INTERNATIONAL STANDARD

ISO 11357-5

Second edition
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Plastics — Differential scanning calorimetry (DSC) —

Part 5: Determination of characteristic reaction-curve temperatures and times, enthalpy of reaction and degree of conversion

Plastiques — Analyse calorimétrique différentielle (DSC) —

Partie 5: Détermination des températures et temps caractéristiques de la courbe de réaction, de l'enthalpie de réaction et du degré de transformation

Reference number
ISO 11357-5:2013(E)

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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 11357-5 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 11357-5:1999), which has been technically revised. Significant technical changes are the following:

— adaption of definition of characteristic temperatures and endo-/exothermic direction in accordance with ISO 11357-1;

— revision of determination of results;

— revision of test report.

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 and glass transition step height*

— *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 5:
Determination of characteristic reaction-curve temperatures and times, enthalpy of reaction and degree of conversion

WARNING — Caution should be observed when working with materials which could give a runaway reaction or exhibit other dangerous behaviour.

1 Scope

This part of ISO 11357 specifies a method for the determination of reaction temperatures and times, enthalpies of reaction, and degrees of conversion using differential scanning calorimetry (DSC).

The method applies to monomers, prepolymers, and polymers in the solid or liquid state. The material can contain fillers and/or initiators in the solid or liquid state.

2 Normative references

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

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 11357-1 and the following apply.

3.1
polymerization
process of converting a monomer or a mixture of monomers into a polymer

3.2
crosslinking
process of multiple intermolecular covalent or ionic bonding between polymer chains

3.3
degree of conversion
quantity of reacted product obtained during a reaction compared with the maximum possible quantity of the product

Note 1 to entry: The degree of conversion will depend on both time and temperature.

4 Principle

The principle is specified in ISO 11357-1.

The test method described indicates the various stages of the reaction by means of DSC curves.

5 Apparatus and materials

The apparatus and materials are specified in ISO 11357-1.

6 Test specimens

The test specimens are specified in ISO 11357-1.

If not specified otherwise, use a mass of 5 mg to 20 mg and adjust the specimen mass if the thermal effect is too high or too low.

7 Test conditions and specimen conditioning

For polymers, the test conditions and specimen conditioning are specified in ISO 11357-1.

For specimens releasing volatile components, it may be necessary to carry out conditioning and testing with the specimen enclosed in a gas-tight specimen crucible which is resistant to high temperature and pressure.

Suitable conditioning procedures shall be agreed between involved parties and included in the test report.

8 Calibration

The calibration is specified in ISO 11357-1.

9 Procedure

9.1 General

The test may use one of two different methods, depending on what information is required:

— temperature-scanning method;

— isothermal method.

9.2 Temperature-scanning method

The temperature-scanning method is specified in ISO 11357-1.

Carry out a temperature scan, from ambient temperature to a temperature high enough to record the whole of the reaction peak, at a scan rate in the range 5 K/min to 20 K/min. Use the same scan rate for all tests which are intended to be comparative.

The final temperature shall be lower than the temperature corresponding to the onset of decomposition of the polymer.

A preliminary test can be useful in defining the decomposition temperature.

9.3 Isothermal method

9.3.1 General

The isothermal method can be carried out in two different ways once the specimen is loaded into the DSC sample holder:

— at constant temperature;

— starting at ambient temperature and heating as quickly as possible to reach the constant measurement temperature.

NOTE The choice of procedure will depend on the model of calorimeter used for the test. The measurement temperature is selected on the basis of a trial run in the temperature-scanning mode. The temperature is intended to be in the vicinity of the temperature at which the peak obtained in the scanning mode begins.

9.3.2 Constant-temperature method

a) Place the reference crucible in the calorimeter.

b) Set the instrument to the desired measurement temperature.

c) Let the calorimeter stabilize at the selected temperature for 5 min.

d) Place the crucible containing the specimen in the calorimeter.

e) Record the DSC curve.

f) Remove the crucible containing the specimen and let it cool down to ambient temperature.

g) Place the crucible containing the specimen back in the calorimeter.

h) Record the DSC curve again (the second curve will be subtracted from the first to correct for the calorimeter perturbation caused by the introduction of the crucible).

NOTE When using this procedure, it is difficult to ensure that the manual operation by which the crucible is introduced into the calorimeter is carried out repeatedly for the determination and the blank run. Also, changes to the state of the specimen can have occurred during the reaction. Subtraction of the two curves can therefore introduce an error.

