PD IEC/TR 60216-7-2:2016

BSI Standards Publication

Electrical insulating materials — Thermal endurance properties

Part 7-2: Results of the round robin tests to validate procedures of IEC TS 60216-7-1 by non-isothermal kinetic analysis of thermogravimetric data

bsi.

National foreword

This Published Document is the UK implementation of IEC/TR 60216-7-2:2016.

The UK participation in its preparation was entrusted to Technical Committee GEL/112, Evaluation and qualification of electrical insulating materials and systems.

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

Published by BSI Standards Limited 2016

ISBN 978 0 580 92883 3
ICS 19.020; 29.020; 29.035.01

This Published Document was published under the authority of the Standards Policy and Strategy Committee on 30 September 2016.

Amendments/corrigenda issued since publication

Date	Text affected

IEC TR 60216-7-2

Edition 1.0 2016-08

TECHNICAL REPORT

colour
inside

Electrical insulating materials – Thermal endurance properties – Part 7-2: Results of the round robin tests to validate procedures of IEC TS 60216-7-1 by non-isothermal kinetic analysis of thermogravimetric data

INTERNATIONAL
ELECTROTECHNICAL
COMMISSION

ICS 19.020; 29.020; 29.035.01

ISBN 978-2-8322-3606-2

CONTENTS

INTERNATIONAL ELECTROTECHNICAL COMMISSION

ELECTRICAL INSULATING MATERIALS – THERMAL ENDURANCE PROPERTIES –

Part 7-2: Results of the round robin tests to validate procedures of IEC TS 60216-7-1 by non-isothermal kinetic analysis of thermogravimetric data

FOREWORD

1) The International Electrotechnical Commission (IEC) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, IEC publishes International Standards, Technical Specifications, Technical Reports, Publicly Available Specifications (PAS) and Guides (hereafter referred to as “IEC Publication(s)”). Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.

2) The formal decisions or agreements of IEC on technical matters express, as nearly as possible, an international consensus of opinion on the relevant subjects since each technical committee has representation from all interested IEC National Committees.

3) IEC Publications have the form of recommendations for international use and are accepted by IEC National Committees in that sense. While all reasonable efforts are made to ensure that the technical content of IEC Publications is accurate, IEC cannot be held responsible for the way in which they are used or for any misinterpretation by any end user.

4) In order to promote international uniformity, IEC National Committees undertake to apply IEC Publications transparently to the maximum extent possible in their national and regional publications. Any divergence between any IEC Publication and the corresponding national or regional publication shall be clearly indicated in the latter.

5) IEC itself does not provide any attestation of conformity. Independent certification bodies provide conformity assessment services and, in some areas, access to IEC marks of conformity. IEC is not responsible for any services carried out by independent certification bodies.

6) All users should ensure that they have the latest edition of this publication.

7) No liability shall attach to IEC or its directors, employees, servants or agents including individual experts and members of its technical committees and IEC National Committees for any personal injury, property damage or other damage of any nature whatsoever, whether direct or indirect, or for costs (including legal fees) and expenses arising out of the publication, use of, or reliance upon, this IEC Publication or any other IEC Publications.

8) Attention is drawn to the Normative references cited in this publication. Use of the referenced publications is indispensable for the correct application of this publication.

9) Attention is drawn to the possibility that some of the elements of this IEC Publication may be the subject of patent rights. IEC shall not be held responsible for identifying any or all such patent rights.

The main task of IEC technical committees is to prepare International Standards. However, a technical committee may propose the publication of a Technical Report when it has collected data of a different kind from that which is normally published as an International Standard, for example "state of the art".

IEC TR 60216-2-7, which is a Technical Report, has been prepared by IEC technical committee 112: Evaluation and qualification of electrical insulating materials and systems.

The text of this Technical Report is based on the following documents:

Enquiry draft	Report on voting
112/354/DTR	112/370/RVC

Full information on the voting for the approval of this Technical Report can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts in the IEC 60216 series, published under the general title *Electrical insulating materials – Thermal endurance properties*, can be found on the IEC website.

The committee has decided that the contents of this publication will remain unchanged until the stability date indicated on the IEC website under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

A bilingual version of this publication may be issued at a later date.

IMPORTANT – The 'colour inside' logo on the cover page of this publication indicates that it contains colours which are considered to be useful for the correct understanding of its contents. Users should therefore print this document using a colour printer.

INTRODUCTION

IEC technical committee 112, (IEC/TC112) has been working on the development of IEC TS 60216-7-1 that considers the use of activation energy determined through thermal analytical tools plus abbreviated conventional heat ageing to determine a thermal index on a polymeric compound. At the same time, the UL LTTA Forum has been discussing alternative methods that could speed up the determination of a thermal index. Members of the IEC/TC112 and of the UL LTTA Forum have joined efforts to determine whether the Technical Specification developed by IEC/TC112 can be used to offer an alternative method of evaluating polymeric compounds for a thermal index.

Members of IEC/TC112 and the UL LTTA Forum decided to conduct a round robin test (RRT) using thermogravimetric analysis (TGA) according to ISO 11358-2 on a known compound, with a known activation energy determined through conventional ageing with a view to validate the acceptability of IEC TS 60216-7-1, and to determine whether a similar thermal index could be calculated. The round robin testing was conducted with conventional TGA by multiple heating rates. However, running isothermal tests can be a follow up of this RRT.

ELECTRICAL INSULATING MATERIALS – THERMAL ENDURANCE PROPERTIES –

Part 7-2: Results of the round robin tests to validate procedures of IEC TS 60216-7-1 by non-isothermal kinetic analysis of thermogravimetric data

1 Scope

The purpose of this part of IEC 60216, which is a Technical Report, is to validate the procedures of IEC TS 60216-7-1 in providing a similar temperature index to conventional methods used in other parts of the IEC 60216 series.

These round robin test results do not provide statistical analysis for precisions. The round robin test focuses on preliminary studies to understand the evaluation and calculation procedures, influence on apparatus, and data variance among laboratories before determination of precisions.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

activation energy
Arrhenius activation energy
E_a
empirical parameter characterizing the exponential temperature dependence of the reaction rate constant

[SOURCE: IUPAC “Goldbook”]

3.2

end-point
limit for a diagnostic property value based on which the thermal endurance is evaluated

3.3

time to end-point
failure time
time to reach the end point or conventional failure

3.4

relative temperature endurance index
RTE
numerical value of the temperature in degrees Celsius at which the estimated time to end-point of the candidate material is the same as the estimated time to end-point of the reference material at a temperature equal to its assessed temperature index

Note 1 to entry: RTE_A is the relative temperature endurance index calculated through the analytical procedure.

3.5
temperature endurance index
TI

numerical value of the temperature in degrees Celsius derived from the thermal endurance relationship at a time of 20 000 h (or other specified time)

Note 1 to entry: TI_A is the temperature index calculated through the analytical procedure.

[SOURCE: IEC 60050-212:2010, 212-12-11, modified – the two notes have been deleted and replaced by a new note.]

3.6
halving interval
HIC

numerical value of the temperature interval in kelvin which expresses the halving of the time to end-point taken at the temperature equal to TI

Note 1 to entry: HIC_A is the halving interval calculated through the analytical procedure.

3.7
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

[SOURCE: ISO 11358-2:2014, 3.3, modified — the notes have been deleted]

4 Test specimens

For the round robin study, one generic type of polymer, liquid crystal polyester (LCP), was pre-selected as the round robin study which assumes one single thermal degradation reaction is predominant and directly correlated to the end-point of dielectric strength as a diagnostic property.

