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Plastics — Thermogravimetry (TG) of polymers —

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

Plastiques — Thermogravimétrie (TG) des polymères —

Partie 3: Détermination de l'énergie d'activation à l'aide du graphique d'Ozawa-Friedman et analyse cinétique de la réaction

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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).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document 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 11358-3:2013), which has been technically revised.

The changes compared to the previous edition are as follows:

— the term "conversion" has been deleted;

— a corresponding reference to ISO 11358-2 has been added in Clause 3;

— details of the gas atmosphere in 8.1 and 8.2 have been clarified.

A list of all parts in the ISO 11358 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The Ozawa-Friedman plot (logarithm of the rate of mass loss versus the reciprocal of absolute temperature at a given mass loss) is a derivative method that can be applied to data obtained by any mode of temperature change in thermal analysis; e.g. isothermal, constant heating rate, sample-controlled thermal analysis, temperature jump, and repeated temperature scanning.

If controlled rate thermogravimetry (CRTG) is used to study the decomposition of polymers, the Ozawa-Friedman method is typically applied to the analysis of data obtained by CRTG and also to that obtained by the combined use of isothermal thermogravimetry (iso–TG) with conventional linear heating rate thermogravimetry (LHTG), i.e. using a constant heating rate.

Plastics — Thermogravimetry (TG) of polymers —

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

1 Scope

This document specifies an analysis method for determining the activation energy using the Ozawa-Friedman plot. It also specifies the preparation of master plots for verification of the reaction kinetics determined by thermogravimetry.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. 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*

ISO 11358-2, *Plastics — Thermogravimetry (TG) of polymers — Part 2: Determination of activation energy*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11358-1, ISO 11358-2 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
generalized time
t_{gen}

$$t_{gen} = \int_0^t \exp\left(-\frac{E_a}{RT}\right) dt$$

where

E_a is the activation energy, expressed in kJ/mol;

R is the gas constant, expressed as 8,314 J/(mol K);

T is the absolute temperature, expressed in Kelvin;

t is time, expressed in minutes.

3.2
generalized rate of conversion
dC/dt_{gen}

$$\frac{dC}{dt_{gen}}=\exp\left(\frac{E_a}{RT}\right)\frac{dC}{dt}$$

Note 1 to entry: For the definition of the degree of conversion, refer to ISO 11358-2.

3.3
master curve
plot that can be used to evaluate the results and investigate the reaction kinetics models

EXAMPLE Conversion versus the generalized time, conversion versus the generalized rate of conversion, generalized time versus the generalized rate of conversion.

4 Principle

Test specimens are heated using any temperature profile and the change in mass is measured as a function of temperature and time. At a given conversion, the logarithm of the rate of conversion is plotted versus the reciprocal of the absolute temperature, and the activation energy is calculated from the slope of the straight line fit to the data thus obtained.

At least two of the master curves enable verification of the reaction kinetics analysis.

5 Apparatus

The apparatus shall be in accordance with ISO 11358-1.

6 Test specimens

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).

7 Mass and temperature calibration

7.1 Mass calibration

The procedure of mass calibration is given in ISO 11358-1.

7.2 Temperature calibration

The procedure of temperature calibration is given in ISO 11358-1.

