air is a concern. Unless effects of moisture are to be studied, use of dry purge gas is recommended and is essential for operation at subambient temperatures.

7.1.2 *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 10 to 20°C/min constant to ±0.1°C/min or at an isothermal temperature constant to ±0.1°C.

7.1.3 *Recording Device*, either digital or analog, capable of recording and displaying any fraction of the heat flow signal (DSC curve) including the signal noise as a function of temperature.

7.1.4 *Containers* (pans, crucibles, vials, and so forth) that are inert to the specimen and reference materials and which are of suitable structural shape and integrity to contain the specimen and reference in accordance with the specific requirements of this test method.

7.1.5 Cooling capability to hasten cool down from elevated temperatures, to provide constant cooling rates of up to 10°C/min, to achieve subambient operation, or to sustain an isothermal subambient temperature, or combination thereof.

7.2 *Balance*, with a capacity of 100 mg or greater to weigh specimens or containers, or both, to ±10 µg.

8. Sample

8.1 *Powdered or Granular Specimens*—Avoid grinding if the preliminary thermal cycle as outlined in 10.1.2 is not performed. Grinding 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 or Pelleted Specimens*—Cut the specimens with a microtome, razor blade, hypodermic punch, paper punch, or cork borer (Size No. 2 or 3) to appropriate size, in thickness or diameter and length that will best fit the specimen capsule and will approximate the desired weight in the subsequent procedure.

8.3 *Film or Sheet Specimens*—For films thicker than 40 µm, see 8.2. For thinner films, cut slivers to fit in the specimen capsules or punch disks, if the circular specimen capsules are used.

9. Calibration

9.1 Calibrate the DSC temperature signal using Practice E 967 and the same heating rates (that is, 10 or 20°C/min, or both) to be used in this test method (see Note 5).

10. Procedure

10.1 *For First-Order Transition*:

10.1.1 Use a specimen mass appropriate for the material to be tested. In most cases 5-mg specimen mass is satisfactory. Avoid overloading. Weigh the specimen to an accuracy of 10 µg.

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[6] The boldface numbers in parentheses refer to the list of references at the end of this test method.

10.1.1.1 Intimate thermal contact between the pan and specimen is essential for reproducible results. Crimp a metal cover against the pan with the sample sandwiched in between to ensure good heat transfer. Take care to ensure flat pan bottoms.

10.1.2 Perform and record a preliminary thermal cycle by heating the sample at a rate of 10°C/min under inert purge gas atmosphere from 50°C below to 30°C above the melting point. The selection of temperature and time are critical when effect of annealing is studied. Minimize the time of exposure to high temperature to avoid sublimation or decomposition. In some cases the preliminary thermal cycle may interfere with the transition of interest, causing an incorrect transition or eliminating a transition. Where it has been shown that this effect is present, omit the preliminary thermal cycle.

NOTE 5—Other heating or cooling rates may be used but shall be reported. It is the responsibility of the user of other rates to demonstrate equivalency to this test method.

NOTE 6—For some polymers, this high-temperature annealing may result in degradation of the specimen. In such cases, shorter annealing times may be used but shall be reported.

10.1.3 Hold temperature for 10 min (10.1.2).

10.1.4 Cool to 50°C below the peak crystallization temperature at a rate of 10°C/min and record the cooling curve.

10.1.5 Repeat heating (10.1.2) as soon as possible under inert purge gas at a rate of 10°C/min, and record the heating curve.

10.1.6 Measure the temperatures for the desired points on the curves: T_{eim}, T_{pm}, T_{efm}, T_{eic}, T_{pc}, and T_{eic} (see Fig. 1). Report two T_{pm}'s or T_{pc}'s if observed.

where:
T_{eim} = melting extrapolated onset temperature, °C,
T_{efm} = melting extrapolated end temperature, °C,
T_{pm} = melting peak temperature,° C,
T_{eic} = crystallization extrapolated onset temperature, °C,
T_{pc} = crystallization peak temperature, °C, and
T_{efc} = crystallization extrapolated end temperature, °C.

