



Standard Test Method for Transition Temperatures of Polymers By Differential Scanning Calorimetry¹

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 and enthalpies of fusion and crystallization of polymers by differential scanning calorimetry.

NOTE 1—True heats of fusion are to be determined in conjunction with structure investigation, and frequently, specialized crystallization techniques are needed.

1.2 This test method is applicable to polymers in granular form or to any fabricated shape from which it is possible to cut appropriate specimens.

1.3 The normal operating temperature range is from the cryogenic region to 600°C. Certain equipment allows the temperature range to be extended.

1.4 The values stated in SI units are the standard.

NOTE 2—This test method does not apply to all types of polymers as written (see 6.8).

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, -2, -3. The ISO procedures provide additional information not supplied by this test method.

2. Referenced Documents

2.1 ASTM Standards:²

- E 473 Terminology Relating to Thermal Analysis
- E 793 Test Method for Enthalpies of Productivity and Crystallization by Differential Scanning Calorimetry
- E 794 Test Method for Melting and Crystallization Tem-

perature by Thermal Analysis

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

E 968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters

E 1142 Terminology Relating to Thermophysical Properties

E 1356 Test Method for Glass Transition Temperatures by Differential Scanning Calorimetry or Differential Thermal Analysis

E 1953 Practice for Description of Thermal Analysis Apparatus

2.2 ISO Standards:³

ISO 11357-1 Plastics—Differential Scanning Calorimetry (DSC)—Part 1: General Principles

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

ISO 11357-3 Plastics—Differential Scanning Calorimetry (DSC)—Part 3: Determination of Temperature and Enthalpy of Melting and Crystallization

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 under a specified purge gas at a controlled flow rate and continuously monitoring with a suitable sensing device the difference in heat input between a reference material and a test material due to energy changes in the material. A transition is 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. Areas under the crystallization exotherm or fusion endotherm of the test materials are compared against the respective areas obtained by the treatment of a well-characterized standard.

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

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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.

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

5. Significance and Use

5.1 Thermal analysis provides a rapid method for measuring transitions due to morphological or chemical changes, in a polymer as it is heated/cooled through a specified temperature range. Change in specific heat capacity, heat flow and temperature values are determined for these transitions. Differential scanning calorimetry is 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 have been measured with the aid of this technique; such reactions include oxidation, curing of thermosetting resins, and thermal decomposition.

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

6. Interferences

6.1 Differences in heating or cooling rate as well as the final heating and cooling temperature have an effect on the measured results, especially on the enthalpy of fusion or crystallization. Therefore, departure from conditions specified for a given polymer is not permitted.

6.2 The presence of impurities is known to affect the transition temperature, particularly if an impurity tends to form solid solutions, or to be miscible in the melt phase.

6.3 Uncertain radiation losses at temperatures higher than 400°C have been known to affect the accuracy of results at times.

6.4 Since particle size has an effect upon detected transition temperatures, the specimens to be compared shall be approximately the same particle size (1-5).⁴

6.5 In cases that specimens react with air during the temperature cycle, provision shall be made for running the test under an inert gas blanket to avoid any incorrect measurement. Since some materials degrade near the melting region, care must be used to distinguish between degradation and transition.

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

6.7 It is possible that toxic or corrosive effluents are released when heating the material, and be harmful to the personnel or to the apparatus.

6.8 Not all polymers lend themselves to the exact terms of this test method. For some polymers such as polyarylamides, crystallization is only possible from solution. For other polymers such as crystallizable polystyrene, annealing is only possible above their glass transition temperatures. When this test method is used for polymers of this type, carefully annealed samples must be tested without conditioning.

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 $\pm 0.01^\circ\text{C}$.

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 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 sub-ambient temperatures.

7.1.2 *Temperature Controller*, 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 0.5 to 20°C/min constant to $\pm 0.1^\circ\text{C}/\text{min}$ or at an isothermal temperature constant to $\pm 0.1^\circ\text{C}$.

7.1.3 *Recording Device*, 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 *Software*, for integrating areas under endothermic valleys or exothermic peaks, or both.

7.1.5 *Containers* (pans, crucibles, 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.

7.1.6 Cooling capability to hasten cool down from elevated temperatures, to provide constant cooling rates of 0.5 - 20 °C/min to obtain repeatable crystallization temperatures, to achieve sub-ambient operation, or to sustain an isothermal sub-ambient temperature, or combination thereof.

7.2 *Balance*, capable of weighing to ± 10 μg .

