
**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*



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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 734 10 79
E-mail copyright@iso.ch
Web www.iso.ch

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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 3.

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 part of ISO 11357 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 11357-5 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 characteristic reaction-curve temperatures and times, enthalpy of reaction and degree of conversion*
- *Part 6: Determination of oxidation induction time*
- *Part 7: Determination of crystallization kinetics*
- *Part 8: Determination of amount of water absorbed*

Plastics — Differential scanning calorimetry (DSC) —

Part 5:

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

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 may contain fillers and/or initiators in the solid or liquid state.

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

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 11357. For dated references, subsequent amendments to, or revisions of, these publications do not apply. However, parties to agreements based on this part of ISO 11357 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

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

ISO 11357-3:1999, *Plastics — Differential scanning calorimetry (DSC) — Part 3: Determination of temperature and enthalpy of melting and crystallization*.

3 Definitions

3.1 polymerization

the process of converting a monomer or a mixture of monomers into a polymer

3.2 crosslinking

the process of multiple intermolecular covalent or ionic bonding between polymer chains

3.3 degree of conversion

the quantity of unreacted product remaining during a reaction compared to the initial quantity of the product

NOTE The degree of conversion will depend on both time and temperature.

4 Principle

See ISO 11357-1:1997, clause 4.

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

5 Apparatus and materials

See ISO 11357-1:1997, clause 5.

6 Test specimens

See ISO 11357-1:1997, clause 6.

If the specimen is a liquid resin or a mixture, use a mass of 5 mg to 20 mg. In the case of thermosets, increase the specimen mass in order to have 5 mg to 20 mg of resin in the specimen.

7 Test conditions and specimen conditioning

For polymers, see ISO 11357-1:1997, clause 7.

For monomers and prepolymers in the liquid phase, particularly those with volatile components, it may be necessary to carrying out conditioning and testing with the specimen enclosed in a gas-tight specimen pan which is resistant to high temperature and pressure.

8 Calibration

See ISO 11357-1:1997, clause 8.

9 Procedure

9.1 General

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

- temperature-scanning method;
- isothermal method.

9.2 Temperature-scanning method

See ISO 11357-1:1997, subclause 9.4.

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 °C/min to 20 °C/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 will 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 inside the calorimeter cell:

- 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 has to be in the vicinity of the temperature at which the peak obtained in the scanning mode begins.

9.3.2 Constant-temperature procedure

- a) place the reference pan 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 pan containing the specimen in the calorimeter;
- e) record the DSC curve;
- f) remove the pan containing the specimen and let it cool down to ambient temperature;
- g) place the pan containing the specimen back in the calorimeter;
- h) record the DSC curve again (the second curve will be subtracted from the first to allow for the calorimeter perturbation caused by the introduction of the pan).

NOTE When using this procedure, it is difficult to ensure that the manual operation by which the pan is introduced into the calorimeter is carried out repeatably for the determination and the blank run. Subtraction of the two curves may therefore introduce a small error.

9.3.3 Procedure starting at ambient temperature

- a) place both pans (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 pans, and record the DSC curve again (the second curve will be subtracted from the first to allow for the calorimeter perturbation caused by the rapid heating process).

9.3.4 Residual enthalpy

At the end of an isothermal run (e.g. a polymerization reaction), allow the instrument to cool to ambient temperature with the specimen still inside it. Then heat up the specimen at the same rate as in a temperature scan in order to determine whether there is any residual enthalpy (i.e. whether any additional polymerization occurs). Add this enthalpy to the isothermal value to give the total enthalpy of reaction.

10 Expression of results

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

See also ISO 11357-3.

