
**Plastics — Differential scanning
calorimetry (DSC) —**

**Part 7:
Determination of crystallization
kinetics**

*Plastiques — Analyse calorimétrique différentielle (DSC) —
Partie 7: Détermination de la cinétique 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 meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: [Foreword - Supplementary information](#).

The committee responsible for this document is ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

This second edition cancels and replaces the first edition (ISO 11357-7:2002), which has been technically revised with the following changes:

- a) values to be recorded for isothermal crystallization revised, starting time of the isothermal step ($t = 0$) added (10.2.1), and Figure 2 to Figure 6 revised accordingly;
- b) Formula (A.1) and Formula (A.2) are corrected;
- c) dated references changed to undated references.

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 7:

Determination of crystallization kinetics

1 Scope

This part of ISO 11357 specifies two methods (isothermal and non-isothermal) for studying the crystallization kinetics of partially crystalline polymers using differential scanning calorimetry (DSC).

It is only applicable to molten polymers.

NOTE These methods are not suitable if the molecular structure of the polymer is modified during the test.

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 472, *Plastics — Vocabulary*

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

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

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472, ISO 11357-1, ISO 11357-3, and the following apply.

3.1

crystallization kinetics

description of the rate of crystallization of a material taking into account the effects of variables such as time, temperature, pressure, stress, and molecular structure

Note 1 to entry: These factors and also any additives, fillers, or contaminants can modify the crystallinity of the polymer at the end of crystallization.

3.2

relative crystallinity

α

ratio between the crystallinity at a particular point in time or a particular temperature and the crystallinity at the end of crystallization

Note 1 to entry: The relative crystallinity can be expressed either as a ratio or as a percentage if multiplied by 100.

Note 2 to entry: In DSC, the relative crystallinity can be determined as the ratio between the partial area of the crystallization peak, at each time or each temperature, and the total area of the peak.

4 Principle

The principle is specified in ISO 11357-1.

5 Apparatus and materials

5.1 Differential scanning calorimeter, according to ISO 11357-1.

5.2 Crucibles, according to ISO 11357-1.

It can be necessary to verify that the material used for the crucibles does not modify the crystallization kinetics of the polymer.

5.3 Balance, according to ISO 11357-1.

5.4 Calibration materials, according to ISO 11357-1.

5.5 Purge gas, according to ISO 11357-1.

6 Test specimens

Test specimens shall be as specified in ISO 11357-1.

7 Test conditions and specimen conditioning

Test conditions and specimen conditioning shall be as specified in ISO 11357-1.

8 Calibration

The calibration shall be done in accordance with ISO 11357-1.

The linearity of the temperature scale in the heating and cooling modes shall be checked using materials which do not supercool. The use of the liquid-liquid transition of liquid crystals, such as 4,4'-azoxyanisole, is recommended.

9 Procedure

9.1 General

The study of the crystallization kinetics of polymers can be done in an isothermal or a non-isothermal mode.

The relative crystallinity is given by the ratio of the partial enthalpy of crystallization, at each time or each temperature, and the total enthalpy of crystallization ΔH_c , as given in Formula (1):

$$\alpha_{t \text{ or } T} = \Delta H_{t \text{ or } T} / \Delta H_c \quad (1)$$

where

- α_t and ΔH_t are the relative crystallinity and the enthalpy of crystallization at a given time in the isothermal mode;
- α_T and ΔH_T are the relative crystallinity and the enthalpy of crystallization at a given temperature in the non-isothermal mode.

9.2 Loading the test specimen into the crucible

The loading of the test specimen shall be done as specified in ISO 11357-1.

To avoid self-heating, the mass of the specimen shall be chosen based on the heat evolved by the crystallization of the material. If the object of the measurements is to compare various grades of a polymer, maintain the mass within $\pm 0,5$ mg.

9.3 Insertion of the crucibles into the instrument

The crucibles shall be inserted into the instrument as specified in ISO 11357-1.