8. Sample

8.1 *Powdered or Granular Specimens*—Avoid grinding if the preliminary thermal cycle as outlined in 10.1.3 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) or other appropriate means to appropriate size, in thickness or diameter and length that will best fit the specimen containers as in 7.1.5 and will approximately meet 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.

8.4 Use any shape or form listed in 8.1-8.3 except when conducting referee tests that shall be performed on films as specified in 8.3.

⁴ The boldface numbers in parentheses refer to the list of references at the end of this test method.

9. Calibration

9.1 The purge gas shall be used during calibration.

9.2 Calibrate the DSC temperature signal using Practice E 967 and the same heating rate to be used in this test method (10°C/min) (see Note 5).

9.3 Calibrate the DSC heat flow signal using Practice E 968 and the same heating rate to be used in this test method (10°C/min) (see Note 5).

9.4 Some instruments allow for the temperature and heat flow calibration to be performed simultaneously. In such cases, use the same heating rate for this method (10°C/min) and follow the manufacturer's instruction.

NOTE 5—Use of other heating rates is permitted but shall be reported. It is the responsibility of the user of other rates to demonstrate equivalency to this test method.

10. Procedure

10.1 *For First-Order Transition (melting and crystallization):*

10.1.1 The purge gas shall be used during testing. The flow rate of the gas shall be the same as used in the calibration (9.1).

10.1.2 Use a specimen mass appropriate for the material to be tested. In most cases a 5-mg specimen mass is satisfactory. Avoid overloading. Weigh the specimen to an accuracy of $\pm 10 \mu\text{g}$.

10.1.2.1 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.

10.1.3 Perform and record a preliminary thermal cycle by heating the sample at a rate of 10°C/min from at least 50°C below to 30°C above the melting temperature to erase previous thermal history.

NOTE 6—The selection of temperature and time are critical when the effect of annealing is studied. Minimize the time of exposure to high temperature to avoid sublimation or decomposition. In some cases it is possible that the preliminary thermal cycle will 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.

10.1.4 Hold the temperature for 5 min (10.1.3).

NOTE 7—In cases that high-temperature annealing cause polymer degradation, the use of shorter annealing times is permitted but shall be reported.

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

10.1.6 Hold the temperature for 5 min.

10.1.7 Repeat heating at a rate of 10°C/min and record the heating curve. Use this curve to calculate the enthalpies of transition.

10.1.8 Measure the temperatures for the desired points on the curves: T_{eim} , T_{pvm} , T_{efm} , T_{eic} , T_{pc} , and T_{efc} (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 8—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 The purge gas shall be used during testing. The flow rate of the gas shall be the same as used in the calibration (9.1).

10.2.2 Use a specimen mass appropriate for the material to be tested. In most cases, a 10 to 20-mg specimen mass is satisfactory. Weigh the specimen to an accuracy of $\pm 10 \mu\text{g}$.

10.2.3 Perform and record a preliminary thermal cycle by heating the sample at a rate of 20°C/min from at least 50°C below to 30°C above the melting temperature to erase previous thermal history.

10.2.4 Hold the temperature for 5 min. (See Note 7.)

10.2.5 Quench cool to at least 50°C below the transition temperature of interest.

10.2.6 Hold the temperature for 5 min.

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

10.2.8 The glass transition is more pronounced at faster heating rates. A heating rate of 20°C/min is used for T_g measurements. The instrument shall be calibrated at this heating rate. If both first- and second-order transitions (T_m and T_g , respectively) are to be determined in the same run, use procedure 10.1 and determine results from the second heating step (10.1.7).

NOTE 9— T_g obtained using Procedure 10.1 will be different from T_g measured using procedures 10.2.3-10.2.7. The heating rate must be reported as described in 12.1.3.

10.2.9 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 10). For most applications, the T_{mg} temperature is more meaningful. In those cases, designate T_{mg} as the glass transition temperature (T_g) in place of the extrapolated onset for the glass transition curve.

NOTE 10—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.