9.3.3 Procedure starting at ambient temperature

a) Place both crucibles (reference and specimen) in the calorimeter at ambient temperature.

b) Increase the calorimeter temperature, at the highest possible rate, to the selected measurement temperature.

c) Record the DSC curve.

d) Allow the calorimeter to cool down to ambient temperature.

e) Repeat the process without removing the crucibles, and record the DSC curve again (the second curve will be subtracted from the first to correct for the calorimeter perturbation caused by the rapid heating process).

NOTE When using this procedure, changes to the state of the specimen can have occurred during the reaction. Subtraction of the two curves can therefore introduce an error.

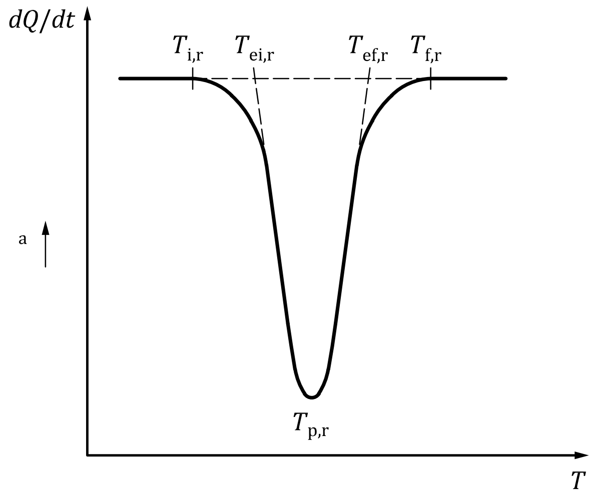
9.3.4 Residual enthalpy

At the end of an isothermal run performed in accordance with 9.3.2 or 9.3.3, cool down the instrument to ambient temperature with the specimen still inside the sample holder. Then, heat up the specimen to a temperature below specimen decomposition at the same rate as in a temperature scan in order to determine whether there is any residual enthalpy (i.e. whether any additional reaction occurs). Add this enthalpy to the isothermal value to obtain the total enthalpy of reaction.

10 Determination of results

10.1 Determination of characteristic temperatures and enthalpy of reaction (temperature-scanning method)

See Figure 1. See also ISO 11357-1.



Key

dQ/dt	heat flow rate
T	temperature
a	Endothermic direction.

Figure 1 — DSC curve with exothermic peak (temperature-scanning method)

The temperatures shown in Figure 1 are:

$T_{i,r}$ onset of reaction, corresponding to the point at which the DSC curve departs from the initial extrapolated baseline;

$T_{ei,r}$ extrapolated onset temperature, corresponding to the point at which the initial extrapolated baseline is intersected by the tangent to the curve at the point of inflection, both on the low-temperature side of the curve;

$T_{p,r}$ maximum reaction rate, corresponding to the top of the peak;

$T_{ef,r}$ extrapolated end temperature, corresponding to the point at which the final extrapolated baseline is intersected by the tangent to the curve at the point of inflection, both on the high-temperature side of the curve;

$T_{f,r}$ end of reaction, corresponding to the return of the DSC curve to the final extrapolated baseline.

The enthalpy of reaction ΔH_r, in joules per gram, is obtained by integrating the area between the reaction peak and the interpolated baseline from $T_{i,r}$ to $T_{f,r}$.

10.2 Determination of characteristic times and enthalpy of reaction (isothermal method)

Each procedure (9.3.2 and 9.3.3) may require a different length of time for the reaction to begin.

