BS ISO 11358-2:2014

BSI Standards Publication

Plastics — Thermogravimetry (TG) of polymers

Part 2: Determination of activation energy

bsi.

...making excellence a habit.™

National foreword

This British Standard is the UK implementation of ISO 11358-2:2014. It supersedes BS ISO 11358-2:2005 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PRI/21, Testing of plastics.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Published by BSI Standards Limited 2014

ISBN 978 0 580 84697 7
ICS 83.080.01

Compliance with a British Standard cannot confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 June 2014.

Amendments/corrigenda issued since publication

Date	Text affected

BS ISO 11358-2:2014

INTERNATIONAL STANDARD

ISO 11358-2

Second edition
2014-06-15

Plastics — Thermogravimetry (TG) of polymers —

Part 2: Determination of activation energy

Plastiques — Thermogravimétrie (TG) des polymères —

Partie 2: Détermination de l'énergie d'activation

Reference number
ISO 11358-2:2014(E)

COPYRIGHT PROTECTED DOCUMENT

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 and chemical properties*.

This second edition cancels and replaces the first edition (ISO 11358-2:2005), of which it constitutes a minor revision. The following are the changes:

— limitation of the term "activation energy" to gas-phase reactions was deleted;

— normative references were changed into undated ones;

— the term "pan" was replaced by "crucible" in the whole text;

— in line with 3.2, the term "energy of activation" was replaced with "activation energy" (see 9.2).

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*

INTERNATIONAL STANDARD **ISO 11358-2:2014(E)**

Plastics — Thermogravimetry (TG) of polymers —

Part 2: Determination of activation energy

1 Scope

This part of ISO 11358 specifies a method for the determination of the activation energy, E_a, in the Arrhenius formula for the decomposition of polymers using a thermogravimetric technique. The method is applicable only if the reaction proceeds by a single mechanism. It is applicable to multistage reactions if they consist of clearly separated single-stage steps.

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 11358-1, *Plastics — Thermogravimetry (TG) of polymers — Part 1: General principles*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11358-1 and the following apply.

3.1
Arrhenius formula
formula representing the temperature dependence of the rate constant of a reaction

Note 1 to entry: The rate constant, k, of a reaction is expressed by the Arrhenius formula, as follows:

$$k = A\exp^{(-E_a/RT)}$$

where

R is the gas constant (= 8,314 J · K^{-1} · mol^{-1});

T is the absolute temperature, in kelvins (K);

A is the pre-exponential factor, in reciprocal seconds (s^{-1});

E_a is the activation energy, in J · mol^{-1};

k is the rate of reaction (= dα/dt), in reciprocal seconds (s^{-1}).

3.2
activation energy
E_a
energy, above that of the ground state, which must be added to an atomic or a molecular system to allow a particular process to take place

Note 1 to entry: It is expressed in J · mol^{-1}.

3.3
degree of conversion
α
quantity of products present at a particular time and temperature during a reaction compared with the final quantity of the products

Note 1 to entry: It is given by the formula

$$\alpha = (M_i - M_t) / (M_i - M_f)$$

where

M_i is the initial quantity, in milligrams;

M_t is the quantity at a particular time and temperature, in milligrams;

M_f in the final quantity, in milligrams.

Note 2 to entry: When multistage reactions occur, the degree of conversion is calculated separately for each stage.

Note 3 to entry: The degree of conversion is dimensionless and varies in value from 0 to 1.

4 Principle

Test specimens are heated at several different heating rates and the change in mass measured as a function of temperature. The temperatures corresponding to given degrees of conversion are determined for each heating rate. For a given degree of conversion, the logarithm of the heating rate is plotted against the reciprocal of the absolute temperature, and the activation energy is calculated from the slope of the straight line thus obtained.

5 Apparatus

See ISO 11358-1.

6 Mass and temperature calibration

6.1 Mass calibration

See ISO 11358-1.

6.2 Temperature calibration

See ISO 11358-1.

7 Test specimens

The test specimens shall be in the form of powder, pellets, flakes, filaments, or film. The test specimens shall be prepared by cutting the material, as necessary, to a size appropriate for the apparatus (see ISO 11358-1). Particles of small size, i.e. of high surface-area-to-volume ratio, are preferred. Grinding in a liquid-nitrogen mill can be used to decrease the particle size.

8 Procedure

8.1 General

See ISO 11358-1.

Perform the procedure at three or more heating rates, using specimens of identical mass (±1 %). The lowest and highest heating rates shall differ by a factor of at least 5.

In order to improve the accuracy of the determination, record the mass of an empty crucible subjected to the same test conditions of atmosphere, gas flow, and heating rate as used in the run with the specimen. If there is a mass change during the run with the empty crucible (which is usually ascribed to buoyancy), subtract the curve obtained with the empty crucible from that obtained with the test specimen to obtain a corrected thermogravimetric curve for the specimen. This procedure shall be repeated for all heating rates. Corrected curves shall be used for the analysis of the results.

NOTE It is preferable to use specimens less than 10 mg in size and heating rates of less than 10 $K \cdot min^{-1}$. For specimens greater than 10 mg and heating rates greater than 10 $K \cdot min^{-1}$, the specimen temperature might not follow the required temperature profile.

