INTERNATIONAL STANDARD

**ISO 11358-1**

First edition
2014-07-15

# Plastics — Thermogravimetry (TG) of polymers —

## Part 1: General principles

*Plastiques — Thermogravimétrie (TG) des polymères —*

*Partie 1: Principes généraux*



Reference number
ISO 11358-1:2014(E)



ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

# Contents

Page

# 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 first edition of ISO 11358-1 cancels and replaces ISO 11358:1997, which has been technically revised.

The main changes are:

a) addition of ISO 472 to the Normative references clause and removal of definitions specified therein;

b) revision of apparatus specifications.

ISO 11358 consists of the following parts, under the general title *Plastics — Thermogravimetry (TG) of polymers*:

— *Part 1: General principles*

— *Part 2: Determination of activation energy*

— *Part 3: Determination of the activation energy using the Ozawa-Friedman plot and analysis of the reaction kinetics*



# Plastics — Thermogravimetry (TG) of polymers —

# Part 1: General principles

## 1 Scope

This part of ISO 11358 specifies general conditions for the analysis of polymers using thermogravimetric techniques. It is applicable to liquids or solids. Solid materials may be in the form of pellets, granules or powders. Fabricated shapes reduced to appropriate specimen size may also be analysed by this method.

Thermogravimetry can be used to determine the temperature(s) and rate(s) of decomposition of polymers, and to measure at the same time the amounts of volatile matter, additives and/or fillers they contain.

The thermogravimetric measurements may be carried out in dynamic mode (mass change versus temperature or time under programmed conditions) or isothermal mode (mass change versus time at constant temperature).

Thermogravimetric measurements may also be carried out using different testing atmospheres, e.g. to separate decomposition in an inert atmosphere from oxidative degradation.

## 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 291, *Plastics — Standard atmospheres for conditioning and testing*

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 the following apply.

**3.1**
**dynamic mass-change determination**
technique for recording the variation of the mass of a test specimen with temperature $T$ which is changing at a programmed rate

**3.2**
**isothermal mass-change determination**
technique for recording the variation of the mass of a test specimen with time $t$ at constant temperature $T$

**3.3**
**Curie temperature**
temperature at which a ferromagnetic material passes from the ferromagnetic state to the paramagnetic state or vice versa

## 4 Principle

A test specimen is heated at specified rates with a controlled temperature programme, and the change in mass is measured as a function of temperature. Alternatively, the specimen is kept at a given constant temperature and the change in mass is measured as a function of time over a given period.

During measurement the test specimen is held in a controlled inert or oxidising atmosphere.

In general, the reactions which cause the mass of a test specimen to change are decomposition or oxidation reactions or the volatilisation of a component. The change in mass is recorded as a thermogravimetric (TG) curve.

The change in mass of a material as a function of temperature and the extent of this change are indicators of the thermal stability of the material. TG data can therefore be used to evaluate the relative thermal stability of polymers of the same generic family and polymer-polymer or polymer-additive interactions, using measurements made under the same test conditions.

NOTE TG data may be used for process control, process development and material evaluation. Long-term thermal stability is a complex function of service and environmental conditions. TG data alone may not be able to describe the long-term thermal stability of a polymer.

## 5 Apparatus

A number of commercial instruments suitable for thermogravimetric measurements are available. The basic apparatus consists of the following.

**5.1 Thermobalance**, meeting the following requirements:

— capability to generate constant heating and cooling rates suitable for intended measurements;

— capability to maintain the test temperature constant (to within ±0,3 K or less for the duration of measurement);

— capability to maintain a constant purge gas flow rate controllable to within ±10 % over a range of flow rates (e.g. 10 ml/min to 150 ml/min);

— temperature and mass range in line with experimental requirements;

— recording device capable of automatically recording the measured curve of mass versus temperature and time;

— measurement of temperature signals with an accuracy of ±2 K or better;

— measurement of time with an accuracy of ±1 s or better;

— measurement of mass with an accuracy of ±20 µg or better.

**5.2 Purge gas**, dry air or oxygen (oxidizing conditions) or a suitable inert gas with an oxygen content of 0,001 % by volume or less (non-oxidizing conditions). In either case, the water content of the purge gas shall be less than 0,001 % by mass.

## 6 Test specimen preparation

### 6.1 General

Test specimens may be liquids or solids. Solids may be in the form of powders, pellets, granules or cut pieces. For finished products, the test specimen shall be in the form normally found in use.

