Designation: D 4591 – 01

Standard Test Method for Determining Temperatures and Heats of Transitions of Fluoropolymers by Differential Scanning Calorimetry[1]

This standard is issued under the fixed designation D 4591; 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 defines conditions for the use of differential scanning calorimetry (DSC) with fluoropolymers. It covers the use of DSC analyses with the fluoropolymers, PTFE, PVDF, PCTFE, and PVF and their copolymers PFA, FEP, ECTFE, EFEP, VDF/HFP, VDF/TFE/HFP, VDF/CTFE. The test method is applicable to the analysis of powders as well as samples taken from semi-finished or finished products. The nature of fluoropolymers is such that special procedures are needed for running DSC analysis and interpreting the results.

1.2 The values stated in SI units as detailed in IEEE/ASTM SI 10 are to be regarded as the standard.

1.3 *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 1—There is currently no ISO standard that duplicates this test method. Pending ISO 12086-1 and ISO 12086-2 cover similar testing and reference this test method for testing conditions.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 1600 Terminology for Abbreviated Terms Relating to Plastics

D 3417 Test Method for Heats of Fusion and Crystallization of Polymers by Thermal Analysis

D 3418 Test Method for Transition Temperatures of Polymers by Thermal Analysis

D 4894 Specification for Polytetrafluoroethylene (PTFE) Granular Molding and Ram Extrusion Materials

D 4895 Specification for Polytetrafluoroethylene (PTFE) Resins Produced From Dispersion

E 473 Terminology Relating to Thermal Analysis

E 793 Test Method for Heats of Fusion and Crystallization by Differential Scanning Calorimetry

IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI) (the Modern Metric System)

2.2 *ISO Standards:*[3]

ISO 12086-1 Plastics—Fluoropolymer Dispersion and Molding and Extrusion Materials—Part 1: Designation and Specification

ISO 12086-2 Plastics—Fluoropolymer Dispersion and Molding and Extrusion Materials—Part 2: Preparation of Test Specimen and Determination of Properties

3. Terminology

3.1 *Definitions:*

3.1.1 *differential scanning calorimetry (DSC)*—a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature, while the substance and reference material are subjected to a controlled increase or decrease in temperature.

3.1.2 Refer to Terminology E 473 for general terminology used in this test method.

3.2 *Abbreviated Terms:*

3.2.1 Abbreviations used in this test method are in accordance with Terminology D 1600.

3.2.2 PTFE—polytetrafluoroethylene.

3.2.3 PFA—perfluoro(alkoxy alkane) resin.

3.2.4 FEP—perfluoro(ethylene-propene) copolymer.

3.2.5 ETFE—ethylene-tetrafluoroethylene copolymer.

3.2.6 PVDF—poly(vinylidene fluoride).

3.2.7 PCTFE—polymonochlorotrifluoroethylene.

3.2.8 ECTFE—ethylene-monochlorotrifluoroethylene copolymer.

3.2.9 EFEP—ethylene-perfluoroethylene-propene copolymer.

3.2.10 VDF/HFP—vinylidene fluoride-hexafluoropropene copolymer.

3.2.11 VDF/TFE—vinylidene fluoride-tetrafluoroethylene copolymer.

3.2.12 VDF/TFE/HFP—vinylidene fluoride-tetrafluoroethylene-hexafluoropropene copolymer.

---

[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.15 on Thermoplastic Materials.

Current edition approved June 10, 2001. Published August 2001. Originally published as D 4591 – 87. Last previous edition D 4591 – 97.

[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.**

3.2.13 VDF/CTFE—vinylidene fluoride-chlorotrifluoroethylene copolymer.

3.2.14 PVF—poly(vinyl fluoride).

3.2.15 SSG—standard specific gravity.

4. Significance and Use

4.1 DSC analysis may be used with fluoropolymers to achieve at least four different objectives as follows:

4.1.1 To measure transition temperatures to aid in the identification of the various fluoropolymers, individually or in mixtures;

4.1.2 To compare the relative levels of crystalline content of two or more specimens of a sample of a fluoropolymer relative to another sample by measuring the heat of fusion;

NOTE 2—Absolute values of crystalline content cannot be determined until values for heats of fusion of the completely crystalline polymers are available.