9.4 Melting of the polymer

Prior to isothermal or non-isothermal crystallization, all crystalline elements in the sample that could modify the crystallization kinetics shall be molten completely.

This is usually achieved by heating at a rate of 10 K/min or 20 K/min to a temperature of 30 K above the extrapolated end melting temperature and holding at this temperature for 3 min to 5 min.

NOTE Preliminary trials can be done to optimize these conditions and to prevent this step from changing the molecular structure of the polymer.

9.5 Isothermal crystallization

At the end of the melting stage, cool the specimen as quickly as possible to the selected temperature at which isothermal crystallization shall be measured.

A schematic representation of an isothermal crystallization run is shown in [Figure 2](#).

The time t_0 , at which the selected temperature is reached, is the start of the isothermal step.

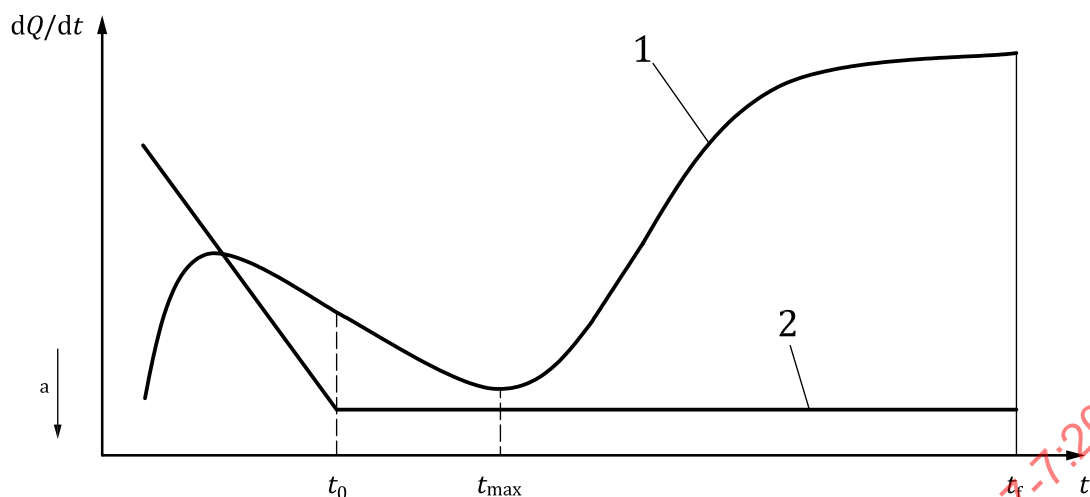
Isothermal crystallization starts at initial crystallization time, t_i , which is obtained by the intersection point of the slope of the crystallization peak onset with a linear baseline obtained by interpolation between peak start and end.

The time t_f at which the isothermal step ends (i.e. the time to obtain a complete crystallization curve) depends on the crystallization rate. If not clear from the DSC curve, it shall be set to five times the time taken to reach the maximum crystallization rate, $t_{\max}$.

Carry out at least three runs at different temperatures.

The isothermal temperatures are limited by the specifications of the instrument and data shall be rejected when the crystallization starts during cooling (see [Figure 1](#)).