LCP originally has very little entwining of molecules which exhibits crystalline properties as a liquid and therefore, there is less thermal transformation between solid and liquid, or between oven ageing conditions of conventional thermal endurance test and TGA conditions at higher temperature range. In addition, LCP molecular chains align themselves when moulded, and this generates a self-reinforcing effect, thereby resulting in high mechanical and electrical stress resistance.

In this round robin, two LCP materials (LCP sample A, LCP sample B) were chosen for test samples which already have the conventional heat oven ageing data of dielectric strength, tensile strength, and impact strength to validate the acceptability of whether or not RTE_A can be similar to RTE. Both sample A and sample B consist of 30 % glass fibres reinforced. Configurations of monomers are only different between the samples which influence the difference in thermal resistance, as shown in Table 1.

The samples were homogenized by freeze-pulverization from the test plaques respectively. 100 mg each of freeze-pulverized powders from the same batch were prepared and provided to eleven testing laboratories for evaluation, after pre-drying at 140 °C for 4 h.

Table 1 – Heat ageing properties of the test specimens by the conventional procedure described in IEC 60216-5

Temperature in ovens	Time to end-point at 50 % retention of initial dielectric strength h		Time to end-point at 50 % retention of initial tensile strength h		Time to end-point at 50 % retention of initial impact strength h	
°C	LCP Sample A	LCP Sample B	LCP Sample A	LCP Sample B	LCP Sample A	LCP Sample B
290		1 141		1 215		1 860
285	2 896		1 789		2 870	
280		1 917		3 229		2 655
275	5 591		3 083		4 164	
270		4 300		4 597		3 920
265	8 255		6 706		8 412	
260		5 848		7 625		6 640
250						9 600
Ea	130,6	142,3	165,2	145,9	134,5	102,9
TI	250,0	241,5	249,1	246,2	249,1	234,7

5 Test apparatus

5.1 Thermogravimetric analyser (TGA)

A thermogravimetric analyser (TGA) in accordance with ISO 11358-1 was used for determination of RTE_A concerning the test samples. In fact, a number of commercial instruments suitable for the document are available and various models of TGAs that the laboratory participants have were used for evaluation of the test samples. Before the RRT, weight and temperature calibrations were implemented based on ISO 11358-1 and TGA apparatus manufacturer’s guidance.

5.2 Purge gas supplied into the TGA furnace

For purge gas into the TGA furnace, air was chosen to assume oxidative thermal degradation, as well as degradation of electrical and mechanical strengths with test specimens in oven ageing. Most of the laboratory participants selected dry air (water content less than 1 ppm[1]), but air supplied from the facility (compressed air with or without air dryer) was used in a few laboratories.

6 Test procedures

6.1 General

Thermal analysis with TGA of the test samples was evaluated with reference to ISO 11358-2 and IEC TS 60216-7-1 in principle. A few modifications of test conditions and more detailed procedures were added as follows.

---

[1] ppm = part per million.

6.2 Preconditioning of test samples

5 mg ± 0,5 mg of the test sample were initially measured in each laboratory and mounted on the empty pan in the furnace opened. Then the furnace was closed and pre-conditioned in equilibrium at 100 °C for 1 h before heating tests were started. The weight value just before the heating test (time at 0 s in the heating run, or 60 min at the end of the equilibrium) was used for calculation on the degree of conversion.

NOTE ISO 11358-2 requires using test samples of identical mass ±1 % of the initial weight in multiple heating conditions which is much narrower than the above. Influence on the initial mass deviation is taken into consideration in 7.2.

6.3 TGA tests with multiple heating rates

Multiple heating rates testing at 1 K/min, 2 K/min, 4 K/min, 6 K/min and 8 K/min were selected for evaluation which gave the lowest and highest heating rates that differ by a factor of 8, in accordance with ISO 11358-2. Evaluation temperature range was set between 100 °C and 700 °C. Each heating rate test was run one time each for sample A and sample B, but 8 K/min was evaluated twice as an approximate check and to consider repeatability.

6.4 Calculation of the activation energy (E_a)

After TGA data with multiple heating rates were obtained, the activation energies were calculated per certain given degrees of conversion in accordance with Equation (2) in ISO 11358-2:2014. Then, both values of degree of conversion and the activation energies were plotted between 1 % and 19 % with 2 % interval of degree of conversion to analyse the cubic approximation for drawing the fitting curve of the plots as shown in Figure 1. Equation (2) in ISO 11358-2:2014 was used for selection of appropriate activation energy and degree of conversion to determine RTE_A.

For example, if the activation energy of a reference material was already determined as 150 kJ/mol by the conventional heat ageing (e.g. dielectric strength), the corresponding degree of conversion of the reference material can be read and obtained with the equation of the fitting curve graph (see Figure 1). Then the corresponding degree of conversion for this reference material can be used for reading the activation energy of a candidate material from another graph which was also evaluated with ISO 11358-2 and had another fitting curve of activation energy and degree of conversion for the candidate material.

All TGA raw data were submitted by eleven laboratories participants and analysis with ISO 11358-2 was carried out by one of the laboratories with their analytical tool, to avoid any discrepancy among various software calculations.

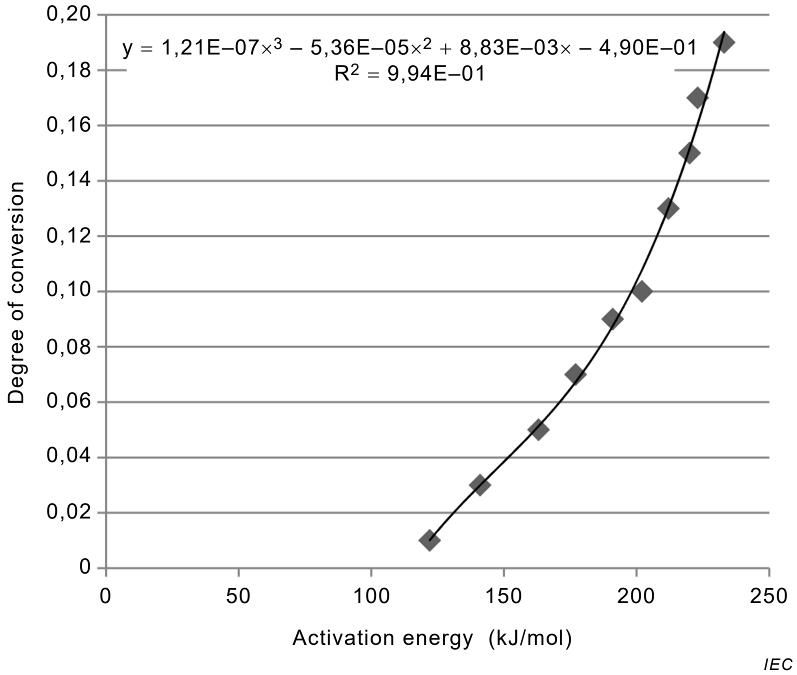


Figure 1 – Fitting curve of plots between degree of conversion and activation energy determined by ISO 11358-2 (example)

6.5 Determination of thermal endurance using TGA

6.5.1 General

The activation energy given by the above procedure can be used for the determination of RTE_A by calculating with time to end-point at the highest temperature which was determined by the conventional heat ageing test under IEC 60216-5, and procedures in accordance with IEC TS 60216-7-1.