4.1.3 To characterize PTFE (DSC thermal curves determined on powders or products of PTFE that have never been melted convey appreciable information about details of morphology and molecular structure);[4]

4.1.4 To supplement the test for standard specific gravity (SSG) described in Specifications D 4894 and D 4895 by using the heat of crystallization of pure PTFE homopolymer, depending on the relative molecular weight of the specimen. The scopes of these specifications, however, include PTFE resins modified with small amounts of comonomers, and many commercial PTFE resins are modified in this manner. These modifications can have profound effects on crystallization behavior. Published relationships[4] between heat of crystallization and molecular weight refer to pure PTFE homopolymers and, therefore, cannot be applied to the modified resins.

5. Apparatus

5.1 *Differential Scanning Calorimeter*, capable of heating and cooling rates of at least 10.0 °C/min and of recording automatically the differential heat flow between a specimen and a reference material as a function of time, both to the required sensitivity and precision. For comparison purposes, the same heating rate shall be used for all calibrations and test runs. Thermal curves are recorded using a computerized data collection system or on a time-based recorder. The resulting curves are used for the measurement of peak areas either by computer integration or an alternative area measuring procedure. The instrument should have a sensitivity for heat flow sufficient to provide a precision of ±1 % when run using a suitable standard for calibration, such as indium. The instrument must have a precision of ±1 % for either the computerized data collections or over a time-base range of 0.1 to 2.0 min/cm of chart.

NOTE 3—Most DSC systems report data with a temperature ordinate. The temperature values are directly related to time based on the heating or cooling rate. Integrated areas measured from the DSC curves will be directly proportional to the differential caloric input.

NOTE 4—Noncomputerized area measurement shall be done with a precision of ±1 % or better.

5.2 *Specimen Holders and Covers*, made from aluminum or other materials of high thermal conductivity that do not react with the specimen. It is preferable to use holders designed for the particular DSC instrument being used. For holders for which the cover has the shape of a small cup, the top should be inserted with the open side of the cup up.

5.3 *Nitrogen*, or other inert gas supply for purging purposes.

5.4 *Balance*, with capacity greater than 15 mg, capable of weighing to the nearest 0.01 mg.

6. Procedure

6.1 *General Requirements*—In general, the detailed methods of Test Method D 3417 or Test Method D 3418 shall be used whenever possible. There are instances, however, when following the procedures of Test Method D 3417 or Test Method D 3418 will not give the desired results, will not provide information needed for proper interpretation of the resultant thermal curve, or will require more time for the analysis than need be spent for results having suitable precision. Examples of these instances include the following:

6.1.1 The requirement that scans be started at room temperature, a provision usually not required with all fluoropolymers;

6.1.2 The practice of running only a heating curve although the cooling curve provides more information with many fluoropolymers, and

6.1.3 At times the thermal curve that results from the analysis provides information that cannot be interpreted in a useful manner by the procedures of Test Method D 3417 or Test Method D 3418 but can be interpreted following the procedures of Section 7.

6.2 *Calibration*—The procedures for calibration provided in Test Method E 793 should be used. The comments in Test Method D 3417 are helpful and should be reviewed. The calibration is carried out by using an appropriate amount of at least two selected standards weighed to the nearest 0.01 mg. The standard materials should be selected so that their range includes the first-order transition temperature(s) of the fluoropolymer being tested. Appropriate materials are given in Table 1 of Test Method E 793 and NIST Standard Reference Materials. The instrument calibration can be validated using only one standard between calibrations.

6.3 A standard specimen mass shall be in the range of 9 to 10 mg weighed to an accuracy of 0.01 mg. For routine analysis, a nonstandard specimen size may be used in cases where equivalence to the standard mass has been established for particular properties. A specimen mass different from the standard shall be reported.

NOTE 5—Thermal curves from such analyses not using the standard specimen mass range may not compare with curves obtained using the standard mass range. Due to the sensitivity of the peak, T_m, to the specimen size, the results may be outside the expected precision and bias.

---

[4] Sperati, C. A., "Polytetrafluoroethylene: History of Its Development and Some Recent Advances" (67 references), *High Performance Polymers: Their Origin and Development*, Seymour and Kirshenbaume (eds), Marcel Deckker, New York, 1986, p. 274.