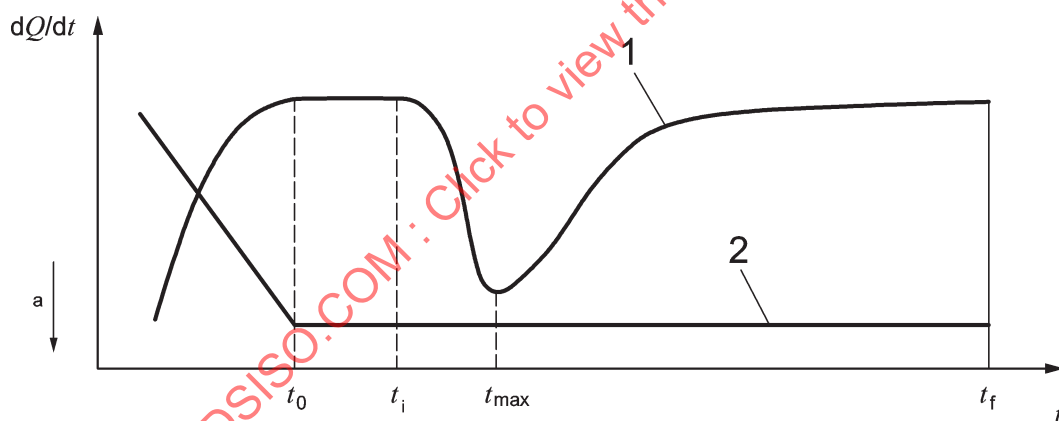
NOTE Limiting instrument factors can be e.g. too high thermal lag or insufficient cooling capabilities.



Key

- 1 DSC signal
- 2 temperature plot
- dQ/dt heat flow rate
- t time
- a Exothermic direction.

Figure 1 — Bad isothermal run: Crystallization started before isothermal temperature reached



Key

- 1 DSC signal
- 2 temperature plot
- dQ/dt heat flow rate
- t time
- a Exothermic direction.

Figure 2 — Good isothermal run

9.6 Non-isothermal crystallization

At the end of the melting stage, cool the specimen at the selected constant cooling rate to at least 10 K to 20 K below the final crystallization temperature.

Carry out at least three runs at different cooling rates.

NOTE It is recommended that the cooling rates used are close to the highest rate at which the instrument is able to maintain the rate linear over the whole cooling-temperature range.

10 Expression of results

10.1 General

See also ISO 11357-3.

NOTE The values calculated in 10.2.1 and 10.2.2 can be used to compare different polymers.

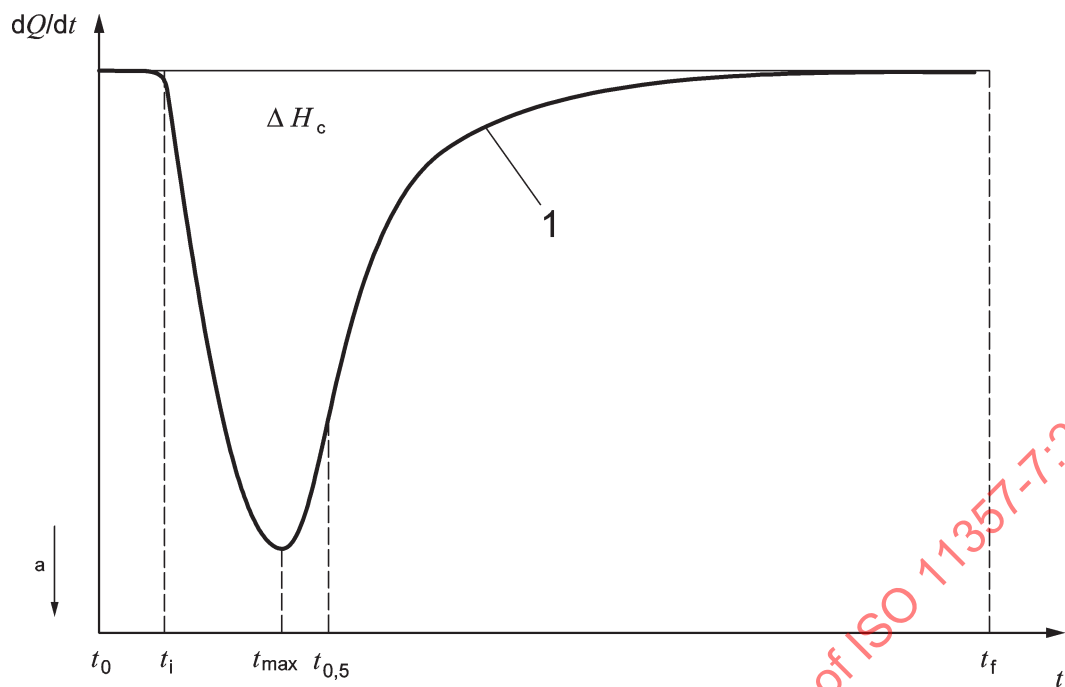
The study of the crystallization kinetics of polymers is still evolving and there are many models to describe the kinetics. The literature has to be used for the actual determination of the kinetics (see [Annex A](#)).