11. Calculation for Heat of Fusion and Crystallization

11.1 Construct a baseline by connecting the two points at which the melting endotherm or freezing exotherm deviate from the relatively straight baseline, caused by a signal that is

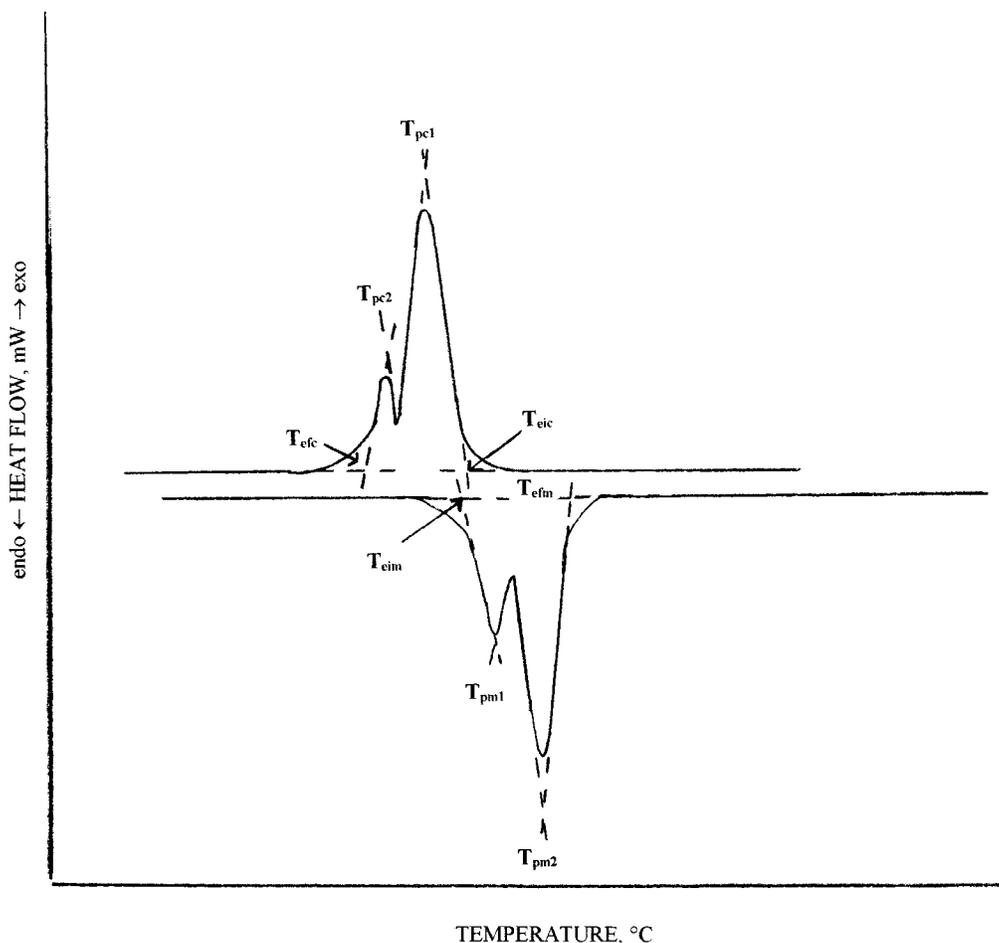


FIG. 1 First-Order Transition of Nylon

proportional to the difference in heat flow between the reference and specimen capsules (Fig. 3 and Fig. 4).

11.2 The method described in 11.1 is not applicable for certain materials. In such cases, other graphical means must be developed for enclosing the peak areas as agreed upon between the manufacturer and the purchaser (4-8).

11.3 Integrate the area under the fusion heat flow endotherm or crystallization exotherm as a function of time to yield enthalpy or heat (mJ) of the transition.

11.4 Calculate the mass normalized enthalpy or heat of transition by dividing the enthalpy obtained in 11.3 by the mass of the test specimen. Report this mass normalized enthalpy of transition (J/g).

12. Report

12.1 Report the following information:

- 12.1.1 Complete identification and description of the material tested, including source, manufacturer's code,
- 12.1.2 Description of instrument used for the test,
- 12.1.3 Statement of the mass, dimensions, geometry, and materials of the specimen container, and the heating rate.
- 12.1.4 Description of temperature calibration procedure,
- 12.1.5 Identification of the sample atmosphere by purge gas flow rate, purity, and composition, including humidity, if applicable,

12.1.6 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} that are commonly used as single characteristic temperatures for the first-order transition of semicrystalline polymers but must be identified by including the subscript.

12.1.7 Heat of fusion or crystallization, or both, and,

12.1.8 Any side reaction (for example, crosslinking, thermal degradation, or oxidation), and the reaction identified if possible.

13. Precision and Bias

13.1 A complete Precision and Bias statement is not available.

13.1.1 The precision of this test method for measuring first-order melting and crystallization temperatures is essentially equivalent to the that of Test Method E 794 (RR:E37-1001).

13.1.2 The precision for measuring the glass transition temperature is essentially equivalent to that of Test Method E 1356 (RR:E37-1013).

