Designation: F2625 – 10

StandardTest Method for Measurement of Enthalpy of Fusion, Percent Crystallinity, and Melting Point of Ultra-High-Molecular Weight Polyethylene by Means of Differential Scanning Calorimetry[1]

This standard is issued under the fixed designation F2625; 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 discusses the measurement of the heat of fusion and the melting point of ultra-high-molecular weight polyethylene (UHMWPE), and the subsequent calculation of the percentage of crystallinity.

1.2 This test method can be used for UHMWPE in powder form, consolidated form, finished product, or a used product. It can also be used for irradiated or chemically-crosslinked UHMWPE.

1.3 This test method does not suggest a desired range of crystallinity or melting points for specific applications.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3418 Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E793 Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry

E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters

E1953 Practice for Description of Thermal Analysis and Rheology Apparatus

3. Terminology

3.1 *Symbols:*

3.1.1 ΔH_f, *n*—theoretical heat of fusion of 100 % crystalline material (J/g).

3.1.2 ΔH_s, *n*—mass normalized heat of fusion of the test sample (J/g).

3.1.3 T_p, *n*—melting temperature at the peak of the melting endotherm (°C).

3.1.4 T_o, *n*—onset temperature of the melting endotherm (°C).

3.1.5 *%X, n*—percentage of crystallinity of material.

4. Summary of Test Method

4.1 This test method consists of placing a known mass of UHMWPE in a sample pan and heating the sample pan at a controlled temperature while measuring the heat flow to the sample pan and an empty reference pan. The area under the melting endotherm, indicative of the enthalpy of melting, is normalized with the sample mass. This value is then normalized with the theoretical enthalpy of melting of 100 % crystalline polyethylene to determine the percentage of crystallinity in the test sample.

5. Significance and Use

5.1 The crystallinity of UHMWPE will influence its mechanical properties, such as creep and stiffness. The reported crystallinity will depend on the integration range used to determine the heat of fusion, and the theoretical heat of fusion of 100 % crystalline polyethylene used to calculate the percent crystallinity in an unknown specimen. Differential scanning calorimetry is an effective means of accurately measuring both heat of fusion and melting temperature.

[1] This test method is under the jurisdiction of ASTM Committee F04 on Medical and Surgical Materials and Devices and is the direct responsibility of Subcommittee F04.15 on Material Test Methods.

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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.

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

6. Interferences

6.1 As machining processes can affect the crystalline structure of UHMWPE, care should be taken to obtain a representative sample away from the surface of a component if bulk measurements are desired.

6.2 The integration range used to measure the area of the melting endotherm will affect the measured value, as can heating rate. Therefore, the same ranges and test conditions must be used to ensure comparative results between laboratories.

6.3 The sample must not be too tall, as temperature gradients can then be generated in the sample, leading to erroneous results. It is suggested that the sample height should be less than 2 mm.

7. Apparatus

7.1 *Differential scanning calorimeter (DSC)*, as described in Test Method D3418 and Practice E1953.

7.2 *Aluminum DSC sample pans, crimpable.* Pans with venting holes are optional. The same type of pan must be used for the sample and reference pan.

7.3 *Analytical balance*, accurate to ±0.01 mg.

NOTE 1—According to Test Method E793, the repeatability standard deviation for the enthalpy of fusion of a polyolefin is 1.2 % when using a balance resolution of 0.01 mg.

8. Sampling, Test Specimens, and Test Units

8.1 The UHMWPE test specimen can be in the form of powder, flake, film, or pellet.

8.2 If a specimen is to be cut from a larger piece of polyethylene, it is recommended that a clean, sharp razor blade or other equivalent tool is used to cut a slice. The specimen must not be cut with a tool that generates enough heat to melt the UHMWPE. A core borer or punch can also be used to cut a sample from a film of UHMWPE.

8.3 The specimen should be fairly flat to ensure good thermal contact with the sample pan.

8.4 It is recommended that a minimum of three specimens per test location are tested.

NOTE 2—"Test location" is defined as the location on the sample where the DSC analysis is performed.

9. Preparation of Apparatus

9.1 The DSC test chamber should be purged with dry nitrogen, argon, or helium at a controlled flow rate during all tests. The same rate and gas should be used for all calibrations and tests. A purge rate of 10 to 50 ml/min is recommended.

10. Calibration and Standardization

10.1 Calibrate the temperature and heat flow signals of the DSC according to Test Method E967 and Practice E968, respectively. Typically, pure indium is used as a reference material. Both onset of the melting endotherm of the reference standard and the heat of fusion shall be reported and compared with published values (T_o = 156.6°C, Δ H_f = 28.57 J/g).[3] The DSC calibration should be verified on at least a monthly basis.

NOTE 3—The value of the ΔH_f will vary with the lot of the indium by as much as 3 %. Users should refer to the certificate of analysis for the ΔH_f of their specific lot of indium.

11. Procedure

11.1 Weigh an UHMWPE specimen on an analytical balance to a resolution of 0.01 mg. The specimen weight should be between 5 and 10 mg. The replicate specimens should all be within ±2 mg of each other.

11.2 Place the specimen into an aluminum DSC sample pan, cover with an aluminum lid, and crimp to seal the sample. If the DSC software allows compensation for the pan weight, record the weight.

11.3 Inspect the bottom of the sample pan to ensure that it is flat. If it is not flat, prepare another sample.

11.4 Place the sample pan into the DSC chamber, along with an empty reference pan.

11.5 Equilibrate the sample at ambient temperature for at least 3 min.

11.6 Heat the sample from ambient to 200°C at 10°C/min. An additional cooling cycle and heating run can be performed if desired.

12. Calculation or Interpretation of Results

12.1 Construct a straight baseline by connecting points from 50 to 160°C on the heating cycle. If the melting endotherm is not complete by 160°C, the user can change the position of the baseline construction on the high end, but must report the change. The area will depend on the integration range selected. An example is shown in Fig. 1.

12.2 Integrate the area under the fusion endotherm from the heating cycle to yield the enthalpy of the transition in units of Joules (J).

12.3 Calculate the mass normalized sample heat of fusion melting transition (ΔH_s) by dividing the calculated enthalpy in 12.2 by the mass of the sample in units of grams (g).

12.4 Calculate the percentage of crystallinity (%X) by dividing the mass normalized sample heat of fusion in 12.3 by the heat of fusion of 100 % crystalline polymer:

$$\%X = \Delta H_s / \Delta H_f \times 100 \quad (1)$$

where:

ΔH_f = 289.3 J/g.[4]

12.5 Calculate the peak melting temperature (T_p) and onset temperature (T_o) as indicated in Fig. 1. The onset temperature is determined from the line drawn from the peak temperature tangent to the melting endotherm and its intersection with the constructed baseline.

[3] Linde, D. R., ed., *CRC Handbook of Chemistry and Physics*, 76th ed, CRC Press, Boca Raton, 1995.

[4] Wunderlich, B. and Cormier, C. M., "Heat of fusion of polyethylene," *J. Polym. Sci.*, Vol A-2, No. 5, 1967, pp. 987–988.