10.2 Methods of determination of crystallization kinetics

10.2.1 Isothermal crystallization

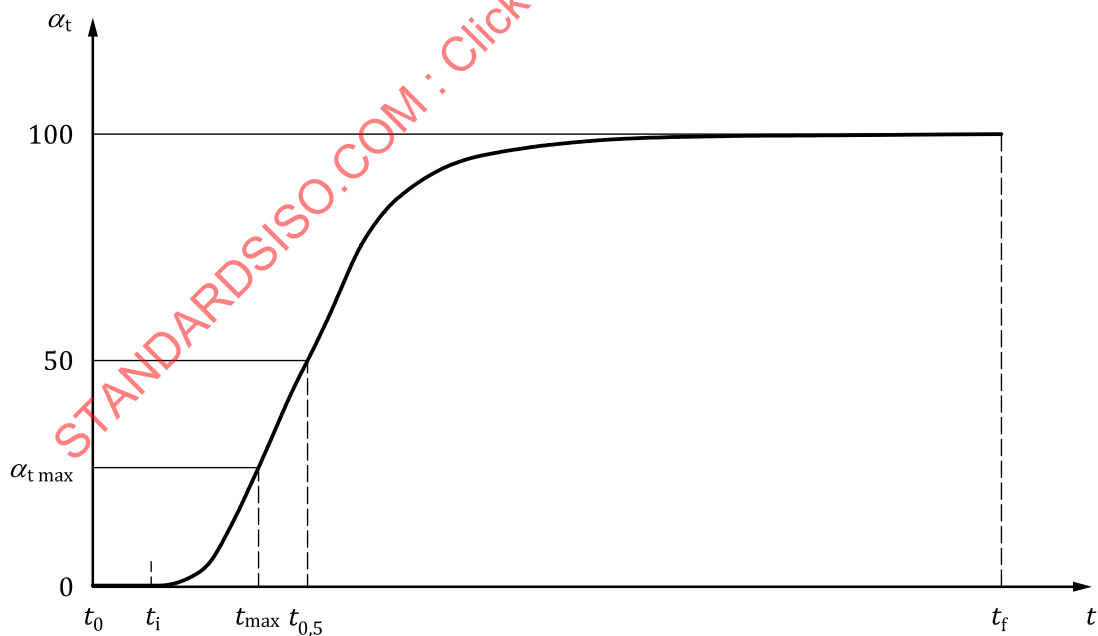
For each run at a specific isothermal temperature, determine the variation in α as a function of time (α_t) and record the following values (see [Figure 3](#) and [Figure 4](#)):

- starting time of the isothermal step ($t = 0$) t_0
- initial crystallization times t_i
- time to reach the maximum crystallization rate $t_{\max}$
(measured to the top of the crystallization peak)
- relative crystallinity at $t_{\max}$ $\alpha_{t_{\max}}$
- time to reach a relative crystallinity of 0,5 $t_{0,5}$
- enthalpy of crystallization ΔH_c
- time to the end of crystallization t_f



Key
1 DSC signal
 dQ/dt heat flow rate
 t time
a Exothermic direction.