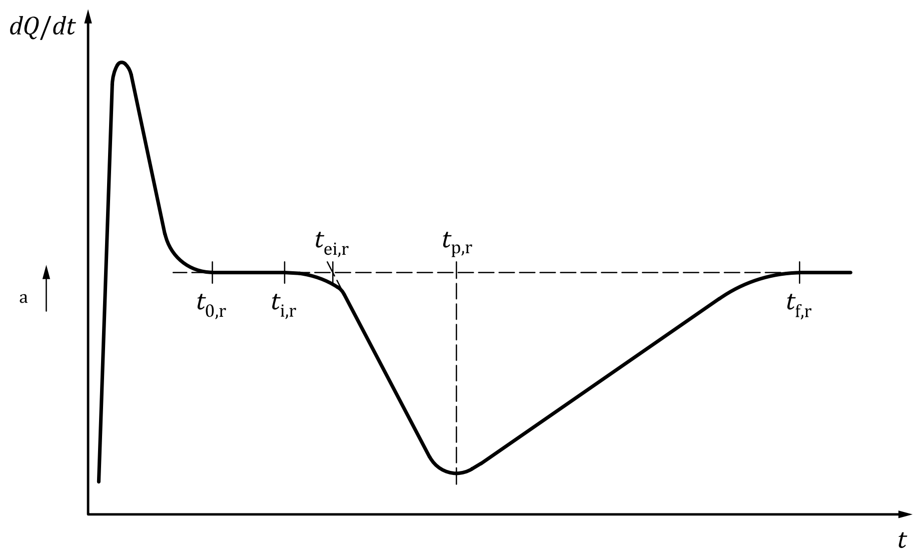
Note the time $t_{0,r}$ when the specimen reaches temperature equilibrium. Typically, $t_{0,r}$ is the time at which the DSC curve comes back to the isothermal baseline obtained by connecting the horizontal parts of the DSC curve before and after the isothermal reaction peak. Measure the following times from this point (see Figure 2):

$t_{i,r}$ onset of reaction, corresponding to the departure of the DSC curve from the initial interpolated baseline;

$t_{ei,r}$ extrapolated onset time, corresponding to the point at which the interpolated baseline is intersected by the tangent to the curve at the point of inflection, both on the short-time side of the curve;

$t_{p,r}$ maximum reaction rate, corresponding to the top of the peak;

$t_{f,r}$ end of reaction, corresponding to the return of the DSC curve to the interpolated baseline.



Key

dQ/dt heat flow rate

t time

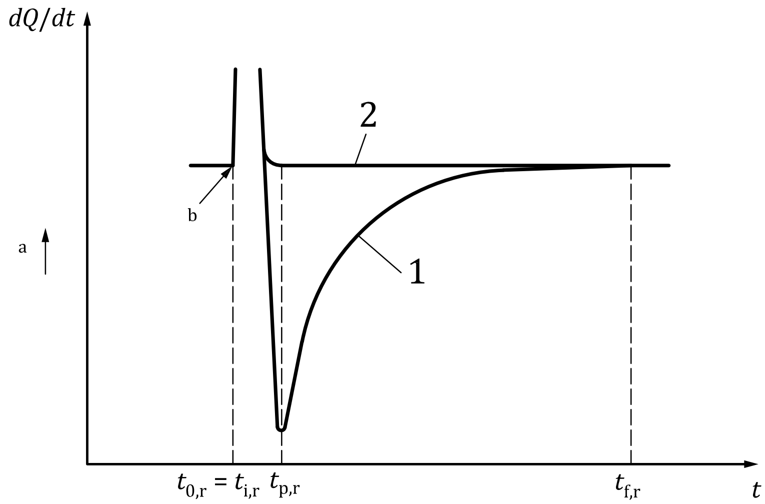
a Endothermic direction.

Figure 2 — DSC curve with exothermic peak (isothermal method)

The enthalpy of reaction during the isothermal stage is obtained by integrating the area between the reaction peak and the interpolated baseline from $t_{i,r}$ to $t_{f,r}$.

NOTE It is necessary to select the temperature of the test in order to get a record of the peak as described in Figure 2. If needed, the temperature of the test can be lowered.

If the reaction starts immediately, the curve will look like Figure 3. In such cases, $t_{i,r}$ and $t_{ei,r}$ cannot be measured. Time $t_{i,r}$ is taken to be equal to $t_{0,r}$.



Key

dQ/dt	heat flow rate
t	time
1	reaction curve
2	reacted specimen
a	Endothermic direction.
b	Introduction of specimen.

Figure 3 — DSC curve with exothermic peak (reaction starting instantaneously)

10.3 Determination of degree of conversion

10.3.1 General

The degree of conversion α, which depends on the temperature (temperature-scanning method) or the time (isothermal method), can be determined from the DSC curve.

