



Designation: D 4591 – 9701

## Standard Test Method for Determining Temperatures and Heats of Transitions of Fluoropolymers by Differential Scanning Calorimetry<sup>1</sup>

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 ( $\epsilon$ ) 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 ~~Practice E 380~~ IEEE/ASTM SI 10 are to be regarded as the ~~standard and the practices of Practice E 380 incorporated herein~~ 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:

D 1600 Terminology for Abbreviated Terms Relating to Plastics<sup>2</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.15 on Thermoplastic Materials. Current edition approved ~~Sept. 10, 1997~~ June 10, 1997; 2001. Published ~~March 1998~~ August 2001. Originally published as D 4591 – 87. Last previous edition D 4591 – 93a7.

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

D 3417 Test Method for Heats of Fusion and Crystallization of Polymers by Thermal Analysis<sup>3</sup>

D 3418 Test Method for Transition Temperatures of Polymers by Thermal Analysis<sup>3</sup>

D 4894 Specification for Polytetrafluoroethylene (PTFE) Granular Molding and Ram Extrusion Materials<sup>4</sup>

D 4895 Specification for Polytetrafluoroethylene (PTFE) Resins Produced From Dispersion<sup>4</sup>

~~E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System) 473 Terminology Relating to Thermal Analysis<sup>5</sup>~~

~~E 473 Terminology Relating to Thermal Analysis<sup>5</sup>~~

~~E 793 Test 793 Test Method for Heats of Fusion and Crystallization by Differential Scanning Calorimetry<sup>5</sup>~~

IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI) (the Modern Metric System)<sup>6</sup>

2.2 *ISO Standards:*<sup>7</sup>

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.

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

<sup>2</sup> *Annual Book of ASTM Standards*, Vol. 08.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 08.02.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 08.03.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>6</sup> Available from American National

<sup>6</sup> *Annual Book of ASTM Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036*, Vol 14.04.

<sup>7</sup> 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,

<sup>7</sup> Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, 1986, p. 274, NY 10036.

convey appreciable information about details of morphology and molecular structure);<sup>8</sup>

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 ~~Specification D 1457~~, these specifications, however, includes 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<sup>8</sup> 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  $\pm 1\%$  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, 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.

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.

<sup>8</sup> 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.

**TABLE 1 Recommended Temperature Limits for DSC Measurements and for Integrating DSC Thermal Curves with Various Fluoropolymers<sup>A, B</sup>**

Fluoropolymer	Heating Curve		Dwell Time, min	Cooling Curve		Rate, °C/min	Typical Values, <sup>C</sup> °C
	Start, °C	End, °C		Start, °C	End, °C		
(homopolymers)							
PTFE	270	380		380	270	10	315–360
PCTFE	180	250	5	250	195	10	
				195	180	0.2	200–225
PVDF	25	210	10	210	25	10	160–175
(copolymers)							
PFA	200	350		350	200	40	300–330
PFA	200	350		350	200	10	280–330
FEP	200	320		320	200	10	240–290
ETFE	200	320		320	200	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	130–165
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

<sup>A</sup> Report peaks (and shoulders) from lowest to highest (for example,  $T_m^1 < T_m^2 < T_m^3 \dots$ ).

<sup>B</sup> 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).

<sup>C</sup> Typical 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.

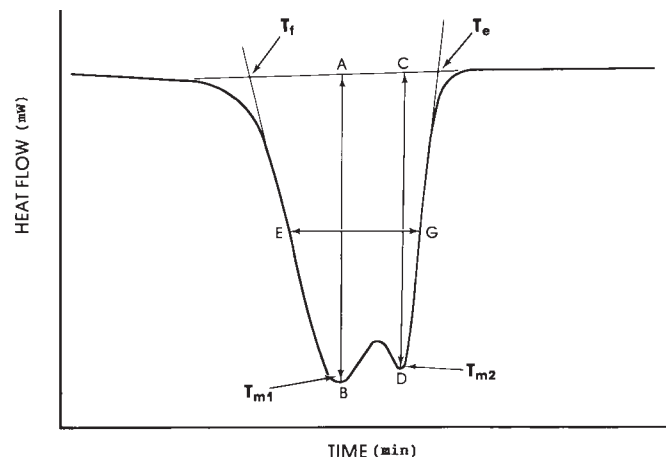
6.6 Before starting the scan at the controlled rate, heat the specimen at the highest rate possible with the instrument being used to the temperature shown in Table 1 for the fluoropolymer being tested. The time required to reach thermal equilibrium at the starting temperature will depend on the particular 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  $T_m$ ,  $T_e$ , and heats of transition.