In accordance with ISO 11358-2, various activation energies can be obtained per certain degrees of conversion calculated with multiple heating rate data of TGA. Therefore, degrees of conversion were chosen appropriately to be correlated to thermal degradation derived by properties and the conventional heat ageing data which are described in 6.5.2 (Method A). On the other hand, the fixed degree of conversion at 0,05 and the activation energy are sometimes used experimentally for prediction of end-point of properties [1][2][2], which is described in 6.5.3 (Method B).

6.5.2 Determination of RTE_A by given degree of conversion from reference material (Method A)

After the cubic approximation between the degree of conversion and the activation energy is determined (see 6.4), the degree of conversion for the reference material is given from the equation where the activation energy is the same as that from the Arrhenius equation of conventional heat ageing data. The activation energy of the candidate material is then determined from the cubic approximation of the candidate material where the degree of conversion for the candidate material is assumed to be the same as the given degree of conversion for the reference material. In Method A, RTE_A can be obtained.

---

[2] Numbers in square brackets refer to the Bibliography.

6.5.3 Determination of TI_A by fixed degree of conversion at 0,05 (Method B)

In Method B, the fixed degree of conversion at 0,05 can be selected to calculate the activation energy of the candidate material, with regard to practical experiences [2][3]. In Method B it is unnecessary to use reference material data to determine the activation energy of the candidate material in accordance with ISO 11358-2 and the thermal indices of materials can be determined as TI_A by the activation energy when the degree of conversion is 0,05.

In this round robin test, TI_A and RTE_A at 20 000 h of LCP sample A and sample B were determined by using Method A and Method B respectively.

7 Round robin test results

7.1 TGA test results

All the raw TGA test data were obtained from eleven laboratories (a, b, c, d, e, f, g, h, I, j and k). Figure 4 shows typical examples of overlay TGA curves of multiple heating rates which are magnified by the degrees of conversion between 0 and 0,02. Figure 5 provides typical examples of logarithm graphs between reciprocal temperatures and heating rates in certain degrees of conversions. Figure 6 shows cubic approximation between degree of conversions and activation energies to read appropriate activation energy for the determination of RTE_A or TI_A.

7.2 Degree of conversion correlated to the activation energy from conventional heat ageing data

Degrees of conversion at the activation energy identical to that from conventional heat ageing were determined with reference to ISO 11358-2 and IEC TS 60216-7-1 which are shown in Table 2.

It was observed that both sample A and sample B had very low initial thermal degradation under TGA (around 3 % or 4 % mass loss) which were correlated to thermal degradation of the dielectric strength under heating oven in terms of the identical activation energies. For reproducibility in laboratories, however, relatively high deviations are observed (around 30 % of the average degree of conversion) for both sample A and sample B. In addition, three laboratories (b, d, and j) were not able to obtain a degree of conversion identical to that of the activation energy of conventional heat ageing, because all of the activation energies were determined as higher than that from heat ageing in the whole range.

Table 2 – Degree of conversion identical to the activation energy of the conventional heat ageing

Laboratory	Degree of conversion identical to activation energy of the conventional heating, sample A	Degree of conversion identical to activation energy of the conventional heating, sample B
a	0,032 7	0,019 9
b	N/A	0,039 3
c	0,040 8	0,043 7
d	N/A	0,037 8
e	0,037 7	0,024 4
f	0,021 9	0,040 6
g	0,036 7	0,024 6
h	0,034 2	0,037 1
i	0,051 5	0,032 1
j	N/A	0,015 0
k	0,060 0	0,031 1
Average	0,032 7	0,031 4
Standard deviation	0,013 6	0,009 3

NOTE N/A means that in the cubic approximation of activation versus the degree of conversion the equation did not provide a solution.

7.3 HIC$_A$ determined by Method A and Method B

HIC$_A$ determined by Method A and Method B according to IEC TS 60216-7-1 is shown in Table 3,Table 4, Table 5 for dielectric strength, tensile strength, and impact strength respectively.

Table 3 – HIC$_A$ determined by Method A and Method B for dielectric strength

Laboratory	Method A		Method B	
	HIC$_A$ of sample A	HIC$_A$ of sample B	HIC$_A$ of sample A	HIC$_A$ of sample B
a	10,4	9,5	9,8	7,9
b	8,8	N/A	8,6	7,6
c	12,1	11,7	11,6	10,6
d	8,6	N/A	7,9	9,7
e	14,4	9,0	12,6	8,1
f	10,6	16,7	10,0	9,1
g	13,5	10,3	10,0	9,0
h	12,2	9,2	11,5	7,0
i	20,7	8,6	13,0	8,8
j	11,0	N/A	9,1	7,7
k	11,7	12,7	10,4	9,6
Average	12,2	11,0	10,4	8,6
Standard deviation	3,2	2,5	1,5	1,0

NOTE N/A means that in the cubic approximation of activation versus the degree of conversion the equation did not provide a solution.

Table 4 – HIC_A determined by Method A and Method B for tensile strength

Laboratory	Method A		Method B	
	HIC_A of sample A	HIC_A of sample B	HIC_A of sample A	HIC_A of sample B
a	10,0	9,1	9,6	7,9
b	8,7	7,5	8,3	7,6
c	11,5	9,3	11,3	10,7
d	8,5	16,4	7,9	9,7
e	13,9	7,8	12,2	8,4
f	10,1	8,8	9,8	9,2
g	12,6	9,1	9,7	7,9
h	11,9	6,3	11,2	7,1
i	18,8	7,9	12,6	8,8
j	10,1	11,0	8,8	7,8
k	11,1	9,3	10,1	9,6
Average	11,6	9,3	10,1	8,6
Standard deviation	2,9	2,6	1,5	1,1

Table 5 – HIC_A determined by Method A and Method B for impact strength

Laboratory	Method A		Method B	
	HIC_A of sample A	HIC_A of sample B	HIC_A of sample A	HIC_A of sample B
a	9,3	8,4	9,8	8,1
b	8,3	6,6	8,5	7,7
c	20,5	11,6	11,6	11,0
d	10,0	N/A	8,1	9,9
e	12,7	9,2	12,6	8,6
f	11,6	16,6	10,0	9,4
g	14,8	10,3	10,0	9,2
h	N/A	8,0	11,5	7,2
i	32,4	8,9	13,0	9,0
j	10,5	N/A	9,0	7,9
k	12,2	16,4	10,4	9,8
Average	14,2	10,7	10,4	8,9
Standard deviation	7,3	3,6	1,6	1,1

7.4 RTE_A determined by Method A and TI_A by Method B

RTE_A determined by Method A and TI_A by Method B are shown in Table 6, Table 7, and Table 8 for dielectric strength, tensile strength, and impact strength respectively.