### 6.2 Test specimens from finished products

Cut the test specimen to appropriate size for the specimen holder. Microtomes or razor blades are suitable for this purpose.

NOTE Test specimen size and shape are generally dependent on the sample holder. Surface area affects the overall results. For instance, in comparing a test specimen of large surface area with a test specimen of smaller surface area, both having the same mass, the smaller surface area test specimen normally changes at a slower rate.

### 6.3 Test specimen conditioning

Unless otherwise specified in a material specification or product standard, test specimens shall be conditioned, prior to measurement, at one of the standard atmospheres specified in ISO 291, or by any other method specified by agreement between the interested parties.

### 6.4 Test specimen mass

Preferably, the mass of the test specimen shall be in the range of 10 mg to 100 mg.

## 7 Calibration

### 7.1 Mass calibration

Without any gas flow through the thermobalance (to prevent any disturbance through buoyancy and/or convection effects), calibrate the thermobalance as follows, using calibrated masses in the range of 10 mg to 100 mg:

Record the temperature at which the mass calibration was carried out.

Zero the thermobalance. Place the calibration weight on the thermobalance and measure the corresponding mass change. If necessary, adjust the thermobalance so that the measured mass is equal to the calibration mass.

If mass calibration is done by procedures included in the instrument control software or by external service providers a valid calibration certificate may be acceptable to demonstrate adequate mass calibration.

### 7.2 Temperature calibration

Carry out the temperature calibration using the same atmosphere, rate of gas flow and heating rate as shall be used in the procedure specified in Clause 8.

If the thermobalance is not coupled with another thermoanalytical method, use the following procedure.

a) Choose two or more calibration materials with a Curie temperature near the temperature range to be examined. If possible, choose the calibration materials in such a way that the temperature range to be examined lies between the Curie temperatures of two of them.

b) Start heating at the same heating rate as will be used in the procedure specified in Clause 8 and carry out a calibration based on the start temperature $T_A$, mid-point temperature $T_C$ and end temperature $T_B$ for the Curie temperature transition.

NOTE 1 The Curie point is the temperature at which a ferromagnetic material becomes paramagnetic on heating. The effect is reversible. Applying a magnetic field (e.g. by placing a strong magnet below the furnace) exerts a downward force on the ferromagnetic sample. This creates an apparent increase of weight which is lost upon heating the sample above its Curie temperature.

NOTE 2 Certified calibration materials traceable to metrology laboratories should be preferably used. Suitable calibration materials may be available via instrument manufacturers or National Metrology Institutes.

If the thermobalance is combined with a DSC (differential scanning calorimetry) detector, it is recommended that the thermobalance is temperature-calibrated using procedures specified in corresponding standards, e.g. ISO 11357-1 for DSC.

NOTE 3 The melting point of a calibration material is defined as the intercept of the extrapolated baseline and the tangent to the slope of the endotherm at the point of inflection of the curve (the so-called onset temperature).

NOTE 4 Calibration is the most critical stage in obtaining reliable thermogravimetry data; the relationship between the temperature sensor, specimen geometry and type of atmosphere, including the rate of gas flow, will affect the calibration of the measurement system.

NOTE 5 The rate of mass loss is dependent upon the rate of oxidation of the test specimen, and therefore dependent in part upon the atmosphere and rate of gas flow to which it is exposed. It is therefore important to use the same atmosphere and rate of gas flow in the calibration as in the procedure specified in Clause 8.

# 8 Procedure

## 8.1 General

Depending on the measurement requirements a suitable instrument setup has to be chosen. Two modes can be used: temperature scanning (see 8.2) and isothermal (see 8.3).

NOTE 1 A change in buoyancy and convection occurs in the thermobalance when the gas flow is operating. Even if there is no actual change in mass, an apparent change in mass is observed and the accuracy of mass measurement is reduced. It is recommended that a preliminary run without the test specimen is carried out at the same heating rate and gas-flow rate as in the actual test in order to observe the apparent change in mass The precision of the mass measurement cannot be better than that obtained from the preliminary test.

NOTE 2 A change of gas is possible during the determination. In this case, it will be necessary to use the same flow rate. In addition, it is recommended that gases with similar densities are used in order to obtain a similar buoyancy effect. If gases of similar densities cannot be used, it may be necessary to make a buoyancy correction.

NOTE 3 When using multiple gases, it is important that the distances between the gas sources and the instrument are as short as possible to minimize the lag-time due to line purging.

Select the gas flow rate.