NOTE 7—The actual temperature displayed on the temperature axis depends upon the instrument type (for example, specimen temperature, program temperature, or specimen-program temperature average). Follow any recommended procedures or guidelines of the instrument manufacturer to obtain specimen temperature at the point of interest.

10.2 *For Glass Transition*:

10.2.1 Use a specimen mass appropriate for the material to be tested. In most cases, a 10 to 20-mg specimen mass is satisfactory. If both first- and second-order transitions are to be determined, use a new specimen for each test. Weigh the specimen to an accuracy of 10 µg.

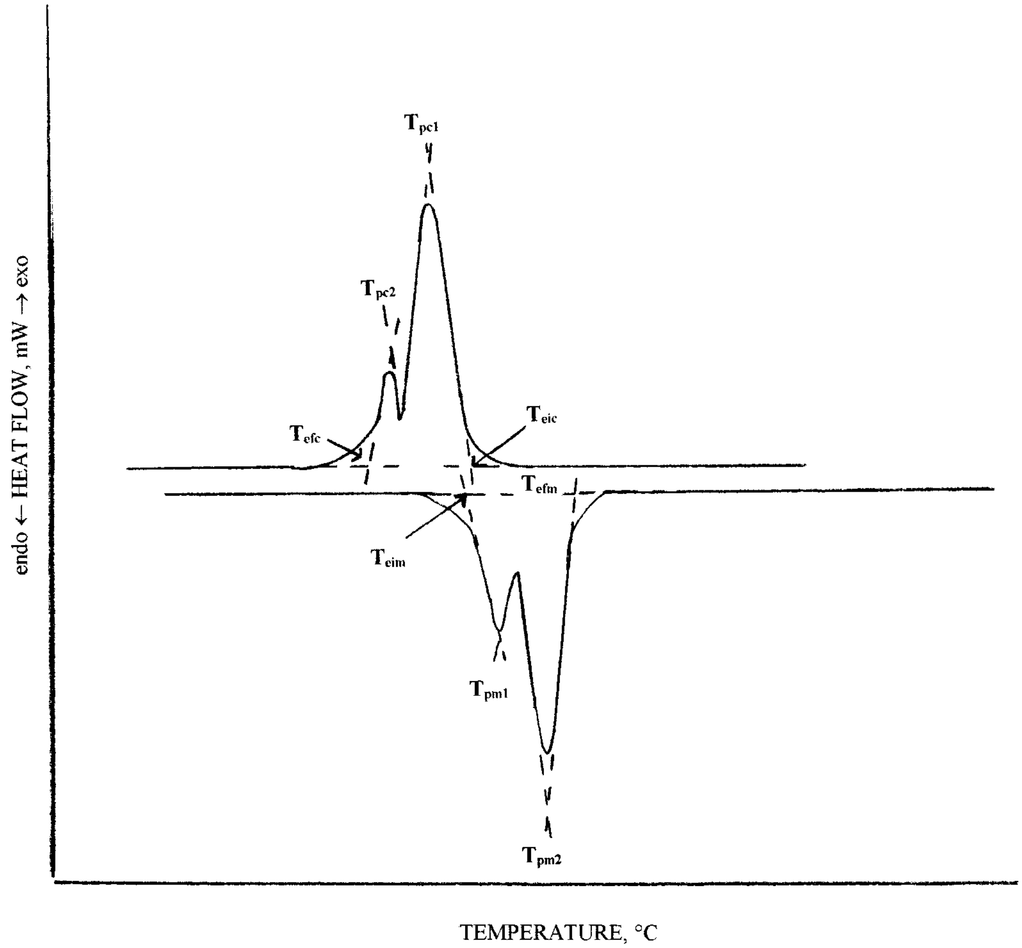

FIG. 1 First-Order Transition of Nylon

10.2.2 Perform and record a preliminary thermal cycle as in 10.1.2 up to a temperature 30°C above the extrapolated end temperature, T_e, to erase previous thermal history, heating at a rate of 20°C/min.