Table 6 – RTE_A determined by Method A and TI_A by Method B for dielectric strength

Laboratory	**Method A**		**Method B**	
	RTE_A of sample A	**RTE_A of sample B**	**TI_A of sample A**	**TI_A of sample B**
a	255,0	249,2	256,7	256,4
b	259,7	N/A	260,4	257,7
c	249,9	238,9	251,2	243,8
d	260,2	N/A	262,3	248,2
e	242,8	251,4	248,3	255,2
f	254,3	213,7	256,1	250,7
g	245,5	245,3	256,2	251,4
h	249,5	250,5	251,6	260,1
i	222,7	253,0	247,1	252,4
j	253,0	N/A	258,8	257,0
k	251,1	234,2	254,9	248,7
Average	249,3	243,1	254,9	253,3
Standard deviation	10,3	13,2	4,9	4,9

Table 7 – RTE_A determined by Method A and TI_A by Method B for tensile strength

Laboratory	**Method A**		**Method B**	
	RTE_A of sample A	**RTE_A of sample B**	**TI_A of sample A**	**TI_A of sample B**
a	250,7	250,7	252,4	256,1
b	255,6	257,8	256,8	257,5
c	245,3	249,6	246,1	243,4
d	256,2	215,2	258,2	247,9
e	236,3	256,5	242,8	253,9
f	250,5	252,0	251,7	250,4
g	241,4	243,6	251,8	250,1
h	243,8	263,2	246,6	259,9
i	216,9	256,3	241.5	252,1
j	250,6	241,8	255,2	256,6
k	247,0	249,8	250,4	248,4
Average	244,9	248,8	250,3	252,4
Standard deviation	11,0	12,7	5,5	4,9

Table 8 – RTE_A determined by Method A and TI_A by Method B for impact strength

Laboratory	Method A		Method B	
	RTE_A of sample A	RTE_A of sample B	TI_A of sample A	TI_A of sample B
a	257,8	259,3	256,3	260,7
b	260,7	266,2	260,1	261,9
c	222,3	247,0	250,7	249,6
d	255,7	N/A	261,5	253,6
e	247,4	256,4	247,8	258,8
f	250,8	227,1	255,7	255,7
g	240,8	252,1	255,7	256,4
h	N/A	260,9	251,1	264,1
i	179,8	257,7	246,6	257,2
j	254,3	N/A	258,8	261,2
k	248,9	227,6	254,5	254,0
Average	241,9	250,5	254,4	257,6
Standard deviation	24,4	14,2	4,9	4,3

7.5 Difference between RTE_A and TI determined by the conventional heat ageing tests

Differences between RTE_A or TI_A and TI, which is a numerical value remaining after TI is deducted from RTE_A or TI_A, are shown in Table 9, Table 10, and Table 11 for dielectric strength, tensile strength, and impact strength respectively.

Table 9 – Difference between RTE_A or TI_A, and TI for dielectric strength

Laboratory	Method A		Method B	
	RTE_A-TI of sample A	RTE_A-TI of sample B	TI_A-TI of sample A	TI_A-TI of sample B
a	5	7,7	6,7	14,9
b	9,7	N/A	10,4	16,2
c	-0,1	-2,6	1,2	2,3
d	10,2	N/A	12,3	6,7
e	-7,2	9,9	-1,7	13,7
f	4,3	-27,8	6,1	9,2
g	-4,5	3,8	6,2	9,9
h	-0,5	9,0	1,6	18,6
i	-27,3	11,5	-2,9	10,9
j	3,0	N/A	8,8	15,5
k	1,1	-7,3	4,9	7,2
Average	-0,6	0,5	4,9	11,4
Mean	1,1	5,8	6,1	10,9
Standard deviation	10,3	13,2	4,9	4,9

Table 10 – Difference between RTE_A or TI_A, and TI for tensile strength

Laboratory	Method A		Method B	
	RTE_A-TI of sample A	RTE_A-TI of sample B	TI_A-TI of sample A	TI_A-TI of sample B
a	0,7	9,2	2,4	14,6
b	5,6	N/A	6,8	16,0
c	-4,7	8,1	-3,9	1,9
d	6,2	N/A	8,2	6,4
e	-13,7	15,0	-7,2	12,4
f	0,5	10,5	1,7	8,9
g	-8,6	2,1	1,8	8,6
h	-6,2	21,7	-3,4	18,4
i	-33,1	14,8	-8,5	10,6
j	0,6	N/A	5,2	15,1
k	-3,0	8,3	0,4	6,9
Average	-5,1	11,2	0,3	10,9
Mean	-3,0	9,8	1,7	10,6
Standard deviation	11,0	5,9	5,5	4,9

Table 11 – Difference between RTE_A or TI_A, and TI for impact strength

Laboratory	Method A		Method B	
	RTE_A-TI of sample A	RTE_A-TI of sample B	TI_A-TI of sample A	TI_A-TI of sample B
a	7,8	17,8	6,3	19,2
b	10,7	N/A	10,1	20,4
c	-27,7	5,5	0,7	8,1
d	5,7	N/A	11,5	12,1
e	-2,6	14,9	-2,2	17,3
f	0,8	-14,4	5,7	14,2
g	-9,2	10,6	5,7	14,9
h	N/A	19,4	1,1	22,6
i	-70,2	16,2	-3,4	15,7
j	4,3	N/A	8,8	19,7
k	-1,1	-13,9	4,5	12,5
Average	-8,2	7,0	4,4	16,1
Mean	-0,1	12,8	5,7	15,7
Standard deviation	24,4	13,8	4,9	4,3

8 Observations from the round robin test results

8.1 General

In the round robin test, the following productive points were observed for the validation of IEC TS 60216-7-1:

- both RTE_A and TI_A determined in these round robin tests mostly had similar values to TI by conventional heat ageing in difference of temperature of 20 °C or less in most cases, and
- Method A using the degree of conversion given by the calculation failed to provide solutions of RTE_A in a few laboratories and their standard deviations were also relatively high, whereas Method B using the fixed degree of conversion based on experiences at 0,05 provided lower standard variations in laboratories.

In particular, the results in difference of temperature within 20 °C from the conventional heat ageing is useful, because the conventional RTE in accordance with the IEC 60216 series also contains this level of reproducibility issues due to variation factors of heating ovens, test plaques and lot-to-lot variation of materials, etc.

As a practical example of implementing long term thermal endurance evaluation according to IEC 60216-8, a certification of the thermal endurance properties provides the industry with a temperature classification with some increments according to the temperature assigned such as 20 °C increments over 180 °C of RTI, 10 °C increments from 130 °C through 180 °C and 5 °C increments up to 130 °C [4].

As TI of the two LCP materials evaluated in this Technical Report have been determined over 180 °C, 20 °C or less difference between RTE_A or TI_A and TI, conformity with the temperature classification in accordance with the above conventional heat ageing methods can be established.

On the other hand, the round robin test also raised technical concerns as follows:

- laboratory i determined an RTE_A of the LCP sample A significantly different from those by other laboratories in all the three properties, and
- a few laboratories could not determine RTE_A of sample B, because the degree of conversion was not appropriately calculated from the fitting curve in 6.4.

The round robin test participants discussed the rationale, and the following potential factors which could have an influence on the above issues were raised and then checked as follows:

1) sample weight variation,
2) humidity and hydrolysis of the sample,
3) repeatability of TGA curves, and
4) baseline drift and spacing between multiple curves of TGA.

8.2 Sample weight variation

ISO 11358-2 provides the tolerance of the sample weight per one run of TGA as ± 1 % with less than 10 mg, however, the round robin test applied a wider tolerance of 5 mg ± 0,5 mg (10 % tolerance). Therefore, the sample weight variation was identified as one of the potential variation factors.

The scatter plot between the standard deviation of sample mass and the difference between TI and RTE_A (TI_A) was evaluated, however, less correlation was observed between the two factors which are shown in Figure 2 and Figure 3.

Because of these facts, the sample weight variation may be considered with respect to ISO 11358-2, but not as a significant factor with regard to the technical concerns of reproducibility in laboratories mentioned above.

