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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

Reference number
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Contents

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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.

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.

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

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 reaction temperatures, reaction times, heats of reaction and degrees of conversion*

— *Part 6: Determination of oxidation induction time*

— *Part 7: Determination of crystallization kinetics*

— *Part 8: Determination of amount of water absorbed by polymers*

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 temperature and enthalpy of melting and crystallization of crystalline or semi-crystalline plastics.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 11357. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 11357 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 291:1997, *Plastics — Standard atmospheres for conditioning and testing*.

ISO 472:—[1)], *Plastics — Vocabulary*.

ISO 11357-1:1997, *Plastics — Differential scanning calorimetry (DSC) — Part 1: General principles*.

3 Definitions

For the purposes of this part of ISO 11357, the definitions given in ISO 11357-1 apply, plus the following:

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

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

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

NOTE 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” should be replaced by “ordered liquid”.

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1) To be published. (Revision of ISO 472:1988)

3.3
enthalpy of fusion
the heat required to melt a material at constant pressure, measured in kJ/kg

3.4
enthalpy of crystallization
the heat released by the crystallization of a material at constant pressure, measured in kJ/kg

3.5
characteristic temperatures
the following temperatures (see figure 1):

— extrapolated onset temperature T_{ei}

— peak temperature T_p

— extrapolated end temperature T_{ef}

NOTE The additional subscript m is used to denote temperatures related to the melting phenomenon and the subscript c to denote temperatures related to the crystallization phenomenon.

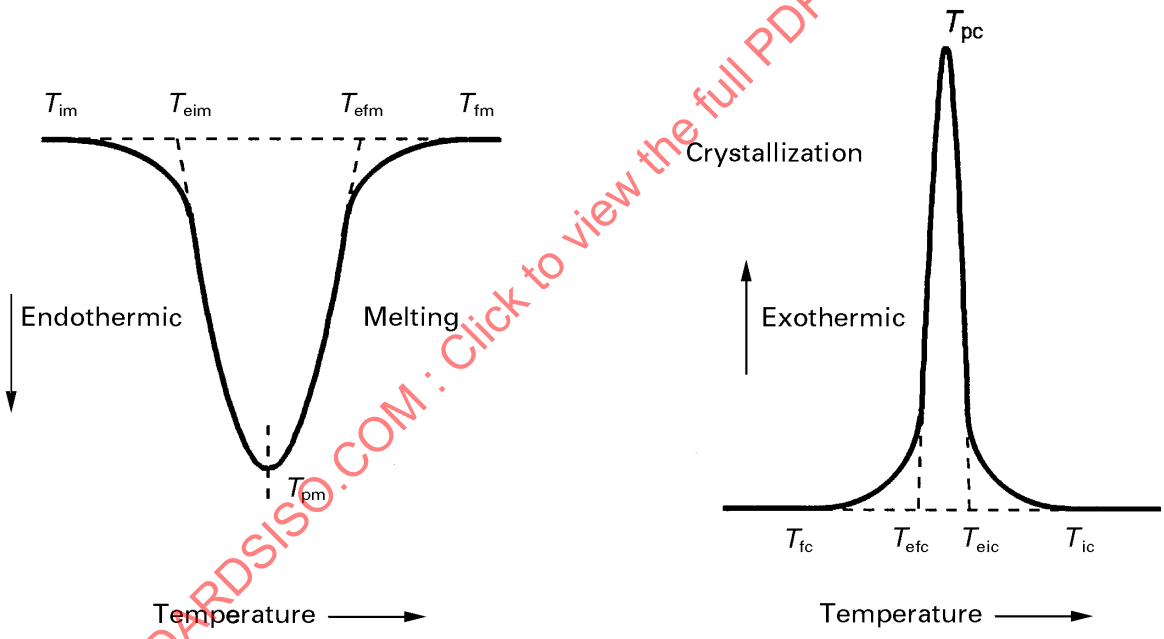

Figure 1 — Examples of characteristic temperature determinations

4 Principle

See ISO 11357-1:1997, clause 4.

5 Apparatus and materials

See ISO 11357-1:1997, clause 5.

The gas supply shall be analytical grade nitrogen or another inert gas.

All specimens and pans shall be handled using clean tweezers.

6 Test specimens

See ISO 11357-1:1997, clause 6.

7 Test conditions and specimen conditioning

See ISO 11357-1:1997, clause 7.

8 Calibration

See ISO 11357-1:1997, clause 8.

9 Procedure

9.1 Setting up the apparatus

See ISO 11357-1:1997, subclause 9.1.

Switch on apparatus and allow it to equilibrate for at least 30 min.

Use the same purge gas flow rate that was used to calibrate the instrument. Any change in flow rate or gas requires re-calibration. Typically, nitrogen gas (analytical grade) at a flow rate of 50 ml/min ± 10 % is used. Other inert gases and flow rates may be used by agreement between the interested parties.

9.2 Loading the test specimen into the pan

See ISO 11357-1, sublause 9.2.