Figure 3 — DSC signal during the isothermal step



Key
 α degree of crystallization
 t time

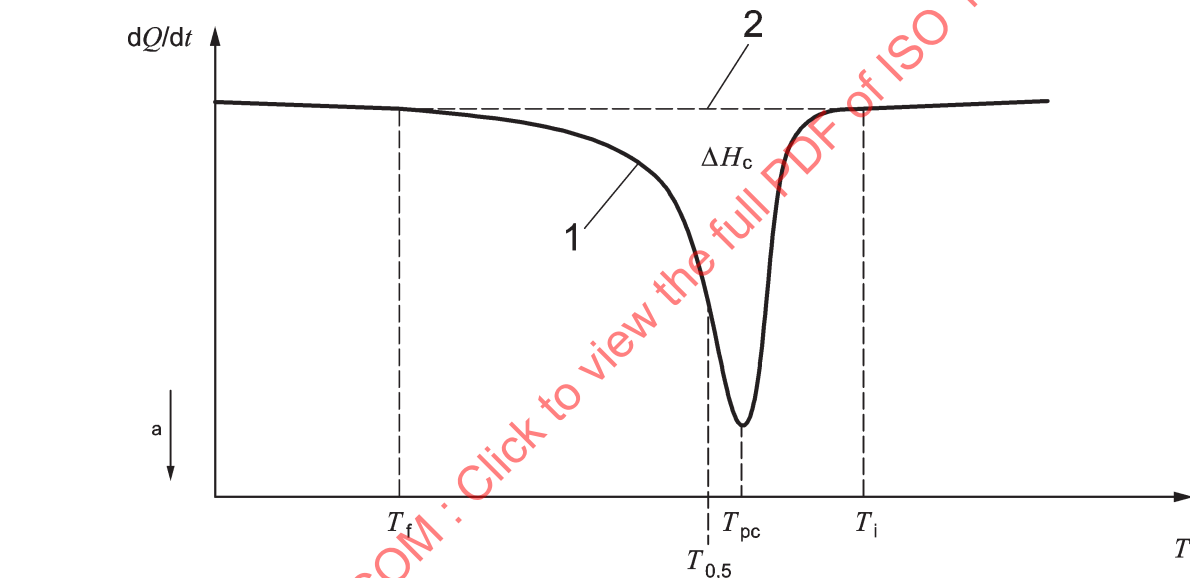
Figure 4 — Variations in α_t during the isothermal step

10.2.2 Non-isothermal crystallization

For each run, specify the cooling rate, determine the variation in α as a function of temperature (α_T) and record at least the following values (see Figure 5 and Figure 6) during the cooling step:

- initial crystallization temperature T_i
- peak crystallization temperature T_{pc}
- temperature to reach a relative crystallinity of 0,5 $T_{0,5}$
- relative crystallinity at T_{pc} $\alpha_{T_{pc}}$
- enthalpy of crystallization ΔH_c
- final crystallization temperatures T_f

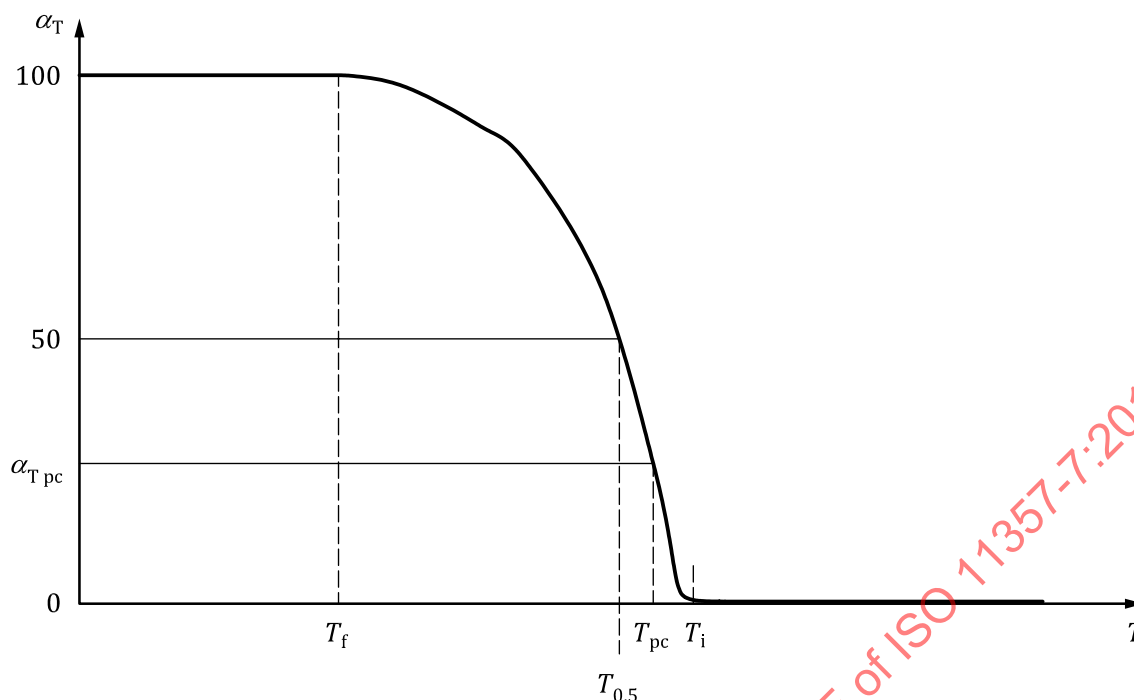
NOTE The initial and the final crystallization temperatures are the points at which the exothermic peak begins to deviate from and returns to the extrapolated straight baseline (see ISO 11357-3).