10.3.2 Calculation of α from a temperature scan

The degree of conversion is calculated, in per cent (%), using Formula (1) (see Figure 4):

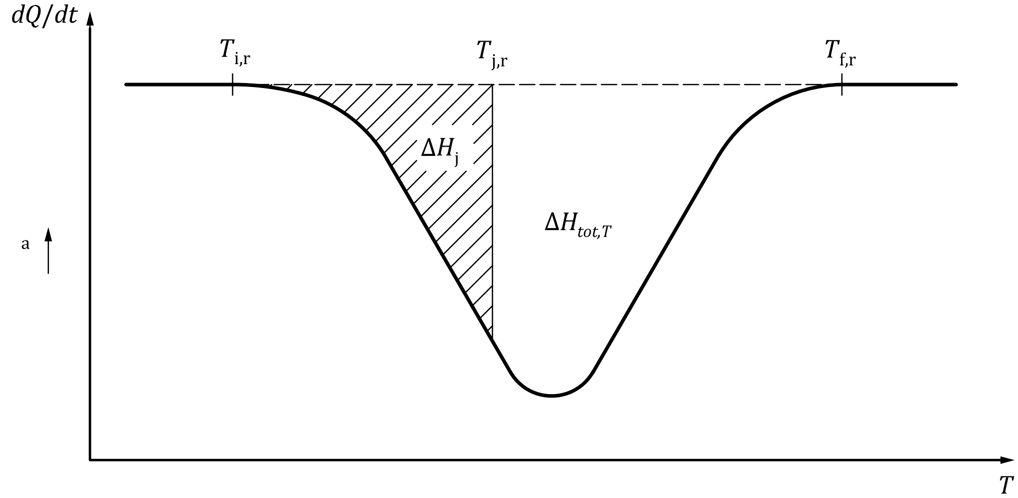
$$\alpha_{\mathrm{j}} = \frac{\Delta H_{\mathrm{j}}}{\Delta H_{\mathrm{tot,T}}} \times 100 \quad (1)$$

where

ΔH_{j} is the part of the enthalpy of reaction to temperature $T_{\mathrm{j,r}}$, corresponding to the part of the peak area between start temperature $T_{\mathrm{i,r}}$ and $T_{\mathrm{j,r}}$;

$\Delta H_{\mathrm{tot,T}}$ is the total enthalpy of reaction measured from a temperature scan, corresponding to the total peak area between start temperature $T_{\mathrm{i,r}}$ and end temperature $T_{\mathrm{f,r}}$ of reaction.

See also ISO 11357-1 for the determination of characteristic temperatures and enthalpies.



Key

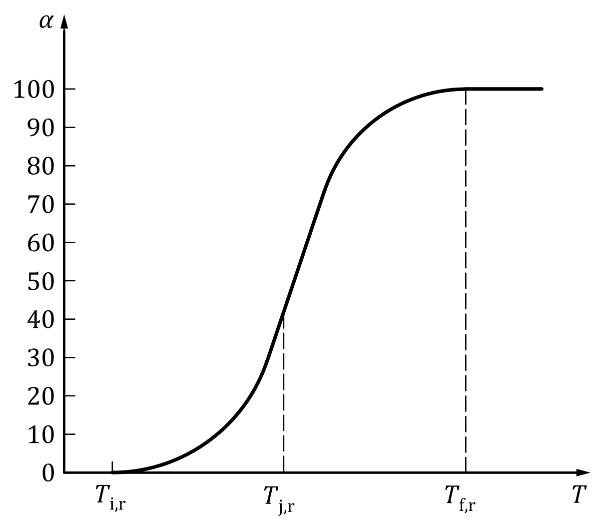
dQ/*dt* heat flow rate

T temperature

a Endothermic direction.

Figure 4 — Calculation of degree of conversion from a temperature scan

The degree of conversion, *α*, increases as the temperature $T_{j,r}$ increases. A typical example is shown in Figure 5.



Key

α degree of conversion

T temperature

Figure 5 — Example of increase in *α* with temperature

10.3.3 Calculation of α from an isothermal curve

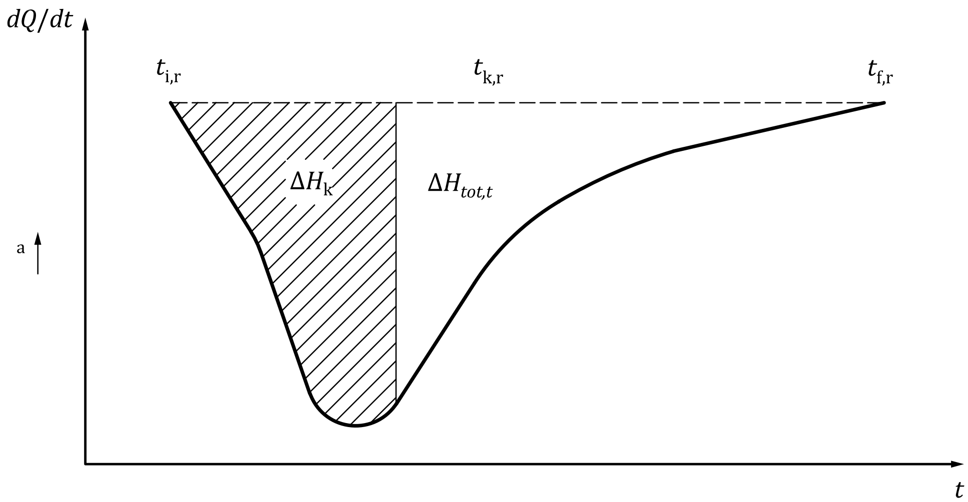
The degree of conversion is calculated, in per cent (%), from Formula (2) (see Figure 6):