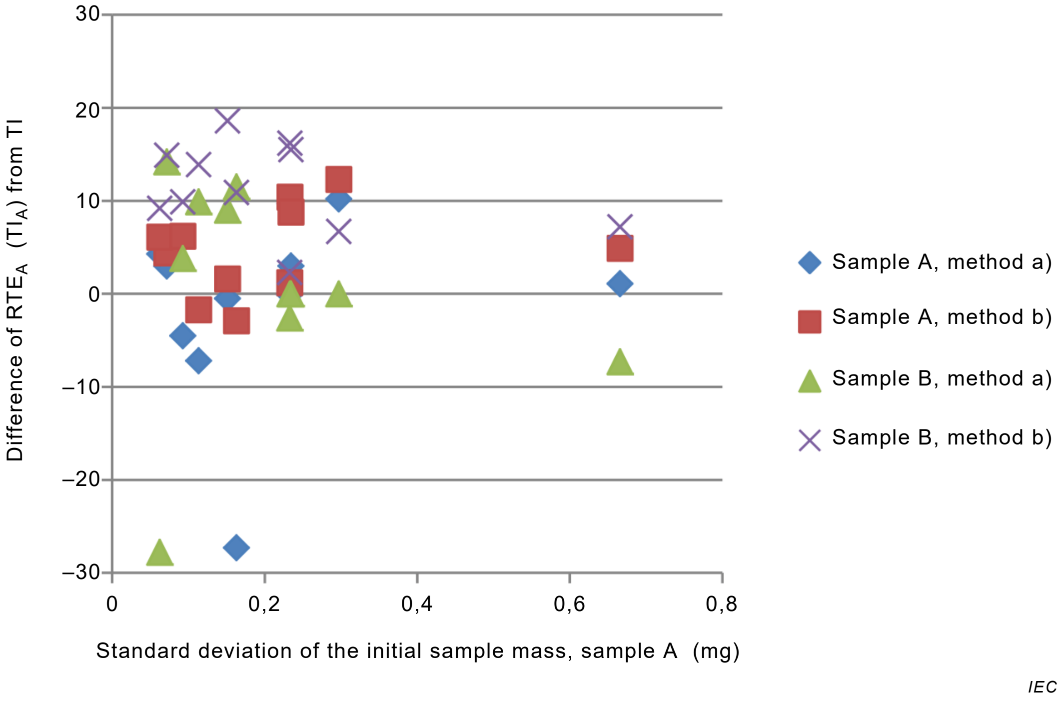


Figure 2 – Correlation between the initial sample mass of sample A and the difference of RTE$_A$ (TI$_A$) from TI

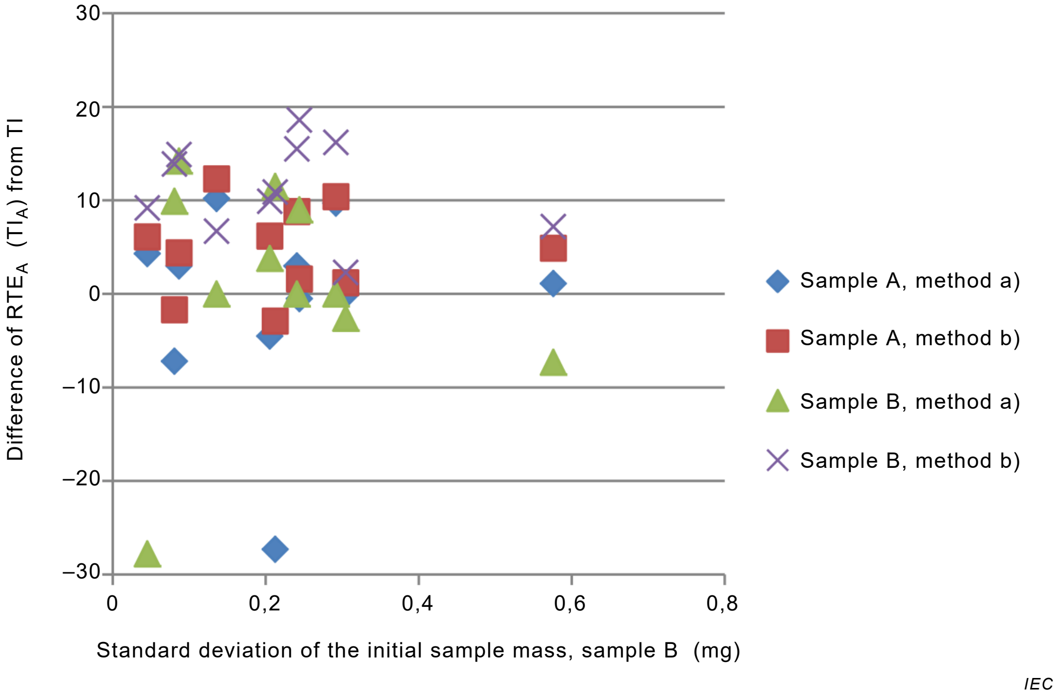


Figure 3 – Correlation between the initial sample mass of sample B and the difference of RTE$_A$ (TI$_A$) from TI

8.3 Humidity and hydrolysis of the sample

The round robin test samples were liquid crystal polyesters, and moisture could accelerate the polymer degradation with hydrolysis and therefore, humidity and hydrolysis were pointed out as the factor of reproducibility to the specific laboratories.

At first, all of sample A and sample B provided to the laboratories were homogenized and pre-dried at 140° for 4 h to remove absorbed water during freeze-pulverization and put into vials before shipment. Natural moisture absorption of LCP is very small, for instance, the equilibrium moisture content of the LCP polymer is approximately 0,03 % (300 ppm) at 23 °C and 50 % RH. Sample A and sample B are 30 % glass filled grades and the actual equilibrium moisture after the vials are opened is expected to be lower than this value. In addition, the sample loaded to TGA was pre-conditioned at 100 °C for 1 h in the furnace. At the above point, absorbed moisture from the sample cannot be considered a major factor of RTE_A and TI_A variation.

Next, atmosphere in the TGA furnace could be another factor which has an influence on hydrolysis of the polymer around the thermal decomposition temperature in the TGA furnace. In fact it was different in laboratories, because the round robin test requested participants to report, if possible, what kind of air was used to supply purge gas into the TGA furnace. Not all laboratories responded, however, and it was determined that some of the laboratories (a, b, and f) used dry air (moisture content guaranteed less than 1 ppm or 2 ppm) while others (laboratories e, g, and h) used compressed air with or without an air dryer. In fact, there was no relation observed between the specific laboratories mentioned above which had different results from the others, in terms of difference in air supply. However, dry air is useful and its use was recommended to all of the participants to decrease a side effect factor of reproducibility issues. For reference, dry air is given as an example of purge gas in ISO 11358-1.

8.4 Consideration on repeatability of TGA curves

In the round robin test based on IEC TS 60216-7-1 and ISO 11358-2, multiple TGA curves with different heating rates were used for the calculation of the degree of conversion and the activation energy of the candidate material. If one TGA curve has low repeatability, correlation between the degree of conversion and the activation energy could also be changed to determine RTE_A or TI_A.

Taking this factor into consideration, supplemental measurement was rerun at 8 K/min for both sample A and sample B in every participating laboratory. A summary of the degree of conversion is shown in Table 12.

NOTE The rerun data at 8 K/min were not reported by laboratory i.