Adjust the zero point of the thermobalance including sample holder using the same purge gas and flow rate as to be used for the sample measurement.

Place the sample holder containing the test specimen on the thermobalance. Start the gas flow and record the initial mass, unless the following paragraph applies.

For investigations under a strictly inert atmosphere, either evacuate the thermobalance with a vacuum pump and then fill or purge with the inert gas to be used for measurement for at least 10 min at the same flow rate to be used for measurement before recording the mass.

## 8.2 Temperature scanning mode

Set the temperature programme to be followed, which shall be as specified by the referring standard, if applicable.

The programme shall include the initial and final temperatures, the duration of the isothermals at these temperatures, and the rates of heating between programmed temperatures, and the purge gas(es) to be used for the different programme steps.

Start the measurement programme and record the thermogravimetric curve.



### 8.3 Isothermal mode

Start the instrument, running at its maximum heating rate in order to reach the specified temperature as quickly as possible.

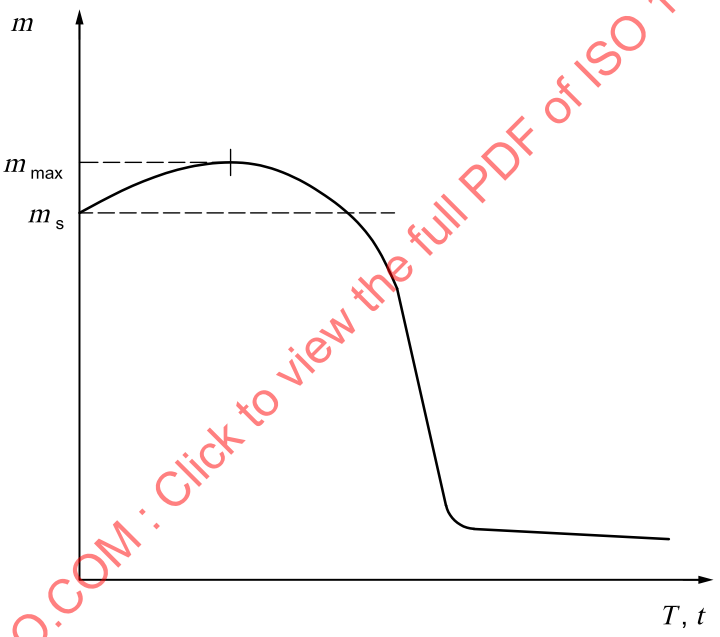
## 9 Expression of results

### 9.1 Graphical representation

Present the thermogravimetry data obtained in the form of a mass or mass change versus time or temperature curve. Determine specific temperatures and masses from the TG curve using the procedures specified in 9.2 and 9.3.

### 9.2 Determination of increase in mass

Determine the maximum mass, $m_{max}$, from the curve. A typical mass gain curve is shown in Figure 1.




**Key**

| | |
|---|---|
| $m$ | mass |
| $T$ | temperature |
| $t$ | time |

**Figure 1 — Example of a TG curve showing an increase in mass**

Calculate the mass gain, $m_g$, expressed as a percentage, using Formula (1):

$$m_g = \frac{m_{max} - m_s}{m_s} \times 100 \quad (1)$$

where

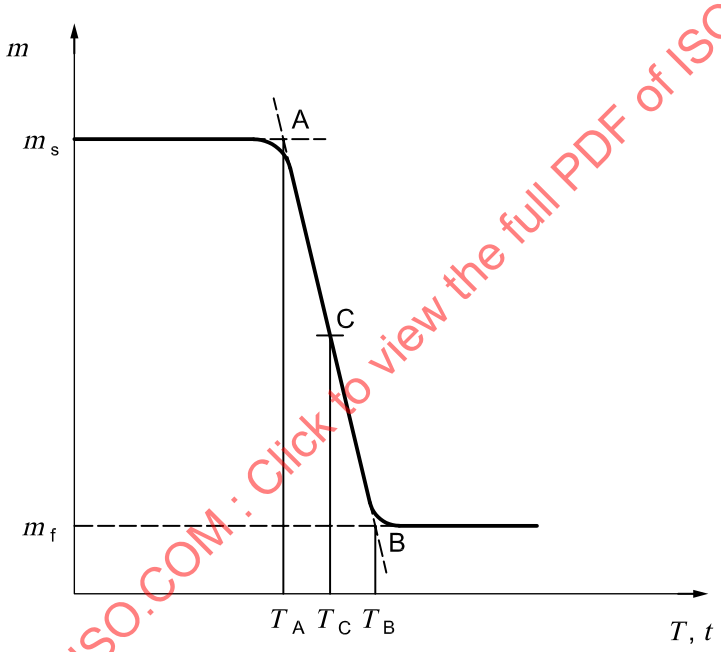
$m_{max}$ is the maximum mass, in milligrams;

$m_s$ is the mass at the starting temperature, in milligrams.