Key

- 1 DSC signal
- 2 baseline
- dQ/dt heat flow rate
- T temperature
- a Exothermic direction.

Figure 5 — DSC signal during the cooling step



Key

- α degree of crystallization
 T temperature

Figure 6 — Variation in α_T during the cooling step

11 Precision

The precision of this method is not known because inter-laboratory data are not available.

12 Test report

The test report shall be as specified in ISO 11357-1. Additionally, the following values calculated in [Clause 10](#) shall be included as test results:

- times, in minutes, to one decimal place;
- temperatures, in °C, to one decimal place;
- cooling rates, in K/min, to two significant figures;
- relative crystallinities, in %, rounded to the nearest whole number;
- enthalpy of crystallization, in kJ/kg or J/g, to two significant figures.

If the kinetics parameters have been determined, specify the model used with the constants and the calculated values. Where the experimental curves can be compared to curves calculated using the model, the curves should be attached to the test report.

Annex A (informative)

Equations for crystallization kinetics of polymers

A.1 Isothermal crystallization

A.1.1 Avrami equation

$$x_t = x_f \times \left[1 - \exp(-kt^n) \right] \quad (\text{A.1})$$

where

x_t is the crystallinity of the polymer at time t ;

x_f is the crystallinity of the polymer at the end of crystallization;

k is the rate constant at the isothermal temperature T ;

n is the Avrami exponent.

A.1.2 Sestak Berggren equation

$$d\alpha/dt = Z\alpha^m(1-\alpha)^n \exp(-E/RT) \quad (\text{A.2})$$

where

n, m are reaction orders;

E is the activation energy;

R is the gas constant;

T is the absolute temperature;

Z is the pre-exponential factor;

α is the relative crystallinity.

A.2 Non-isothermal crystallization

A.2.1 Ozawa equation

$$\alpha(T) = 1 - \exp \left[-K_0(T) \frac{1}{C^m} \right] \quad (\text{A.3})$$

where

$\alpha(T)$ is the relative crystallinity at temperature T ;

C is the cooling rate $(-dT/dt)$

$K_0(T)$ is the function describing the cooling process;

m is the Ozawa exponent.

A.2.2 Nakamura equation

$$\alpha(T) = 1 - \exp \left\{ - \left[\frac{1}{C} \int_{T(0)}^{T(t)} (k(T))^{1/n} dT \right]^n \right\} \quad (\text{A.4})$$

where

$\alpha(T)$ is the relative crystallinity at temperature T ;

C is the cooling rate $(-dT/dt)$;

$k(T)$ is the rate constant at temperature T ;

n is the Avrami exponent.

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