Table 12 – Comparison of degree of conversion with original or rerun data at 8 K/min

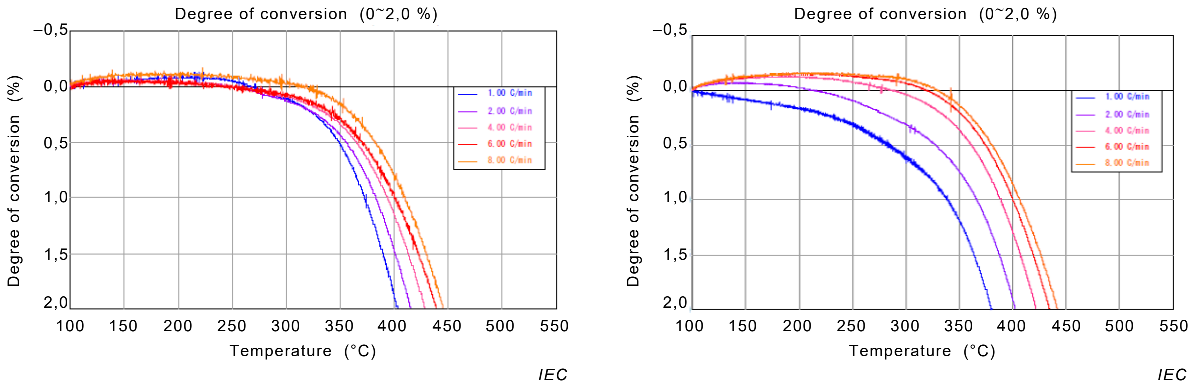
Laboratory	Degree of conversion for E_a of sample A at 130,6kJ/mol		Degree of conversion for E_a of sample B at 142,3kJ/mol	
	Original data at 8K/min	Rerun data at 8K/min	Original data at 8K/min	Rerun data at 8K/min
a	0,032 7	0,084 7	0,019 9	0,019 5
b	N/A	N/A	0,039 3	0,033 6
c	0,040 8	0,022 1	0,043 7	0,038 4
d	N/A	N/A	0,037 8	0,037 2
e	0,037 7	0,051 7	0,024 4	0,024 4
f	0,021 9	0,020 5	0,040 6	0,040 1
g	0,036 7	0,035 1	0,024 6	0,020 9
h	0,034 2	0,037 2	0,037 1	0,017 2
i	0,051 5	-	0,032 1	-
j	N/A	N/A	0,016 7	0,013 7
k	0,060 0	N/A	0,031 1	0,026 0
Average	0,039	0,042	0,032	0,027
Standard deviation	0,012	0,024	0,009	0,010

As shown in Table 12, two laboratories (a and e) had significant change in the given degree of conversion for sample A by rerun data at 8K/min, which exceeded the degree of conversion at 0,05 (Method B). Another laboratory k could not obtain the results of the degree of conversion for sample A , even though the laboratory obtained the given degree of conversion with the original data at 8 K/min. From those observations, it is suggested that the repeatability of TGA raw data can have a significant impact on the calculation of the degree of conversion which affects repeatable determination of RTE_A or TI_A, as well. In this study, only one test condition of heating rates (8K/min) was retested for a preliminary review of repeatability check. The repeatability should be further evaluated also with retesting at other heating rates for an assessment of the precision.

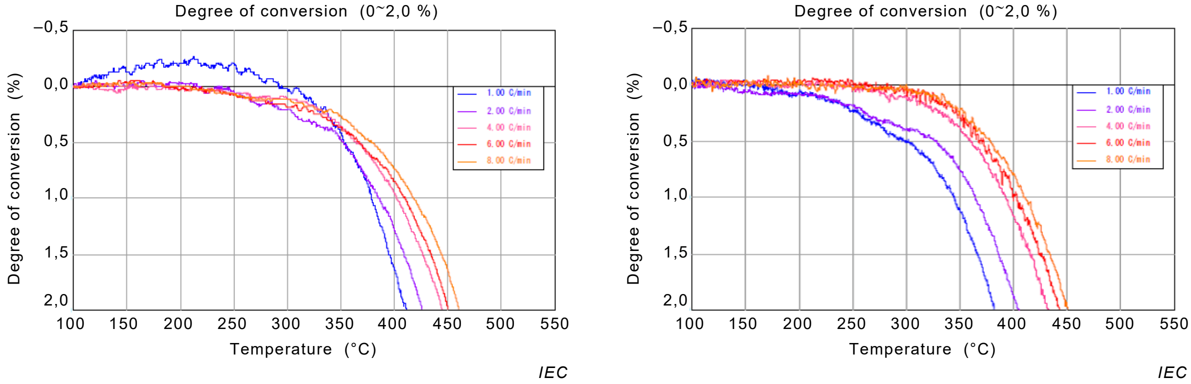
On the above point, population of the TGA raw curve data (e.g. evaluation of 2 or 3 runs at the same heating rate) and normalization of those raw data can be further considered before analysis in accordance with ISO 11358-2 is conducted in each laboratory, if repeatability and reproducibility improvements are necessary.

8.5 Baseline drift and responsiveness to heating rates of TGA

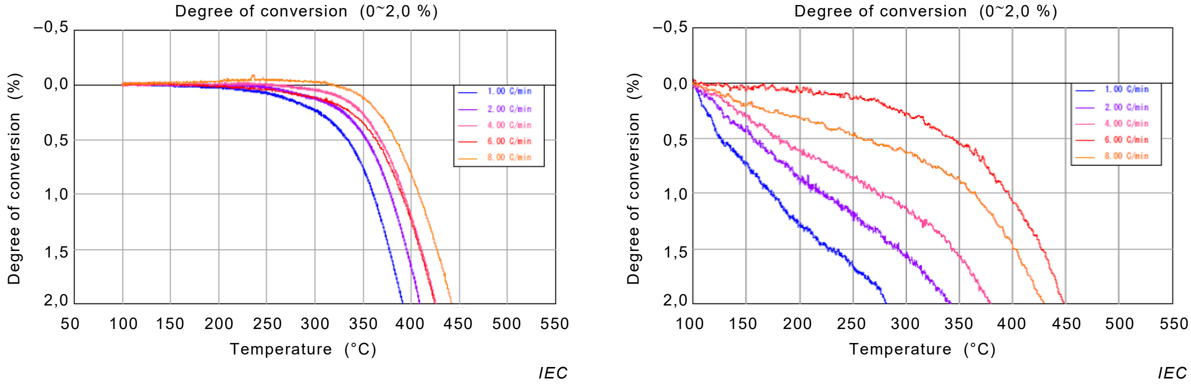
To examine the remaining reasons why no result of degree of conversion and RTE_A by Method A was provided to sample A in three laboratories (b, d and j) for dielectric strength, the raw TGA curves, logarithm graphs according to ISO 11358-2, and the fitting curve example given in Figure 1 were observed as shown in Figure 4, Figure 5 and Figure 6 respectively, with the comparative examples of three other laboratories data which obtained a degree of conversion and RTE_A.



