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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

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

This third edition cancels and replaces the second edition (ISO 11357-3:2011), which has been technically revised. The main changes compared to the previous edition are as follows:

- the normative references in Clause 2 have been updated;
- the sample mass is referring to polymer matrix;
- the procedure has been extended to cover materials with wider crystallisation ranges;
- the calculation of heats of transition has been clarified to include computer aided methods.

A list of all parts in the ISO 11357 series can be found on the ISO website.

Plastics — Differential scanning calorimetry (DSC) —

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

1 Scope

This document 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 documents are referred to in the text in such a way that some or all of their content constitutes requirements 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, *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.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at https://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

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

Note 1 to entry: The transition, also referred to as “fusion”, is characterized by an endothermic peak in the DSC curve. An exception to this definition is the case of liquid crystals, where the term “amorphous liquid” is replaced by “ordered liquid”.

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

Note 1 to entry: The transition is characterized by an exothermic peak in the DSC curve. An exception to this definition is the case of liquid crystals, where the term “amorphous liquid” is replaced by “ordered liquid”.

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

Note 1 to entry: It is expressed in kilojoules per kilogram (kJ/kg) or joules per gram (J/g).

3.4

enthalpy of crystallization

heat released by the crystallization of a material at constant pressure

Note 1 to entry: It is expressed in kilojoules per kilogram (kJ/kg) or joules per gram (J/g).

4 Principle

See ISO 11357-1.

5 Apparatus and materials

Apparatus and materials shall be in accordance with ISO 11357-1.

6 Test specimen

The test specimen shall be in accordance with ISO 11357-1.

7 Test conditions and specimen conditioning

The test conditions and specimen conditioning shall be in accordance with ISO 11357-1.

8 Calibration

Calibration shall be in accordance with ISO 11357-1.

9 Procedure

9.1 Setting up the apparatus

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

9.2 Loading the test specimen into the crucible

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

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 lower or higher than 5 mg to 10 mg, respectively, may be used. In case of polymer compounds the mass shall refer to the matrix polymer.

9.3 Insertion of crucibles

The insertion shall be in accordance with ISO 11357-1.

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 larger effects of the recorded transition. On the other hand, low scanning rates provide higher 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, heating the cell to a temperature high enough to erase the test material's previous thermal history, typically 30 K above the extrapolated end melting temperature, $T_{\mathrm{ef,m}}$. Preferred heating rates for the first heating run are 10 K/min or 20 K/min, but also higher heating rates may be used to delete the thermal and mechanical history of a sample within the first heating run.

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). 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 can be acceptable or needed provided degradation of the polymer does not result.

9.4.5 Perform and record a cooling run at preferably 10 K/min or 20 K/min to approximately 50 K below the extrapolated end crystallization temperature, $T_{\mathrm{ef,c}}$ or lower if required by the polymer to be measured.

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

If glass transitions are to be evaluated, too, cooling shall be done 50 K below the glass transition temperature or lower if required by the polymer to be measured.

9.4.6 Hold the temperature for 5 min.

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

9.4.7 Perform and record a second heating run at preferably the same heating rate as the cooling run (see 9.4.5) to approximately 30 K higher than the extrapolated end melting temperature, $T_{\mathrm{ef,m}}$.

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.

In case of significant weight loss repetition of measurements with stronger dried specimens shall be considered.

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, $T_{\mathrm{i,m}}$, and end temperature, $T_{\mathrm{f,m}}$, 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 shall be drawn, covering all peaks. If possible, the evaluation shall then be divided between each peak, in order to get the most accurate enthalpy. Suitable peak separation techniques may be used and shall then be mentioned in the test report.

For a melting transition curve, measure and report the peak melting temperature, $T_{\mathrm{p,m}}$, 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, $T_{\mathrm{ei,c}}$;
- the peak crystallization temperature, $T_{\mathrm{p,c}}$.

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

10.2 Determination of enthalpies

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

Figure 1 shows the determination of the heat of transition for the example of a melting peak. The same procedure is used for crystallisation peaks pointing to the opposite direction.