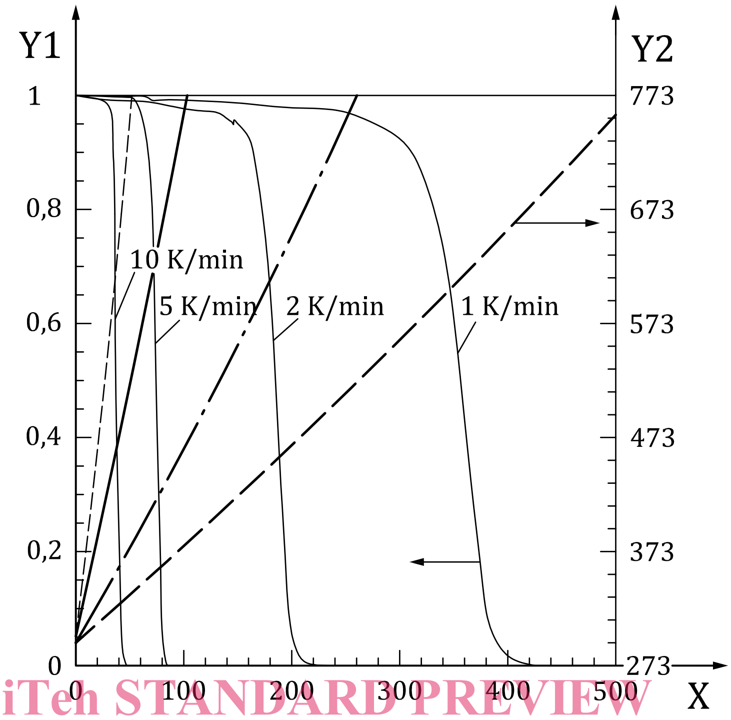
8 Procedure

8.1 General

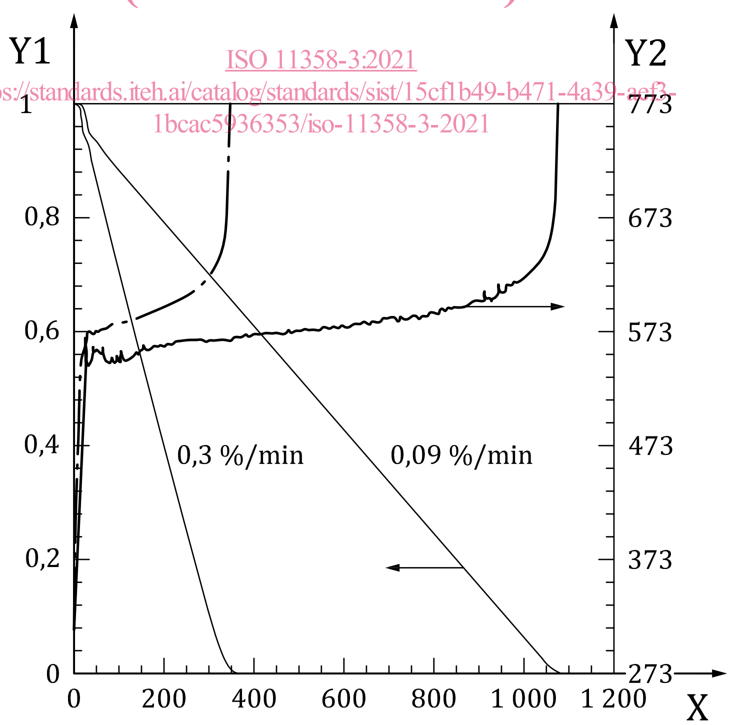
The determination of the rate of conversion dC/dt is necessary for the analysis in this document. The rate of conversion versus absolute temperature shall be determined.

See ISO 11358-1 and ISO 11358-2.

Perform tests using either an isothermal run, constant rate heating, sample mass controlled rate thermal analysis, temperature jump, repeated temperature scanning, or any combination of the above, using specimens of similar mass (±1 %). For examples of linear heating rate thermogravimetry (LHTG) and sample mass controlled rate thermogravimetry (CRTG), see Figure 1 a) and Figure 1 b), respectively.



a) Example of linear heating rate thermogravimetry (LHTG) measurements of PMMA



b) Example of sample mass controlled rate thermogravimetry (CRTG) measurements of PMMA

Key

X *t*/min

Y1 (*1* – *C*)

Y2 *T*/K

NOTE The units of %/min indicate the percentage weight loss per minute of the mass controlled rate.

Figure 1 — Examples of linear heating rate thermogravimetry (LHTG) measurements and sample mass controlled rate thermogravimetry (CRTG) measurements of PMMA

Preferably, the specimen mass should be between 1 mg and 10 mg and the temperature scanning rate between 2 K min^{-1} and 10 K min^{-1}.

Determine the rate of conversion (or rate of change of mass loss fraction with time) at a given conversion (or given mass loss fraction).

8.2 Non-oxidative reactions

The inert gas atmosphere shall be in accordance with ISO 11358-2.

8.3 Oxidative reactions

The oxidative gas atmosphere shall be in accordance with ISO 11358-2.

9 Expression of results

9.1 Graphical presentation

For a given conversion (or mass loss fraction), present the thermogravimetry data in the form of a plot of the logarithm of the rate of conversion (or rate of change of mass loss fraction with time) versus the reciprocal of the absolute temperature, i.e. the Ozawa-Friedman plot, see Figure 2.

9.2 Determination of activation energy

The conversion (or the mass loss fraction) is not directly related to the quantity of reacted pieces, for example as in the random scission of the main chain of polymers, but the conversion, *C*, of a reacting material is expressed as a function of the fraction of a structural quantity, such as a group, a constituent, a broken bond, etc., which is represented by α[1].

Generally, the rate formulae are as shown in Formulae (1) and (2):

$$C = f(\alpha) \tag{1}$$

and

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E_a}{RT}\right)g(\alpha) \tag{2}$$

where

- α is the reacted fraction at time t;
- $f(\alpha)$ is an arbitrary function describing the relationship between the conversion C and the fraction of the reacted structural quantity;
- A is the pre-exponential factor;
- $g(\alpha)$ is a function describing the reaction mechanism.

By taking the logarithm of both sides of Formula (2), Formula (3) can be obtained as follows:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\{Ag(\alpha)\} - \frac{E_a}{RT} \tag{3}$$

When plotted for fixed values of α, with various conversion rate values determined for different experimental temperature control profiles, the slope of the plot of $\ln\left(\frac{d\alpha}{dt}\right)$ versus $\frac{1}{T}$ has the value $-E_a/R$ and is used to determine the activation energy E_a, as the first term in the right side of Formula (3) is constant.

As an example, the experimental data presented in Figures 1a and 1b have been analysed, assuming an n^{th} order type reaction and thus $C = f(\alpha) = \alpha$ (see Annex A), the results of which are presented in Table 1 and Figure 2.

Table 1 — Rate of conversion d*C*/d*t* and estimated activation energy E_a at different conversion levels[a]

	1 000/*T*	ln(d*C*/d*t* (% min^{-1}))	1 000/*T*	ln(d*C*/d*t* (% min^{-1}))	1 000/*T*	ln(d*C*/d*t* (% min^{-1}))
	(K^{-1})	at C = 0,2	(K^{-1})	at C = 0,5	(K^{-1})	at C = 0,8
CRTG, 0,09 %/min	1,779	−2,425	1,735	−2,411	1,677	−2,448
CRTG, 0,3 %/min	1,731	−1,161	1,693	−1,183	1,641	−1,288
Activation energy (kJmol^{-1})						
Ozawa-Friedman plot	207,3		232,8		261,9	
[a] Determined from the controlled rate thermogravimetry (CRTG) data presented in Figure 1 b).						