



Designation: D4591 – 22

Standard Test Method for Determining Temperatures and Heats of Transitions of Fluoropolymers by Differential Scanning Calorimetry¹

This standard is issued under the fixed designation D4591; 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 U.S. Department of Defense.

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, MFA, 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—There is currently no ISO standard that duplicates this test method. ISO 20568-1 and ISO 20568-2 cover similar testing and reference this test method for testing conditions.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

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 March 15, 2022. Published March 2022. Originally approved in 1987. Last previous edition approved in 2017 as D4591 - 17. DOI: 10.1520/D4591-22.

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.

[D1600 Terminology for Abbreviated Terms Relating to Plastics](#)

[D3418 Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry](#)

[D4894 Specification for Polytetrafluoroethylene \(PTFE\) Granular Molding and Ram Extrusion Materials](#)

[D4895 Specification for Polytetrafluoroethylene \(PTFE\) Resin Produced From Dispersion](#)

[E473 Terminology Relating to Thermal Analysis and Rheology](#)

[E793 Test Method for Enthalpies 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 20568-1 Plastics—Fluoropolymer Dispersion and Molding and Extrusion Materials—Part 1: Designation and Specification](#)

[ISO 20568-2 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 [E473](#) 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 [D1600](#).

3.2.2 PTFE—polytetrafluoroethylene.

3.2.3 PFA—perfluoro(alkoxy alkane) resin.

3.2.4 FEP—perfluoro(ethylene-propene) copolymer.

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

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

- 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.
- 3.2.13 VDF/CTFE—vinylidene fluoride-chlorotrifluoroethylene copolymer.
- 3.2.14 PVF—poly(vinyl fluoride).
- 3.2.15 MFA—perfluoromethylvinylether-tetrafluoroethylene copolymer.
- 3.2.16 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 The heat of crystallization of pure PTFE homopolymer is depending on the relative molecular weight of the specimen. Some PTFE resins are modified with small amounts of comonomers. These modifications have profound effects on crystallization behavior and shall be considered when evaluating the results.

4.1.4 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

4.1.5 To supplement the test for standard specific gravity (SSG) described in Specifications **D4894** and **D4895** 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 relationships⁴ between heat of crystallization and molecular weight refer to pure PTFE homopolymers and, therefore, cannot be applied to the modified resins.

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 Dekker, New York, 1986, p. 274.

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 $\pm 1\%$ when run using a suitable standard for calibration, such as indium. The instrument must have a precision of $\pm 1\%$ 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 $\pm 1\%$ 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, Test Method **D3418** shall be used whenever possible. There are instances, however, when following Test Method **D3418** 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 At times the thermal curve that results from the analysis provides information that cannot be interpreted in a useful manner by Test Method **D3418**, but can be interpreted following the procedures of Section 7.

6.2 *Calibration*—The procedures for calibration provided in Test Method **E793** shall be used. The comments in Test Method **D3418** are helpful when reviewed. The calibration is carried out by using an appropriate amount of at least two selected standards weighed to the nearest 0.01 mg. Select the standard materials so that their range includes the first-order transition temperature(s) of the fluoropolymer being tested. It has been

found that only one standard is needed to validate the instrument 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.

6.4 Place the test specimen in the DSC sample pan, cover with pan cover, and crimp. Place the pan with specimen in the DSC sample holder or cell at the heating cycle starting temperature.

6.5 Heating and cooling rates of 10°C/min shall be standard (except as noted in Table 1). Other heating rates may be useful for some routine analyses. Any rates different from the standard must be reported and thermal curves from such analyses must not be used in comparison with curves obtained using the standard rate.

NOTE 6—Other heating rates will change the observed melting and cooling temperature values.

6.6 Before starting the scan at the controlled rate, heat the specimen at the highest rate possible with the instrument being used to the temperature shown in Table 1 for the fluoropolymer being tested. The time required to reach thermal equilibrium at the starting temperature will depend on the particular instrument being used. If heats of crystallization are being determined, stop the heating at the end temperature given in

Table 1. Use a dwell time long enough to remove (or normalize) any homogenous crystal nucleation effects of the polymer before starting the cooling. For PVDF a dwell time of ten minutes at 210°C is required. DSC analysis used to determine the presence of other components in the specimens should usually be started at room temperature.

NOTE 7—Residual homogeneous crystal nuclei can affect the values of T_m , T_c , and heats of transition.