$$\alpha_k = \frac{\Delta H_k}{\Delta H_{tot,t}} \times 100 \tag{2}$$

where

ΔH_k is the part of the enthalpy of reaction to time $t_{k,r}$, corresponding to the part of the peak area between start time $t_{i,r}$ and $t_{k,r}$;

$\Delta H_{tot,t}$ is the total enthalpy of reaction measured isothermally, corresponding to the total peak area between start time $t_{i,r}$ and end time $t_{f,r}$.



Key

dQ/dt heat flow rate

t time

a Endothermic direction.

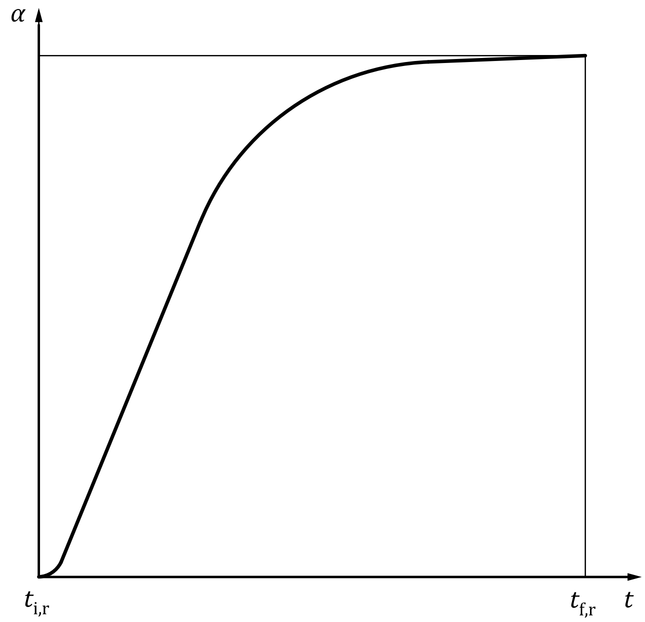
Figure 6 — Calculation of degree of conversion from an isothermal curve

See 10.2 for the determination of characteristic times and enthalpies.

The enthalpy change $\Delta H_{tot,t}$ measured from an isothermal curve shall be compared to the enthalpy change $\Delta H_{tot,T}$ measured from a temperature scan (see 10.3). If $\Delta H_{tot,t}$ is less than $\Delta H_{tot,T}$, replace $\Delta H_{tot,t}$ by $\Delta H_{tot,T}$ in Formula (2) in order to obtain the true degree of conversion, provided no change of reaction characteristics has occurred.

NOTE The comparison of the isothermally measured enthalpy change to that measured in a temperature scan is done in order to capture residual conversion that can occur only at increased temperatures.

The degree of conversion, α, increases with time as shown in Figure 7.



Key

α	degree of conversion
t	time
$t_{i,r}$, $t_{f,r}$	start, end time of reaction

Figure 7 — Increase in α with time

11 Precision

The precision of this test method is not known because interlaboratory data are not available. When interlaboratory data are obtained, a precision statement will be added in a revision of this part of ISO 11357.

12 Test report

The test report is specified in ISO 11357-1.

Include as item k) details of the procedure used including, as appropriate:

— temperature-scanning or isothermal method;

— scan rate;

— isothermal temperature (for isothermal methods);

— details of loading and test procedure and conditions such as loading temperature, heating rate up to test temperature (for isothermal methods).

Include as the test results [item m)]:

— the characteristic temperatures or times measured;

— when an isothermal run was carried out, the residual enthalpy of reaction, if any (see 9.3.4);

— the total enthalpy of reaction;

— the degree of conversion, and the temperature or time at which it was measured.

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