Unless otherwise specified in the materials document, use a mass of 5 mg to 10 mg for the measurement. The accuracy of weighing shall be to the nearest 0,1 mg.

Ensure that the bottoms of the pans are flat. Good contact between the pans and the specimen holders is crucial to obtaining good data.

Do not handle the test material or pan with bare hands; either use tweezers or wear gloves.

9.3 Insertion of pans

See ISO 11357-1:1997, subclause 9.3.

9.4 Temperature scan

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

9.4.2 Perform and record a preliminary thermal cycle at a rate of 20 °C/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 is performed and that the measurements are taken from the second heat scan (see annex B of 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.

9.4.3 Hold the temperature for 5 min.

9.4.4 Perform and record a cooling cycle at a rate of 20 °C/min to approximately 50 °C below the extrapolated end crystallization temperature (T_{efc}).

NOTE 1 Other heating or cooling rates may be used by agreement between 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 and may be appropriate in the resolution of closely overlapping transitions.

NOTE 2 Because of supercooling, crystallization does not occur until a sufficient temperature gradient is available, usually significantly below the melting temperature.

9.4.5 Hold the temperature for 5 min.

9.4.6 Perform and record a second heating cycle at a rate of 20 °C/min (see note 1 to 9.4.4) to approximately 30 °C higher than the extrapolated end melting temperature(T_{efm}).

9.4.7 Bring the apparatus to ambient temperature and remove the pans to determine if deformation of the pan or specimen overflow has occurred.

9.4.8 Reweigh the pan, with the test specimen, to within ± 0,1 mg.

9.4.9 If any weight loss has occurred, a chemical change should be suspected. Open the pan and inspect the test specimen. If the specimen has degraded, discard the test results and retest, selecting a lower maximum temperature.

Do not reuse pans showing signs of deterioration for another measurement.

If the test specimen overflows during measurement, clean the specimen holder assembly, following the instrument manufacturer's instructions, and confirm that the calibration is still valid using at least one temperature and enthalpy reference standard.

9.4.10 Process the data in accordance with the instrument manufacturer's instructions.

9.4.11 Repeat testing shall be decided by the user.

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 by joining the two points at which the peak (endothermic peak for fusion, exothermic peak for crystallization) begins to deviate from the relatively straight baseline, as shown in figure 1. If multiple peaks are present, draw a baseline to each.

For a melting transition curve, measure and report the following for each peak:

— the extrapolated onset melting temperature T_{eim}

— the peak melting temperature T_{pm}

— the extrapolated end melting temperature T_{efm}

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

— the extrapolated onset crystallization temperature T_{eic}

— the peak crystallization temperature T_{pc}

— the extrapolated end crystallization temperature T_{efc}

NOTE The extrapolated onset temperature (T_{ei}) is where the extrapolated baseline is intersected by the tangent to the curve at the point of inflection and corresponds to the start of the transition.

The extrapolated end temperature (T_{ef}) is where the extrapolated baseline is intersected by the tangent to the curve at the point of inflection and corresponds to the end of the transition.

The peak temperature (T_p) is the temperature at which the peak reaches a maximum (or minimum).

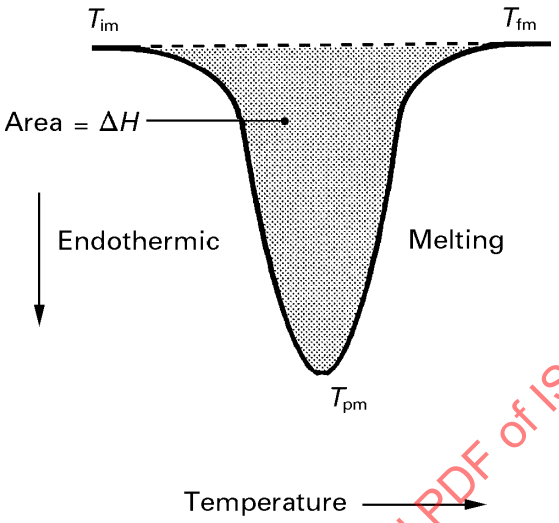

Figure 2 — Determination of the enthalpy of a transition

10.2 Determination of enthalpies (see figure 2)

Measure the area under the peak to the baseline constructed as described in 10.1

Calculate the enthalpy of fusion ΔH_f (enthalpy of crystallization ΔH_c), in kJ/kg, using the following equation:

$$\Delta H = \frac{ABT}{W} \times \frac{\Delta H_S W_S}{A_S B_S T_S}$$

where

ΔH is the enthalpy of fusion or crystallization of the specimen (kJ/kg);

ΔH_S is the enthalpy of fusion or crystallization of the standard (kJ/kg);

A is the peak area for the specimen (mm^2);

A_S is the peak area for the standard (mm^2);

W is the mass of the specimen (mg);

W_S is the mass of the standard (mg);

T is the y-axis sensitivity of the specimen (mW/mm);

T_S is the y-axis sensitivity of the standard (mW/mm);

B is the x-axis sensitivity (time base) of the specimen (s/mm);

B_S is the x-axis sensitivity (time base) of the standard (s/mm).