7. Calculation

7.1 Determining Transition Temperatures—As illustrated in both Fig. 1 and in Test Method D3418, the temperature of a melting peak on a DSC thermal curve shall be designated T_m^1 , T_m^2 , etc., numbered in order of increasing temperature. The temperature at which a tangent to the curve intercepts an extension of the base line on the low-temperature side shall be designated T_f , and the temperature at which a tangent to the curve intercepts an extension of the base line on the high-temperature side shall be designated T_e .

NOTE 8—Fluoropolymers can have various crystal forms or undergo reorganization. Therefore, the resulting DSC curve can have two or more peaks or peaks with pronounced shoulders. The T_m^1 value of one sample with one peak may be the same as the T_m^2 value of another sample with two peaks.

7.1.1 Fig. 1 was selected to show two endothermic peaks during a melting cycle, and the peaks are identified on the figure. Determination of the temperatures for crystallization is carried out in a comparable manner, as shown both in Fig. 2 and in Figure 1 of Test Method D3418.

7.2 Determining Heats of Transition—Calculation of heats of fusion or crystallization shall be done in accordance with Test Method D3418. Instrumental determination of heats of transition requires temperature ranges to determine heat content. Due to instrument start-up effects that can last up to 1 or 2 min, the integration range should be 10 to 20°C above the starting and below the final temperature. A smaller integration range would be $T_f - 20$ or 30°C and $T_e + 10$ or 20°C . The calculated heat value should not be sensitive to small changes (5°C in the integration range).

NOTE 9—Multiple crystal forms and the complicated morphology of

TABLE 1 Recommended Temperature Limits for DSC Measurements for Various Fluoropolymers^{A, B}

Fluoropolymer	Heating Curve		Dwell Time, min	Cooling Curve		Rate, °C/min	Typical Values, °C
	Start, °C	End, °C		Start, °C	End, °C		
(homopolymers)							
PTFE	270	380	5	380	270	10	315–360
PCTFE	130	250		250	195	10	200–225
				195	130	0.2	
PVDF	25	210	10	210	25	10	155–180
(copolymers)							
PFA	200	350		350	200	10	280–330
MFA	200	350		350	200	10	260–290
FEP	200	320		320	200	10	240–290
ETFE	140	320		320	140	10	210–270
ECTFE	200	300		300	200	10	230–250
VDF/HFP	25	210	10	210	25	10	130–165
VDF/CTFE	25	210	10	210	25	10	90–170
VDF/TFE	25	200	10	200	25	10	100–150
VDF/TFE/HFP	25	150	10	150	25	10	<130
VDF/TFE/HFP	25	210	10	210	25	10	>130

^AReport peaks (and shoulders) from lowest to highest (for example, $T_m^1 < T_m^2 < T_m^3 \dots$).

^BThe integration range should be 10 to 20°C above the starting and below the final temperature. A smaller integration range would be $T_f - 20$ or 30°C and $T_e + 10$ or 20°C . The calculated heat value should not be sensitive to small changes (5°C in the integration range).

^CTypical values cited represent an expected range of peak values for this test. These values shall not be used for specifications. Copolymer peak values (and intensities) will vary with comonomer ratios and may not be within the cited ranges.

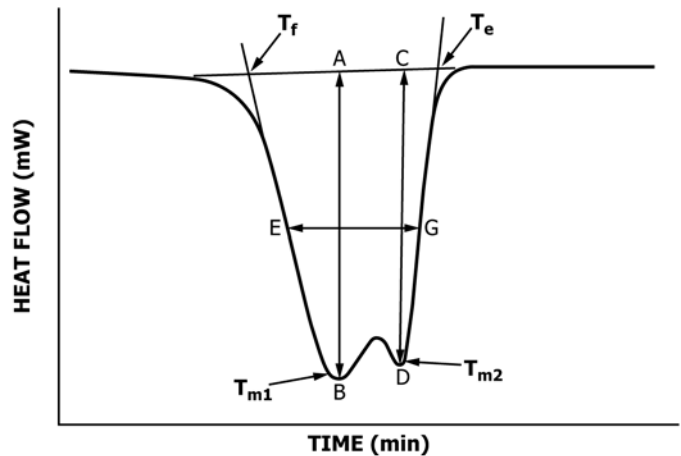


FIG. 1 Heating Curve