13.1.3 The precision for measuring the enthalpies of melting and crystallization is essentially equal to the precision stated in Test Method E 793.

13.2 Precision:

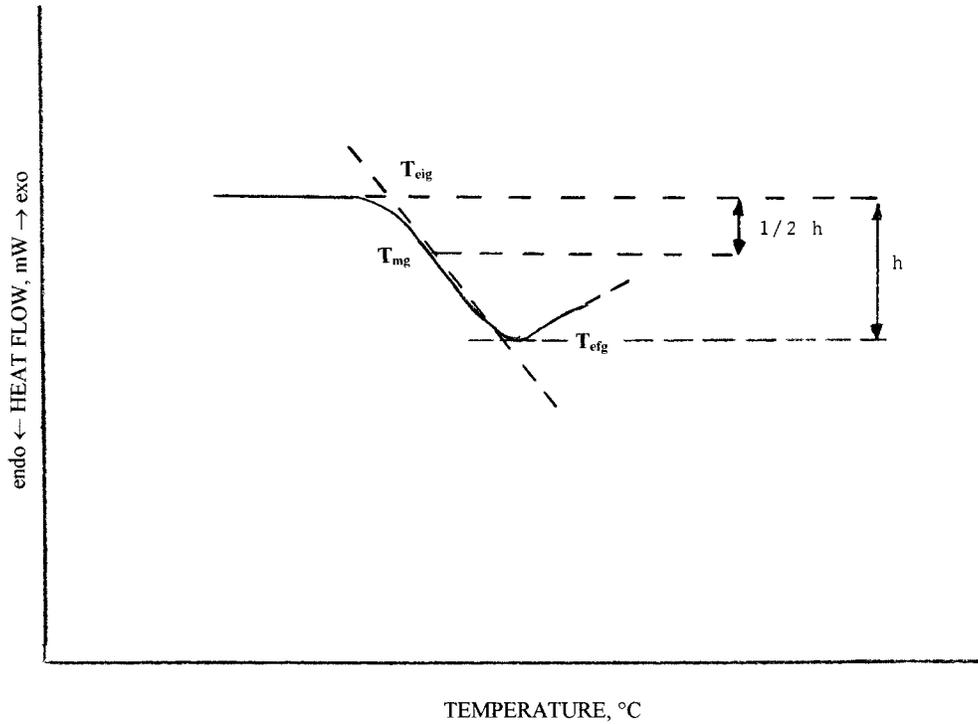


FIG. 2 Assignment of Glass Transition of Poly(Methyl Methacrylate) (PMMA)