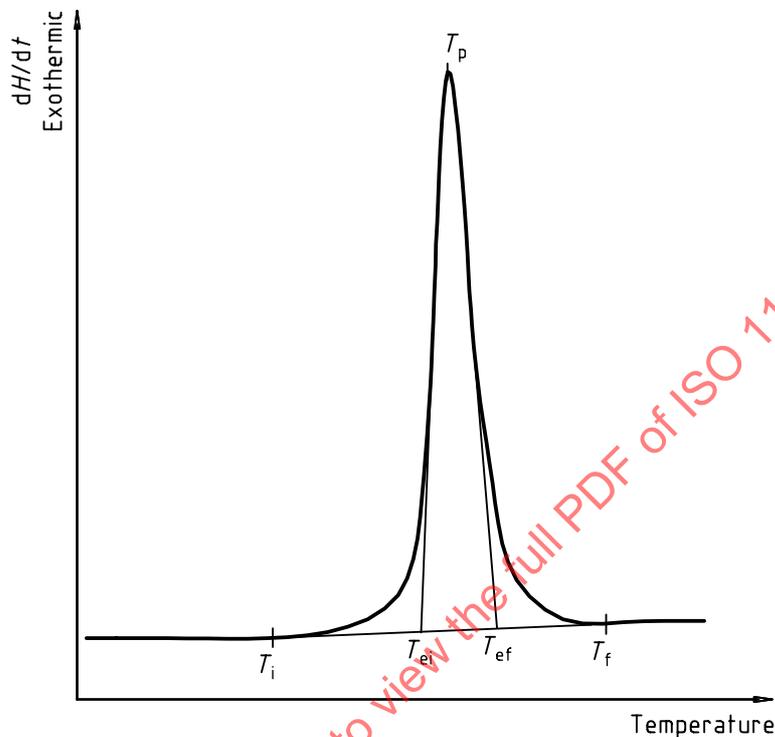


Figure 1 — DSC curve with exothermic peak (temperature-scanning method)

The temperatures shown in Figure 1 are:

- T_i onset of reaction, corresponding to the point at which the DSC curve departs from the initial baseline;
- T_{ei} extrapolated onset temperature, corresponding to the point at which the extrapolated baseline on the low-temperature side of the curve is intersected by the tangent to the curve at the point of inflection;
- T_p maximum reaction rate, corresponding to the top of the peak;
- T_{ef} extrapolated end temperature, corresponding to the point at which the extrapolated baseline on the high-temperature side of the curve is intersected by the tangent to the curve at the point of inflection;
- T_f end of reaction, corresponding to the return of the DSC curve to the final baseline.

The enthalpy of reaction ΔH_R , in joules per gram, is obtained by integrating the area between the reaction peak and the baseline from T_i to T_f .

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

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

Note the time t_0 when the specimen reaches temperature equilibrium. Measure the following times from this point (see Figure 2):

- t_i onset of reaction, corresponding to the departure of the DSC curve from the initial baseline;
- t_{ei} extrapolated onset time, corresponding to the point at which the extrapolated baseline on the low-temperature side of the curve is intersected by the tangent to the curve at the point of inflection;
- t_p maximum reaction rate, corresponding to the top of the peak;
- t_f end of reaction, corresponding to the return of the DSC curve to the baseline.

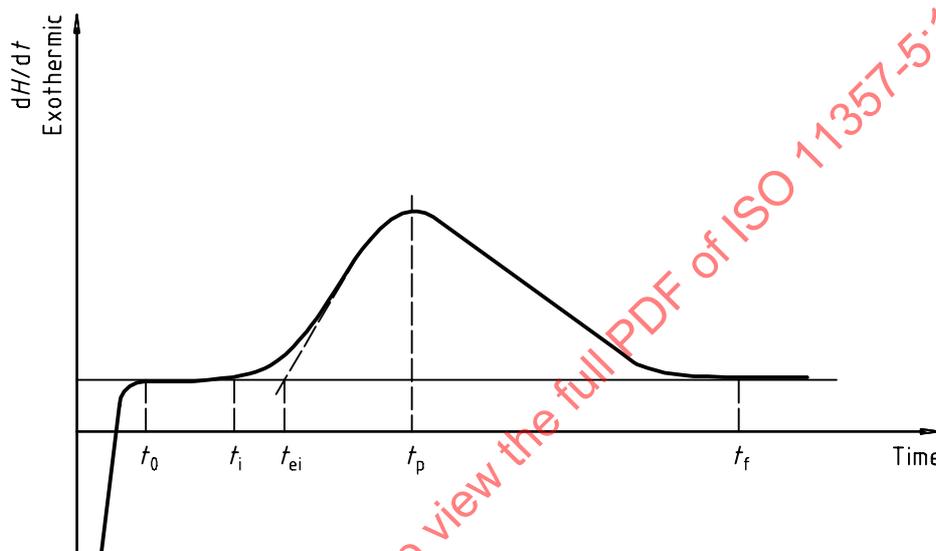


Figure 2 — DSC curve with exothermic peak (isothermal method)

The enthalpy of reaction during the isothermal stage is obtained by integrating the area between the reaction peak and the baseline from t_i to t_f .

