INTERNATIONAL STANDARD

ISO 11357-3

Second edition
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Plastics — Differential scanning calorimetry (DSC) —

Part 3:
Determination of temperature and enthalpy of melting and crystallization

Plastiques — Analyse calorimétrique différentielle (DSC) —

Partie 3: Détermination de la température et de l'enthalpie de fusion et de cristallisation

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 11357-3 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

This second edition cancels and replaces the first edition (ISO 11357-3:1999), which has been technically revised. It also incorporates the Amendment, ISO 11357-3:1999/Amd 1:2005. The most important changes are the following:

- a specification of the preferred scanning rates of 10 K/min or 20 K/min has been given;
- Figure 1 has been updated to better reflect the profile of a real melting peak and y-axis directions specified in ISO 11357-1.

ISO 11357 consists of the following parts, under the general title *Plastics — Differential scanning calorimetry (DSC)*:

- *Part 1: General principles*
- *Part 2: Determination of glass transition temperature*
- *Part 3: Determination of temperature and enthalpy of melting and crystallization*
- *Part 4: Determination of specific heat capacity*
- *Part 5: Determination of characteristic reaction-curve temperatures and times, enthalpy of reaction and degree of conversion*
- *Part 6: Determination of oxidation induction time (isothermal OIT) and oxidation induction temperature (dynamic OIT)*
- *Part 7: Determination of crystallization kinetics*

Plastics — Differential scanning calorimetry (DSC) —

Part 3:
Determination of temperature and enthalpy of melting and crystallization

WARNING — The use of this part of ISO 11357 may involve hazardous materials, operations or equipment. This part of ISO 11357 does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this part of ISO 11357 to establish appropriate health and safety practices and to determine the applicability of regulatory limitations prior to use.

1 Scope

This part of ISO 11357 specifies a method for the determination of the temperatures and enthalpies of melting and crystallization of crystalline or partially crystalline plastics.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 472, *Plastics — Vocabulary*

ISO 11357-1:2009, *Plastics — Differential scanning calorimetry (DSC) — Part 1: General principles*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472 and ISO 11357-1 and the following apply.

3.1
melting
transition stage between a fully crystalline or partially crystalline solid state and an amorphous liquid of variable viscosity

NOTE The transition, also referred to as “fusion”, is characterised by an endothermic peak in the DSC curve.

3.2
crystallization
transition stage between an amorphous liquid state and a fully crystalline or partially crystalline solid state

NOTE The transition is characterised by an exothermic peak in the DSC curve. An exception to this definition is the case of liquid crystals, where the term “amorphous liquid” should be replaced by “ordered liquid”.

3.3
enthalpy of fusion
heat required to melt a material at constant pressure

NOTE It is expressed in kilojoules per kilogram (kJ/kg).

3.4
enthalpy of crystallization
heat released by the crystallization of a material at constant pressure

NOTE It is expressed in kilojoules per kilogram (kJ/kg).

4 Principle

See ISO 11357-1:2009, Clause 4.

5 Apparatus and materials

Apparatus and materials shall be in accordance with ISO 11357-1:2009, Clause 5.

6 Test specimen

The test specimen shall be in accordance with ISO 11357-1:2009, Clause 6.

7 Test conditions and specimen conditioning

The test conditions and specimen conditioning shall be in accordance with ISO 11357-1:2009, Clause 7.

8 Calibration

Calibration shall be in accordance with ISO 11357-1:2009, Clause 8.

9 Procedure

9.1 Setting up the apparatus

The setting up of the apparatus shall be in accordance with ISO 11357-1:2009, 9.1.

9.2 Loading the test specimen into the crucible

The loading of the test specimen shall be in accordance with ISO 11357-1:2009, 9.2.

Unless otherwise specified in the material standard, preferably use a mass of 5 mg to 10 mg for the measurement. In the case of high or low heats of transition, masses higher or lower than 5 mg to 10 mg may be used.

9.3 Insertion of crucibles

The insertion shall be in accordance with ISO 11357-1:2009, 9.3.

9.4 Temperature scan

9.4.1 Heating and cooling rates other than those recommended here may be used by agreement between the interested parties. In particular, high scanning rates result in better sensitivity of the recorded transition. On the other hand, low scanning rates provide better resolution in temperature and may be appropriate in the resolution of closely overlapping transitions.

9.4.2 Allow 5 min for a nitrogen pre-purge prior to beginning the heating cycle.

9.4.3 Perform and record a first heating run, preferably at a rate of 10 K/min or 20 K/min, heating the cell to a temperature high enough to erase the test material's previous thermal history, typically 30 °C above the extrapolated end melting temperature, T_{efm}.

DSC measurements on polymers are greatly affected by the thermal history and morphology of the sample and the test specimen. It is important that the preliminary heat cycle be performed and the measurements be taken from the second heat scan (see ISO 11357-1:2009, Annex E). In cases where the material is reactive or where it is desired to evaluate the properties of a specially pre-conditioned specimen, data may be taken during the first heating cycle. This deviation from the standard procedure shall be recorded in the test report.

9.4.4 Hold the temperature for 5 min.

NOTE Longer times may be acceptable or needed provided degradation of the polymer does not result.

9.4.5 Perform and record a cooling run at preferably the same rate used for the first and second heatings to approximately 50 °C below the extrapolated end crystallization temperature, T_{efc}.

NOTE Because of supercooling, crystallization does not occur until a sufficient temperature gradient is available, usually significantly below the melting temperature.