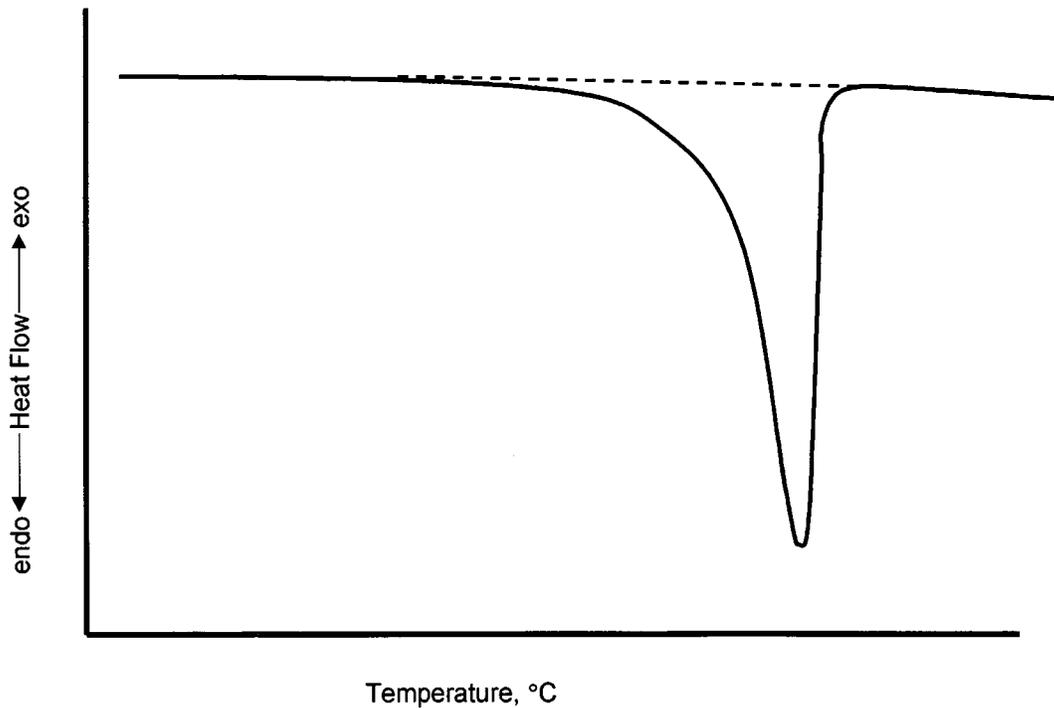


FIG. 3 Typical Heating Curve for Polyethylene

13.2.1 Describe the within laboratory variability using the repeatability value (r) obtained by multiplying the standard deviation by 2.8. The repeatability value estimates the 95 % confidence limit.

13.2.2 An interlaboratory study was conducted in 1998 in which the temperature of melting and crystallization of a

polypropylene sample were determined in nine laboratories. Repeatability values of $r = 2.3$ and 1.0°C were obtained for the melting and crystallization onset temperatures, respectively.

13.2.3 An interlaboratory study was conducted in 1984 in which glass transition temperature for three materials were determined in six laboratories. Repeatability values of $r = 2.2$,

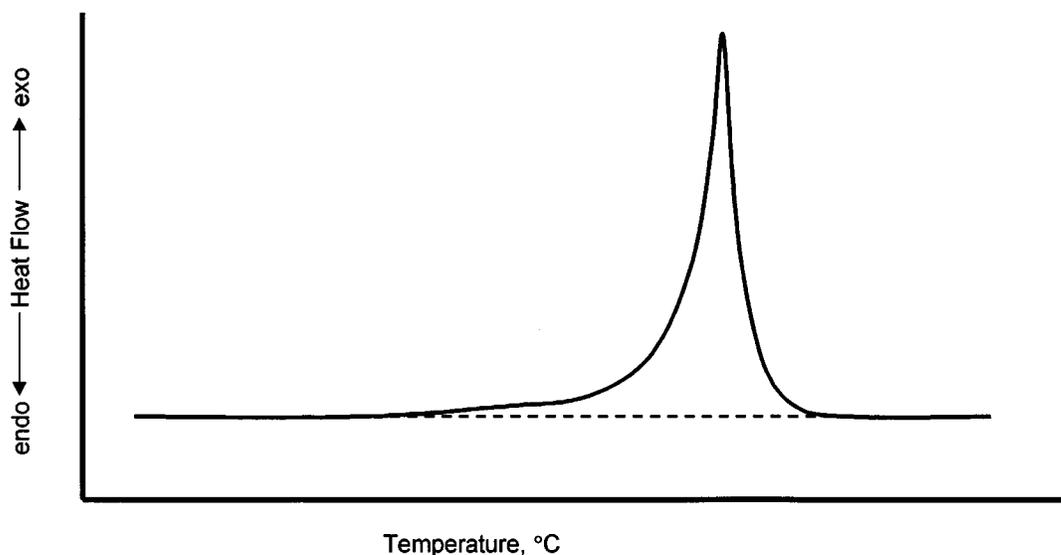


FIG. 4 Typical Freezing Curve for Polyethylene

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.

13.2.4 An interlaboratory study was conducted in 1998 in which the enthalpy of fusion and crystallization for a polypropylene and a metallic sample was tested by nine laboratories. Repeatability values of $r = 10$ and 3.4 % were obtained for enthalpy of fusion and crystallization, respectively.

13.2.5 Describe the between-laboratory variability using the reproducibility value (R) obtained by multiplying the standard deviation by 2.8. The reproducibility value estimates the 95 % confidence limit.

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

13.2.7 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.

13.2.8 Reproducibility values of $R = 22$ and 7.3 % were obtained for the enthalpy of melting and crystallization, respectively.

13.3 Bias:

13.3.1 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 794 and is estimated to be $\pm 1.1^\circ\text{C}$ (RR:E37-1001).

13.3.2 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.

13.3.3 An estimation of bias was obtained by comparing the enthalpy of fusion obtained for a metallic tin sample to literature values for this material. The bias was found to be less than 0.1 %. This indicates an absence of significant bias.

14. Keywords

14.1 crystallization; crystallization temperature; differential scanning calorimetry (DSC); enthalpy; first-order transition; glass transition; heat of crystallization; heat of fusion; heat of transition; melting; melting temperature; polymer; transition temperature

REFERENCES

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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 D20 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 – 03:

- (1) Combined D 3417 and D 3418 into one standard.
- (2) Updated the reference documents.

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, 12, and 13.

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