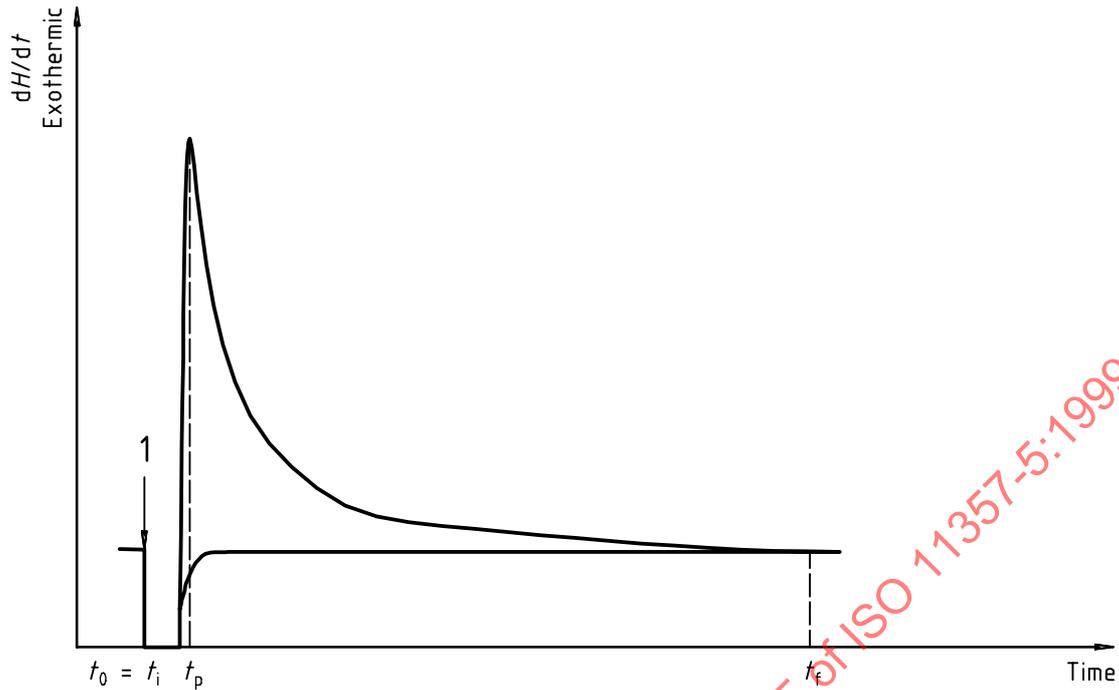
NOTE It is necessary to select the temperature of the test in order to get the record of the peak as described on Figure 2. If needed, the temperature of the test may be lowered. If the reaction starts instantaneously, use Figure 3.

When the reaction starts immediately, the curve will look like Figure 3. In such cases, t_i and t_{ei} cannot be measured. Time t_i is taken to be equal to t_0 .

10.3 Determination of degree of conversion

10.3.1 General

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



Key

- 1 Introduction of specimen

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

10.3.2 Calculation of α from a temperature scan

The degree of conversion is calculated from the following equation (see Figure 4):

$$\alpha \text{ (in \%)} = \frac{\Delta H_j}{\Delta H} \times 100$$

where

ΔH_j is the part of the enthalpy of reaction to temperature T_j , corresponding to the part of the peak area between T_i and T_j ;

ΔH is the total enthalpy of reaction, corresponding to the total peak area between T_i and T_f .

See also ISO 11357-3 for the determination of characteristic temperatures and enthalpies.

Use a slow scan rate (preferably lower than 5 °C/min) or distortion of the curve may occur (see also ISO 11357-1:1997, annex B).

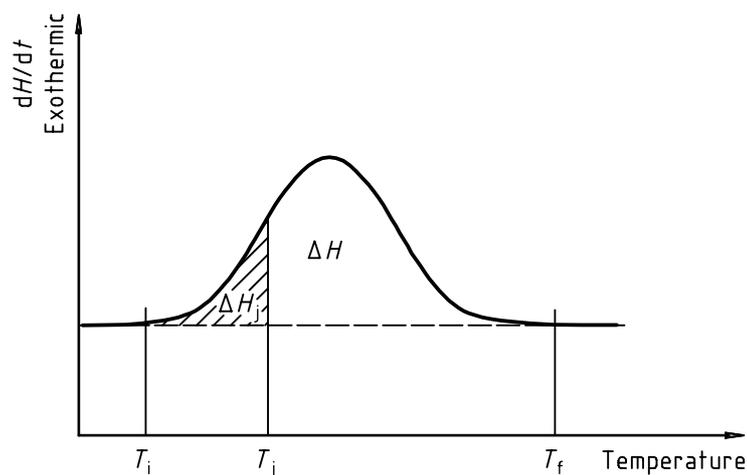


Figure 4 — Calculation of degree of conversion from a temperature scan

The degree of conversion α increases as the temperature T_j increases. A typical example is shown in Figure 5.