9.4.6 Hold the temperature for 5 min.

9.4.7 Perform and record a second heating run at preferably the same heating rate as the first heating and cooling runs (see 9.4.1) to approximately 30 °C higher than the extrapolated end melting temperature, T_{efm}.

NOTE It is important to create a defined thermal history in order to evaluate correct results.

9.4.8 Bring the apparatus to ambient temperature and remove the crucibles to determine if deformation of the crucible or specimen overflow has occurred.

9.4.9 Reweigh the crucible, with the test specimen, unless it is known that the material will suffer no loss in mass during the experiment.

10 Expression of results

10.1 Determination of transition temperatures

Scale the plot so that the peak covers at least 25 % of full scale. Construct a baseline to the peak (see Figure 1) by joining the peak initiation temperature, T_{im}, and end temperature, T_{fm}, at which the peak (endothermic peak for fusion, exothermic peak for crystallization) begins to deviate from the relatively straight baseline. If multiple peaks are present, a baseline should be drawn, covering all peaks. The evaluation should then be divided between each peak, in order to get the most correct enthalpy.

For a melting transition curve, measure and report the peak melting temperature, T_{pm}, for each peak.

Reporting onset of melting is acceptable if requested.

For a crystallization transition curve, measure and report for each peak:

- the extrapolated onset crystallization temperature, T_{eic};
- the peak crystallization temperature, T_{pc}.

Extrapolated onset and end temperatures need to be reported if the width of the peak is of interest.

10.2 Determination of enthalpies (see Figure 1)

Measure the area under the peak to the baseline constructed in accordance with 10.1.

Calculate the enthalpy of fusion, ΔH_{f} [enthalpy of crystallization, ΔH_{C}], in kilojoules per kilogram (kJ/kg), using the following equation:

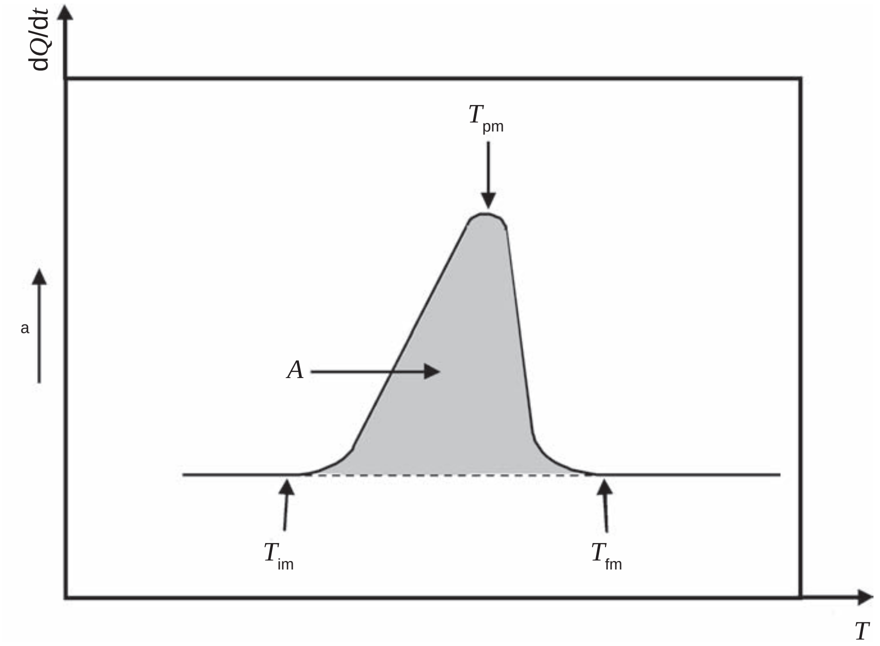
$$\Delta H = \Delta H_{\mathrm{C}} \frac{m_{\mathrm{C}} \cdot A \cdot B \cdot \sigma}{m \cdot A_{\mathrm{C}} \cdot B_{\mathrm{C}} \cdot \sigma_{\mathrm{C}}}$$

where

ΔH	is the enthalpy of fusion or crystallization of the specimen (kJ/kg);
ΔH_{C}	is the enthalpy of fusion or crystallization of the calibration material (kJ/kg);
A	is the peak area for the specimen (mm^2);
A_{C}	is the peak area for the calibration material (mm^2);
m	is the mass of the specimen (mg);
m_{C}	is the mass of the calibration material (mg);
σ	is the y-axis sensitivity of the specimen (mW/mm);
σ_{C}	is the y-axis sensitivity of the calibration material (mW/mm);
B	is the x-axis sensitivity (time base) of the specimen (s/mm);
B_{C}	is the x-axis sensitivity (time base) of the calibration material (s/mm).

NOTE 1 Modern equipment can be used to perform this calculation.

NOTE 2 In the event of significant differences between the specific heat capacities of the solid and liquid states of the polymer, the use of special types of baseline, such as sigmoid baselines, may improve the results.



Key

dQ/dt	heat flow rate
T	temperature
A	peak area

[a] Endothermic direction.

Figure 1 — Determination of enthalpy of transition

11 Precision

The precision of this test method is not known because inter-laboratory data are not available. When inter-laboratory data do become available, it is intended that a precision statement be added to a revision of this part of ISO 11357.

12 Test report

The test report shall be in accordance with ISO 11357-1:2009, Clause 10, with the following addition.

Include as the test results in item m):

— the characteristic transition temperatures T_{pm}, T_{eic} and T_{pc} and, if required, T_{eim}, T_{efm} and T_{efc} for each peak, and the enthalpy change, ΔH, for each peak, in kJ/kg, to one decimal place.

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