8.2 Non-oxidative reactions

When required, an inert-gas atmosphere (e.g. nitrogen) shall be maintained during the determination to prevent oxidation of the specimen. Only purified gas (purity at least 99,95 %) shall be used to create the inert atmosphere.

8.3 Oxidative reactions

An oxidative gas atmosphere (oxygen or air) shall be used when testing polymers that undergo oxidation reactions. Details of the type and purity of the gas used shall be included in the test report.

9 Expression of results

9.1 Graphical presentation

Present the thermogravimetry data obtained in the form of a mass change or percentage mass change versus temperature curve. Determine specific temperatures from the TG curve using the procedures described in ISO 11358-1.

9.2 Determination of activation energy

Check that the final mass reached at the end of each measurement run is constant, thereby indicating completion of the reaction, and that the percentage change in mass from the start of the run to the end of the run for each of the heating rates is also the same.

For a given degree of conversion, α, determine, from the TG curves, the absolute temperatures for each of the heating rates, β. Repeat for other degrees of conversion. Typical curves are shown in Figure 1.

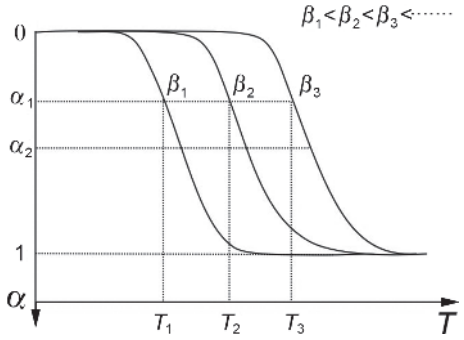

Figure 1 — Determination of absolute temperature for a given degree of conversion and heating rate

The approximate relationship given by Formula (1) was derived by Ozawa and later by Flynn and Wall (see References [1] and [2] in the Bibliography) and is used to determine the activation energy, E_a.

$$\log\beta + 0{,}456\,7\left(E_a / RT\right) = \text{constant} \tag{1}$$

where E_a and R are the activation energy and the gas constant (R = 8,314 J · K^{-1} · mol^{-1}), respectively.

For heating rates β_1, β_2, β_3, ..., and temperatures T_1, T_2, T_3, ..., Formula (2) is obtained for a given degree of conversion, α_1:

$$\log\beta_1 + 0{,}456\,7\left(E_a / RT_1\right) = \log\beta_2 + 0{,}456\,7\left(E_a / RT_2\right) = \log\beta_3 + 0{,}456\,7\left(E_a / RT_3\right) \tag{2}$$

Plotting the logarithm of the heating rate, logβ, against the reciprocal of the absolute temperature, T^{-1}, for each degree of conversion α gives a series of straight-line curves (see Figure 2), and the activation energy, E_a, is calculated from the slope (−0,456 7E_a/R) in each case.

NOTE 1 This method is not suitable for very high degrees of conversion.

NOTE 2 This method is not reliable when the value of E_a varies widely from one degree of conversion to another and/or the logβ versus T^{-1} relationship is not linear.

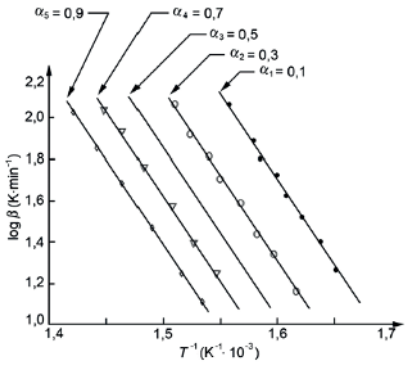

Figure 2 — Heating rate versus the reciprocal of the absolute temperature

10 Precision

See Reference [3] in the Bibliography.

11 Test report

The test report shall include the following information:

a) a reference to this part of ISO 11358, i.e. ISO 11358-2:2014;

b) all details necessary for complete identification of the material analysed;

c) the form and dimensions (if applicable) of the test specimen;

d) the mass of the test specimen;

e) details of the conditioning of the specimen prior to the test;

f) the specimen crucible size and material of construction;

g) the atmosphere and gas-flow rate used;

h) the heating rates used;

i) the standard reference material used for temperature calibration;

j) the activation energy determined using the formula in Note 1 to entry in 3.1 or Formula (1);

k) any observations regarding equipment, test conditions, or test specimen behaviour;

l) the date of the determination.

Bibliography

[1] Ozawa T. A new method of analyzing thermogravimetric data. *Bull. Chem. Soc. Jpn.* 1965, **38** p. 1881

[2] Flynn J.H., & Wall L.A. A quick, direct method for the determination of activation energy from thermogravimetric data. *J. Polym. Sci.* 1966, **4** p. 323

[3] Anderson H.L., Kemmler A., Hohne G.W.H., Keldt K., Strey R. Round robin test on the kinetic evaluation of a complex solid state reaction from 13 European laboratories — Part 1: Kinetics TG-analysis. *Thermochim. Acta*. 1999, **332** p. 33

ICS 83.080.01
Price based on 6 pages

This page deliberately left blank

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards -based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email bsmusales@bsigroup.com.

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Copyright

Useful Contacts:

Customer Services
Tel: +44 845 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 845 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

bsi.

...making excellence a habit.™