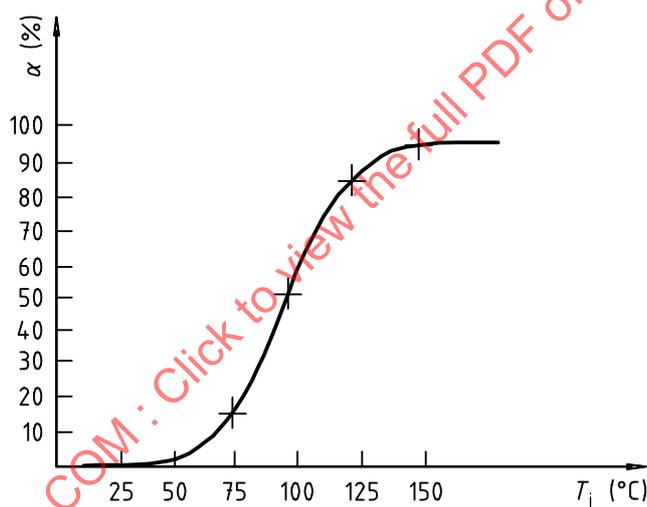


Figure 5 — Example of increase in α with temperature

10.3.3 Calculation of α from an isothermal curve

The degree of conversion is calculated from the following equation (see Figure 6):

$$\alpha \text{ (in \%)} = \frac{\Delta H_k}{\Delta H_i} \times 100$$

where

ΔH_k is the part of the enthalpy of reaction to time t_k , corresponding to the part of the peak area between t_i and t_k ;

ΔH_i is the total enthalpy of reaction, corresponding to the total peak area between t_i and t_k .

See 10.2 for the determination of characteristic times and enthalpies.

If the enthalpy change ΔH_i measured from an isothermal curve is less than the enthalpy change ΔH measured from a temperature scan (see 10.2), then replace ΔH_i by ΔH in the above equation in order to obtain the true degree of conversion.

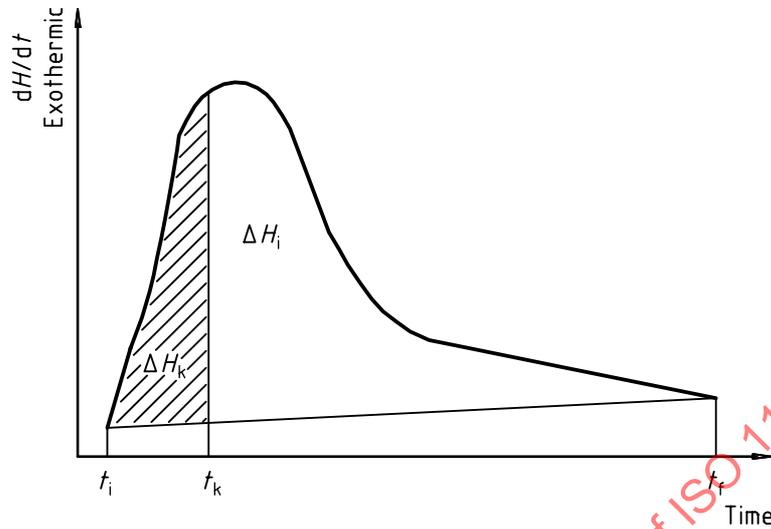


Figure 6 — Calculation of degree of conversion from an isothermal curve

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

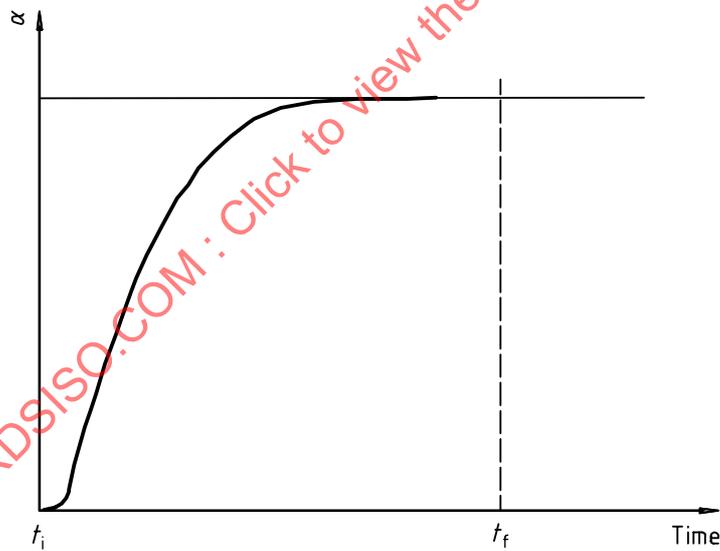


Figure 7 — Increase in α with time

11 Precision

The precision of this test method is not known because inter-laboratory data are not available. When inter-laboratory data are obtained, a precision statement will be added at the following revision.

12 Test report

See ISO 11357-1:1997, clause 10.