Laboratory b Laboratory f



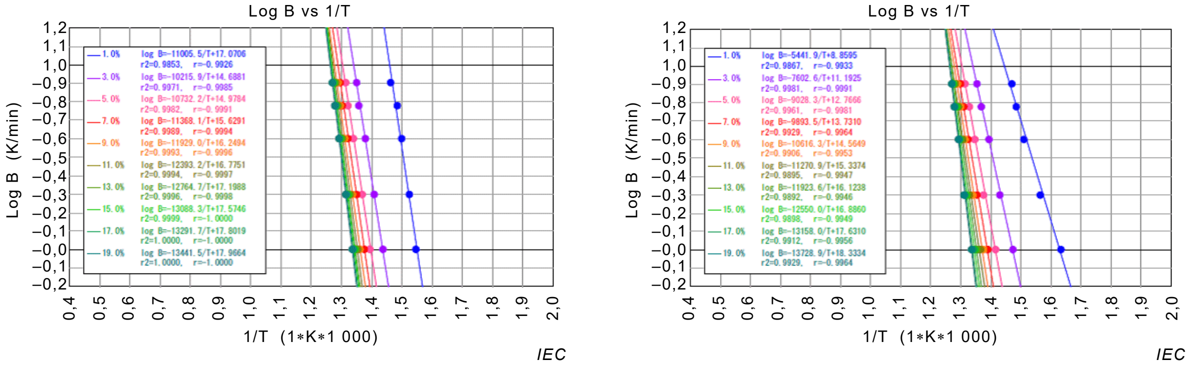
Laboratory d Laboratory g



Laboratory j Laboratory i

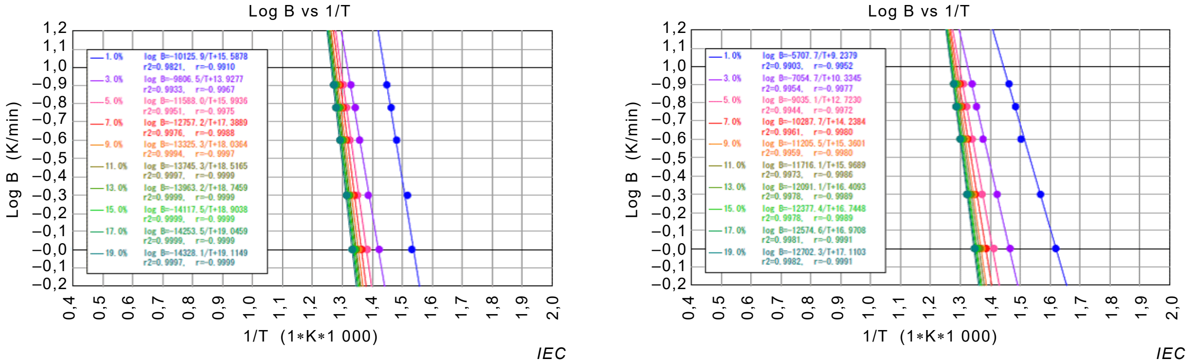
Figure 4 – Overlay charts of TGA curves in multiple heating rates in multiple laboratories (enlarged)

The three graphs on the left in Figure 4 and Figure 5 were evaluated in the laboratories which had no result of the degree of conversion to E_a and RTE$_A$ to Sample B in accordance with the fitting curve example given in Figure 1. The other three graphs on the right in Figure 4 and Figure 5 were tested in the laboratories which all obtained a result of the degree of conversion, although different trends were observed in the final determination of RTE$_A$. It was observed that the three graphs of overlay TGA curves on the left commonly showed a smaller difference in multiple heating rates (narrower range in temperature between the curves) than the three graphs on the right. It appears that the three graphs of logarithm on the left presented a steeper slope than that from the three graphs on the right. When the responsiveness of degradation to change in heating rates is significantly low, the activation energy is to be calculated at a significantly high value. And in fact, the data in Figure 4 and Figure 5 from those laboratories on the left gave higher activation energies in the whole range of degree of conversion in TGA, as shown in Figure 6.



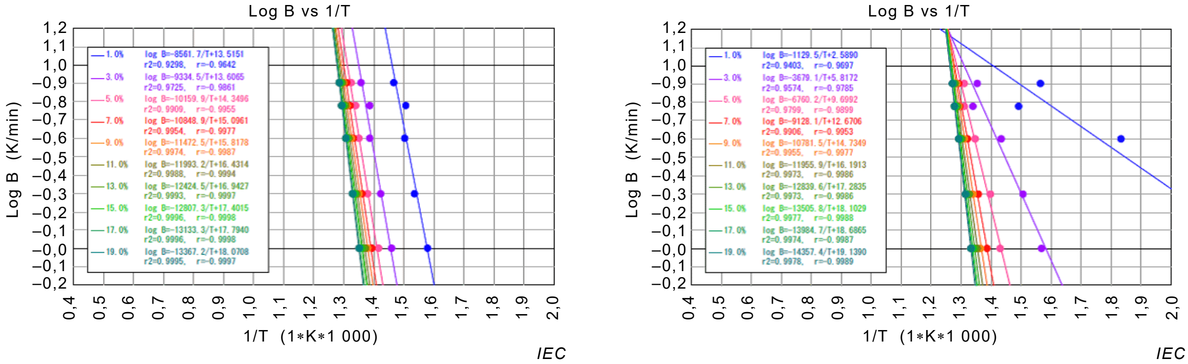
Laboratory b

Laboratory f



Laboratory d

Laboratory g



Laboratory j

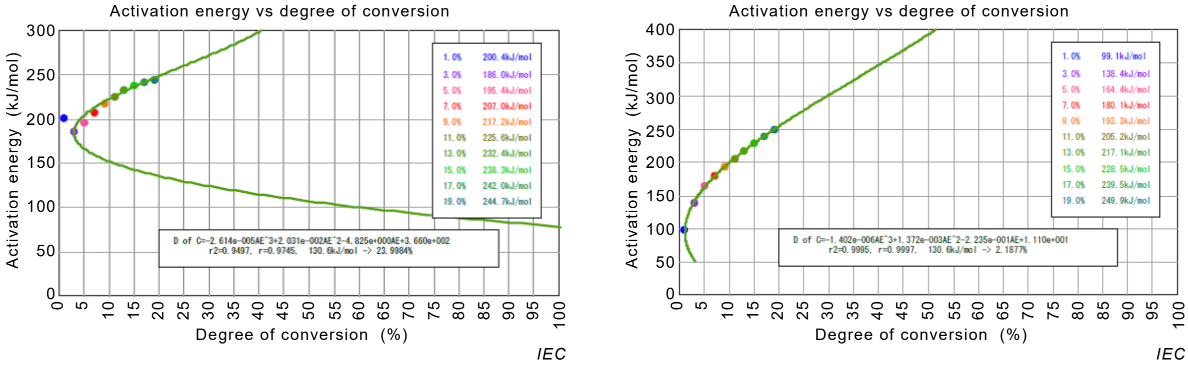
Laboratory i

Figure 5 – Logarithm plots for activation energy calculation

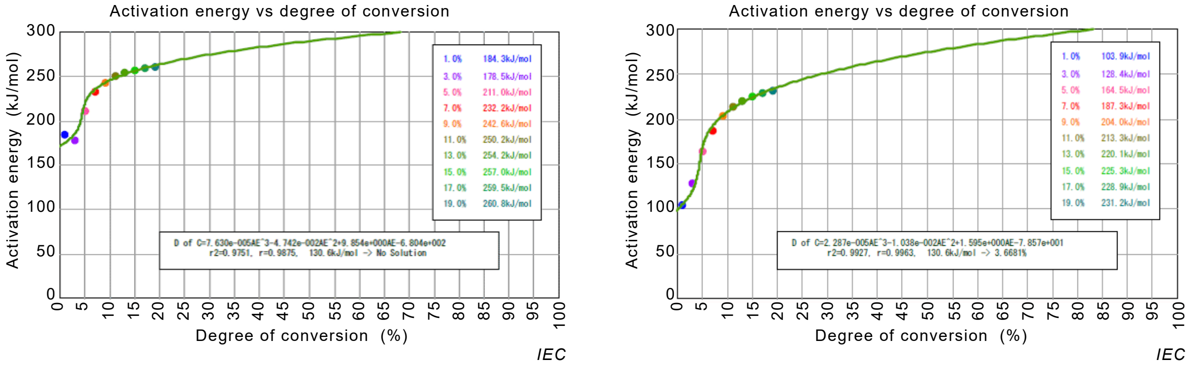
It was not clarified why laboratories b, d, and j obtained lower differences of TGA curves in multiple heating rates, but it is suggested that repeatability of TGA curves in the same heating rate could affect the results as observed in 8.3. It was indeed confirmed that laboratory d and laboratory f in Figures 4 and 5 above used an identical model of TGA apparatus with the same dry air conditions (moisture content less than 1 ppm) which cannot be considered as the rationale of responsiveness. In fact these two laboratories showed similar TGA curves at 8 K/min, but the same approach of repeatability check would be recommended at lower heating rates for the next step if further reproducibility improvement is needed.