Calculate the enthalpy of fusion, ΔH_{f}, or the enthalpy of crystallization, ΔH_{c}, in kilojoules per kilogram (kJ/kg) or joules per gram (J/g), using Formula (1):

$$\Delta H_{\mathrm{f}}, \Delta H_{\mathrm{c}} = \Delta H_{\mathrm{Cal}} \cdot \frac{A \cdot m_{\mathrm{Cal}}}{A_{\mathrm{Cal}} \cdot m} \tag{1}$$

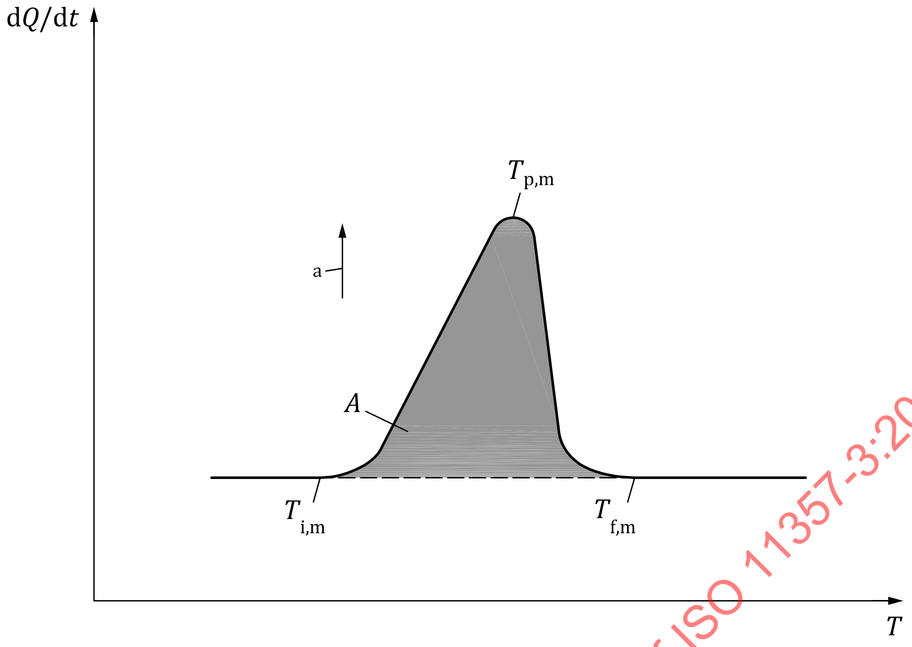
where

ΔH_{f}, ΔH_{c}	are respectively the enthalpy of fusion and the enthalpy of crystallization of the specimen in kilojoules per kilogram (kJ/kg) or joules per gram (J/g);
ΔH_{Cal}	is the enthalpy of fusion or crystallization of the calibration material in kilojoules per kilogram (kJ/kg) or joules per gram (J/g);
A	is the peak area for the specimen;
A_{Cal}	is the peak area for the calibration material;
m	is the mass of the specimen;
m_{Cal}	is the mass of the calibration material.

Units of area and mass used for calibration and measurement shall be the same.

NOTE 1 The enthalpy calculation can be facilitated using computer aided analysis.

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 sigmoidal baselines, can improve the results.



Key

d*Q*/d*t*	heat flow rate	$T_{i,m}$	initial temperature of melting peak
T	temperature	$T_{p,m}$	melting peak temperature
A	peak area	$T_{f,m}$	end temperature of melting peak
– – –	interpolated baseline		

[a] Endothermic direction.

Figure 1 — Determination of enthalpy of transition shown for the example of melting

11 Precision

The precision of this test method is not known because interlaboratory data are not available. It is intended that a precision statement be added when interlaboratory data do become available.

12 Test report

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

Include as the test results in item m):

- the characteristic transition temperatures $T_{p,m}$, $T_{i,m}$ and/or $T_{f,m}$, $T_{p,c}$, $T_{i,c}$ and $T_{f,c}$ and, if required, $T_{ei,m}$, $T_{ef,m}$ and/or $T_{ei,c}$, $T_{ef,c}$ for each peak in °C, and the enthalpy change, ΔH_f and/or ΔH_c, for each peak, in kJ/kg (or J/g), to one decimal place;
- peak separation technique, if applicable.