NOTE 8—Stress relaxation peaks, caused by annealing, that appear in some polymers above the glass transition are normally eliminated by the preliminary thermal cycle and a new baseline will be established after the transition.

10.2.3 Hold temperature for 10 min.

10.2.4 Quench cool to 50°C below the transition temperature of interest.

10.2.5 Hold temperature for 10 min.

10.2.6 Repeat heating (10.2.2) at a rate of 20°C/min, and record the heating curve until all desired transitions have been completed. (See Note 5.)

10.2.7 Measure temperatures T_{eig}, T_{mg}, and T_{efg} (see Fig. 2):

where:
T_{eig} = extrapolated onset temperature, °C,
T_{mg} = midpoint temperature, °C, and
T_{efg} = extrapolated end temperature, °C.

A new baseline will likely be established after the transition, rather than a peak (see Note 8). For most applications, the T_{mg} temperature is more meaningful and may be designated as the glass transition temperature (T_g) in place of the extrapolated onset for the glass transition curve.

11. Report

11.1 Report the following information:

11.1.1 Complete identification and description of the material tested, including source, manufacturer's code,

11.1.2 Description of instrument used for the test,

11.1.3 Statement of the mass, dimensions, geometry, and materials of the specimen capsule; and the average rate of linear temperature change,

11.1.4 Description of temperature calibration procedure,

11.1.5 Identification of the sample atmosphere by purge gas flow rate, purity, and composition, including humidity, if applicable,

11.1.6 Results of the transition measurements using the temperature parameters cited in Fig. 1, or any combination of parameters suitable for the purpose in hand. T_{pm} and T_{eic} are commonly used as single characteristic temperatures for the first-order transition of semicrystalline polymers but must be identified by including the subscript, and,

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

12. Precision and Bias

12.1 No independent interlaboratory test was conducted. However, the precision of this test method for measuring first-order melting and crystallization temperatures is essentially equivalent to the that of Test Method E 793 (RR:E37-1001).

12.1.1 An interlaboratory study was conducted in 1998 in which the temperature of melting and crystallization of a polypropylene sample were determined in nine laboratories.

12.2 No independent interlaboratory test was conducted. However, the precision of this test method for measuring the glass transition temperature is essentially equivalent to that of Test Method E 1356 (RR:E37-1013).