The baseline drift of TGA curves (very slight increase in mass at initiation of heating) was observed in some laboratories but not in others. Obviously the drift affects the difference in temperature at the same degree of conversion between the TGA curves of multiple heating rates, and it also has an influence on the unusual ascending order of the temperature to heating rates. Treatment or cancelation of the baseline may therefore be further discussed to decide on the next opportunity of investigation in order to fine tune the round robin test conditions.

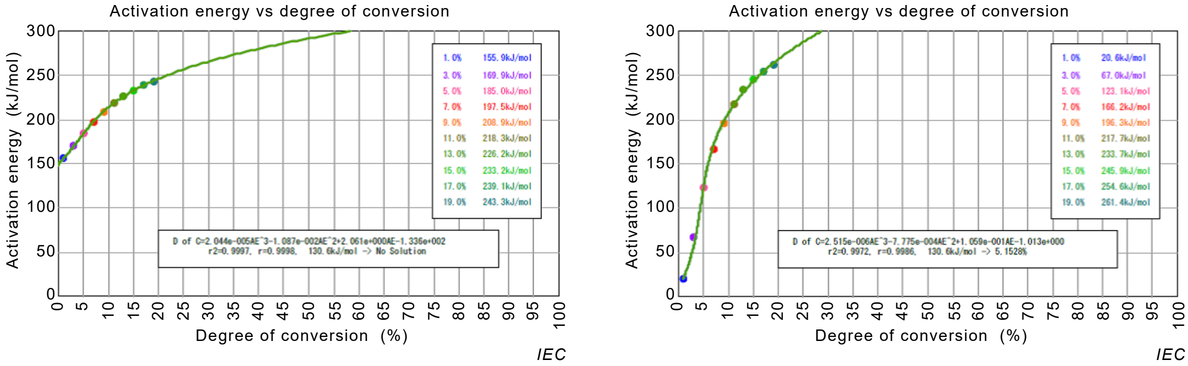
Other observations showed that laboratory i had significantly different TGA curves than all the others, in terms of very rapid mass loss at initiation of heating from 100 °C, which gave very low activation energy at a small degree of conversion, as shown in Figure 6 and a significantly lower RTE_A to sample A. As no other laboratory showed a same or similar trend of the phenomena, their data has to be considered outside the scope of this technical report until additional information on apparatus and conditions during test is provided by the laboratory.



Laboratory b **Laboratory f**



Laboratory d **Laboratory g**



Laboratory j **Laboratory i**

Figure 6 – Fitting curves of degree of conversion vs. activation energy by TGA

9 Conclusion and recommendation

This round robin test applied to one material category of liquid crystal polyester (LCP) and in which eleven laboratories from four countries participated, provided extremely useful findings to accelerate the evaluation of thermal endurance properties in the IEC 60216 series. These findings are as follows.

- By selecting a specific material category where one single reaction to heat is predominant, the two samples of LCP had very similar RTE_A or TI_A (based on IEC TS 60216-7-1) to the

TI of the conventional heat ageing (based on the existing IEC 60216 series), within a small difference, except for one laboratory.

- RTE_A determination by using the degree of conversion corresponding to the activation energy of the reference material based on past conventional heat ageing provided closer results to TI, whereas TI_A determination by using the fixed degree of conversion at 5 %, which is not dependent on the control material, provided more reproducible results to TI, even when higher temperatures were assigned in total. In addition, TI_A provided a solution to obtain tangible results when RTE_A was not determined by this method due to repeatability issues of TGA.
- It was found that TGA curves may not always be repeatable in the same material and at the same heating rates with the same test condition, depending on apparatus condition. Sufficient differences in temperatures detected at the same degree of conversion and provided by change in multiple heating rates gave more confidence in the analysis based on ISO 11358-2 and IEC TS 60216-7-1. Confirmation of TGA curves per heating rate would therefore be recommended with a few populations of the TGA runs, to check the raw data variation for fine tuning of the repeatable results.
- Identical mass of test sample (± 1 %), dry air for purge gas into the TGA furnace (H_2O content less than a few ppm) and cancelation of the base line drift of the TGA curves may be further considered as questionable factors which may affect the determination of RTE_A and TI_A.
- A good criterion to foresee the robustness of the testing procedure and thus the accuracy of TI_A and RTE_A is to repeat at least one test and check that the variance compared to the first run of TGA is small, for example, less than 10 % of the degree of conversion at a certain temperature or activation energy.

Bibliography

[1] IUPAC *“Gold Book”* (http://goldbook.iupac.org/)

[2] ASTM E1641-15, *Standard Test Method for Decomposition Kinetics by Thermogravimetry Using the Ozawa/Flynn/Wall Method*

[3] ASTM E1877-15, *Standard Practice for Calculating Thermal Endurance of Materials from Thermogravimetric Decomposition Data*

[4] UL 746 B, *Standard for safety, Polymeric Materials – Long term Property Evaluations*

IEC 60050-212, *International Electrotechnical Vocabulary – Part 212: Electrical insulating solids, liquids and gases* (available at http://www.electropedia.org)

IEC 60216-1, *Electrical insulating materials – Thermal endurance properties – Part 1: Ageing procedures and evaluation of test results*

IEC 60216-5, *Electrical insulating materials – Thermal endurance properties – Part 5: Determination of relative thermal endurance index (RTE) of an insulating material*

IEC TS 60216-7-1, *Electrical insulation materials – Thermal endurance properties – Part 7-1: Accelerated determination of relative thermal endurance using analytical test methods* (*RTE_A*) *– Instructions for calculations based on activation energy*

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

ISO 11358-2:2014, *Plastics – Thermogravimetry (TG) of polymers – Part 2: Determination of activation energy*

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.

Copyright in BSI publications

All the content in BSI publications, including British Standards, is the property of and copyrighted by BSI or some person or entity that owns copyright in the information used (such as the international standardization bodies) and has formally licensed such information to BSI for commercial publication and use.

Save for the provisions below, you may not transfer, share or disseminate any portion of the standard to any other person. You may not adapt, distribute, commercially exploit, or publicly display the standard or any portion thereof in any manner whatsoever without BSI's prior written consent.

Storing and using standards

Standards purchased in soft copy format:

- A British Standard purchased in soft copy format is licensed to a sole named user for personal or internal company use only.
- The standard may be stored on more than 1 device provided that it is accessible by the sole named user only and that only 1 copy is accessed at any one time.
- A single paper copy may be printed for personal or internal company use only.

Standards purchased in hard copy format:

- A British Standard purchased in hard copy format is for personal or internal company use only.
- It may not be further reproduced – in any format – to create an additional copy. This includes scanning of the document.

If you need more than 1 copy of the document, or if you wish to share the document on an internal network, you can save money by choosing a subscription product (see 'Subscriptions').

Reproducing extracts

For permission to reproduce content from BSI publications contact the BSI Copyright & Licensing 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 subscriptions@bsigroup.com.

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.

Useful Contacts

Customer Services
Tel: +44 345 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 345 086 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 Group Headquarters

389 Chiswick High Road London W4 4AL UK