NOTE An increase in mass according to 9.2 is observed in exceptional cases only where absorption of purge gas components occurs.

## 9.3 Determination of loss in mass

### 9.3.1 Single-stage decrease in mass (see Figure 2)




**Key**

| | | | |
|---|---|---|---|
| $m$ | mass | A | starting point |
| $T$ | temperature | B | end point |
| $t$ | time | C | mid-point |

**Figure 2 — Example of a TG curve showing a single-stage decrease in mass**

From the TG curve, determine points A, B and C, where:

— A is the starting point — the point of intersection of the starting-mass baseline and the tangent to the TG curve at the point of maximum gradient;

— B is the end point — the point of intersection of the final-mass baseline and the tangent to the TG curve at the point of maximum gradient;

— C is the mid-point — the point of intersection of the TG curve with the temperature at which both baselines are equidistant.

Determine masses $m_s$ and $m_f$ and temperatures $T_A$, $T_B$ and $T_C$ corresponding to points A, B and C.



Calculate the mass loss $m_l$, expressed as a percentage, using Formula (2):

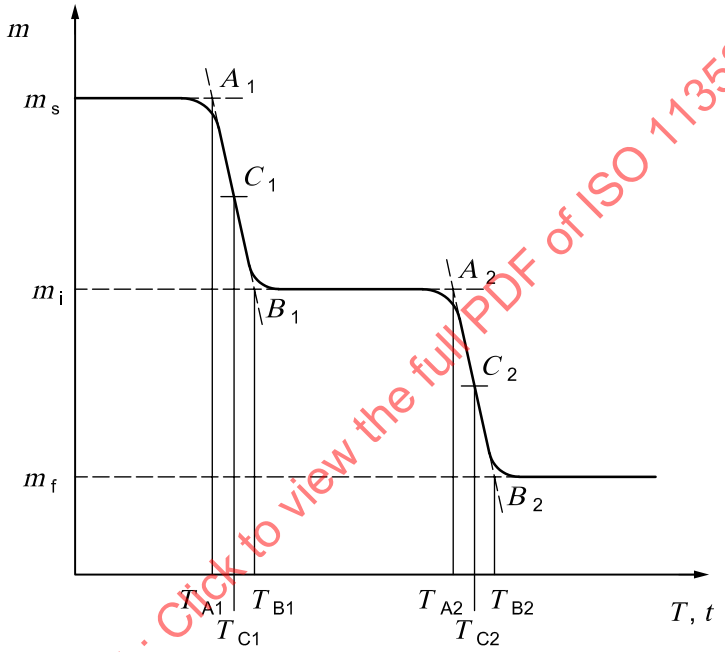
$$m_l = \frac{m_s - m_f}{m_s} \times 100 \quad (2)$$

where

$m_f$ is the mass, in milligrams, at the end point B;

$m_s$ is the mass, in milligrams, at the starting point A.

### 9.3.2 Multi-stage decrease in mass (see Figure 3)




**Key**

$m$ mass

$T$ temperature

$t$ time

**Figure 3 — Example of a TG curve showing a multi-stage decrease in mass**

Determine points $A_1$, $B_1$, $C_1$, $A_2$, $B_2$, $C_2$, and so on (if there are more than two stages) as described in 9.3.1.

Determine masses $m_s$, $m_i$ and $m_f$ and temperatures $T_{A1}$, $T_{B1}$, $T_{C1}$, $T_{A2}$, $T_{B2}$, $T_{C2}$, and so on, corresponding to these points.

If the TG curve does not indicate constant mass in the part of the curve between the primary and secondary stage (see Figure 4), the point of intersection of the tangent to this part of the curve at the point of minimum gradient and the tangent to the first-stage part of the curve at the point of maximum gradient shall be taken as end point of the first stage $B_1$ and the point of intersection of this minimum-gradient tangent and the maximum-gradient tangent to the second-stage part of the curve shall be taken as starting point of the second stage $A_2$. The mass $m_i$ shall be taken as the mid-point between $m_{B1}$ and $m_{A2}$.