## 7. Calculation

7.1 *Determining Transition Temperatures*—As illustrated in both Fig. 1 and in Test Method D 3418, 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. 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.



**FIG. 1 Heating Curve**

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 D 3418.

7.2 *Determining Heats of Transition*—Calculation of heats of fusion or crystallization shall be done in accordance to the procedure of Test Method D 3417. 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 VDF based copolymers can make it difficult to determine heats of transition on this polymer.

7.3 *Calculation of Results of Determinations* made in accordance with the objectives of 4.1 may include transition peaks or shoulders and transition heats. Additional determinations may use the steps listed in 7.3.1 and 7.3.2.

7.3.1 The ratio of peak heights may be useful in characterizing materials that show two or more distinct peaks or shoulders. This ratio is determined by dividing the height of a higher-temperature peak by the height of a peak at a lower temperature. Since this characteristic is reported as a ratio, the heights can be measured in any convenient units. This measurement is illustrated as  $CD/AB$  in Fig. 1.

NOTE 10—Great care must be taken to control the prior thermal history of the specimen before testing due to the sensitivity of this parameter on peak height obtained with polymorphic polymers.

7.3.2 A value for width at half-height of an endothermic peak is defined as a value (in degrees Celsius) that represents the width of a peak at a point one-half the distance between the base line and the maximum of the peak that is being characterized. Peak width at half-height is illustrated by the value of the line, EG, in Fig. 1.

## 8. Report

8.1 In addition to the items required by Test Method D 3417, the report for specimens analyzed in accordance with the objective of 4.1.3 may include values for ratio of peak heights and for width at half-height of the endothermic peak(s).

## 9. Precision and Bias

### 9.1 Precision:

9.1.1 *Repeatability*—See Test Methods D 3417 and D 3418.

9.1.2 *Reproducibility*—See Test Methods D 3417 and D 3418.

9.2 *Bias*—See Test Methods D 3417 and D 3418.

## 10. Keywords

10.1 differential scanning calorimetry; DSC; fluoropolymer(s); heats of fusion; melting point; thermal analysis

## SUMMARY OF CHANGES

This section identifies the location of selected changes to this test method. For the convenience of the user,

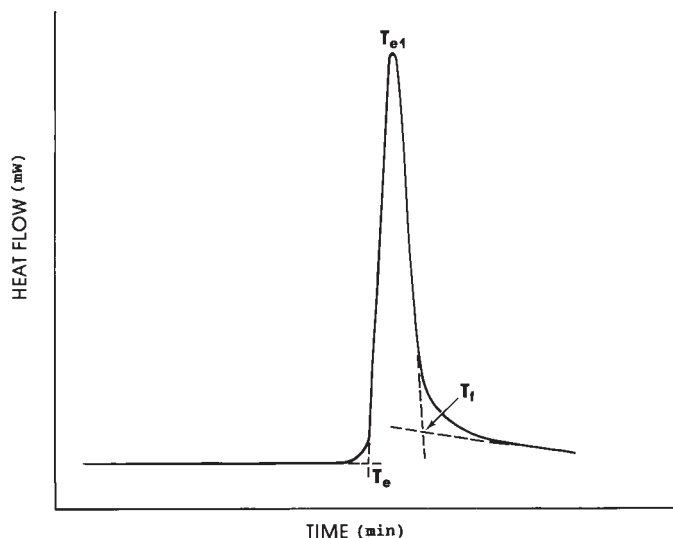


FIG. 2 Cooling Curve

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 4591 – 01:

(1) Reference to Practice E380 has been removed from the standard. IEEE/ASTM SI 10 has been added in its place.

(2) The typical temperature values range for PFA in Table 2 has been adjusted.

D 4591 – 97:

- (1) The ISO equivalency statement was corrected and the ISO standards were added to 2.2.
- (2) Reference to Specification D 1457 was deleted from 2.1 and 4.1.4.

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