12.2.1 An interlaboratory study was conducted in 1984 in which the midpoint temperature for three polymeric materials

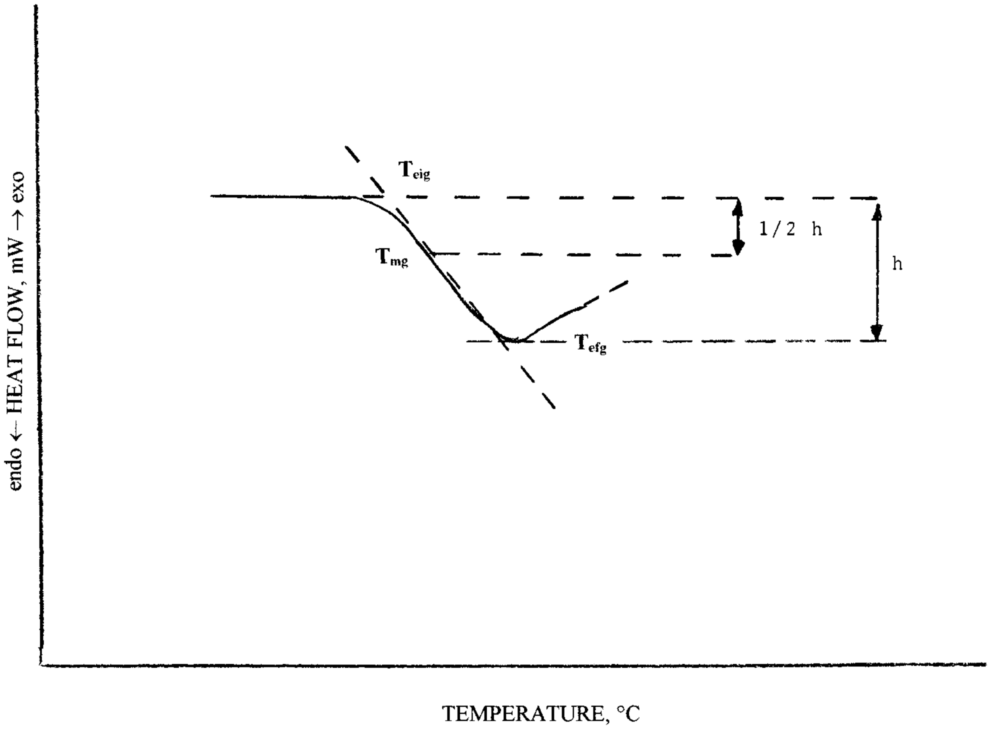

FIG. 2 Assignment of Glass Transition of Poly(Methyl Methacrylate) (PMMA)

(polyurethane, polystyrene, and epoxy glass composite) were determined in six laboratories.

12.3 *Precision*:

12.3.1 Within laboratory variability may be described using the repeatability value (*r*) obtained by multiplying the standard deviation by 2.8. The repeatability value estimates the 95 % confidence limit.

12.3.1.1 Repeatability values of *r* = 2.3 and 1.0°C were obtained for the melting and crystallization onset temperatures for polypropylene, respectively.

12.3.1.2 Repeatability values of *r* = 2.2, 1.9, and 2.8°C were obtained for the glass transition midpoint temperature for a polyurethane, a polystyrene, and a epoxy glass composite, respectively.

12.3.2 Between-laboratory variability may be described using the reproducibility value (*R*) obtained by multiplying the standard deviation by 2.8. The reproducibility value estimates the 95 % confidence limit.

12.3.2.1 Reproducibility values of *R* = 2.7 and 4.2°C were obtained for melting and crystallization onset temperatures for polypropylene, respectively.

12.3.2.2 Reproducibility values of *R* = 4.2, 2.0, and 5.2°C were obtained for the glass transition midpoint temperature for a polyurethane, a polystyrene, and a epoxy glass composite, respectively.

12.4 *Bias*:

12.4.1 The bias of this test method for determining the first-order melting and crystallization temperature is essentially the same as the bias for Test Method E 793 and is estimated to be ±1.1°C (RR:E37-1001).

12.4.2 The bias for this test method for determining the glass transition temperature is undetermined as there are no reference values available for the materials tested.

13. Keywords

13.1 crystallization temperature; glass transition; differential scanning calorimetry (DSC); first-order transition; melting temperature; polymer; transition temperature

REFERENCES

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(**3**) Garn, P. D., *Thermoanalytical Methods of Investigation*, Academic Press, New York, NY, 1965, p. 95.

(**4**) Wunderlich, B., *Differential Thermal Analysis in Physical Methods of Chemistry*, Vol 1, Part V, A. Weissberger and B. W. Rossiter, eds., John Wiley and Sons, Inc., New York, NY, 1971.

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SUMMARY OF CHANGES

This section identifies the location of selected changes to this test method. For the convenience of the user, Committee D-20 has highlighted those changes that may impact the use of this test method. This section may also include descriptions of the changes or reasons for the changes, or both.

D 3418 – 99:

(*1*) Revisions have been made to modernize this test method and make it compatible with Practice E 1953. Upgrades have been made to the title and Sections 1, 2, 5, 7, 9, 10, 11, and 12.