IEC TR 60216-7-2

Edition 2.0 2024-09
REDLINE VERSION

TECHNICAL REPORT

colour inside

Electrical insulating materials – Thermal endurance properties – Part 7-2: Accelerated determination of relative thermal endurance using analytical test methods (RTEA) – Results of the round robin tests to validate procedures of IEC TS 60216-7-1 by non-isothermal kinetic analysis of thermogravimetric data

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ELECTRICAL INSULATING MATERIALS – THERMAL ENDURANCE PROPERTIES –

Part 7-2: Accelerated determination of relative thermal endurance using analytical test methods (RTEA) – Results of the round robin tests to validate procedures of IEC TS 60216-7-1 by non-isothermal kinetic analysis of thermogravimetric data

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This redline version of the official IEC Standard allows the user to identify the changes made to the previous edition IEC TR 60216-7-2:2016. A vertical bar appears in the margin wherever a change has been made. Additions are in green text, deletions are in strikethrough red text.

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

This second edition cancels and replaces the first edition published in 2016. This edition constitutes a technical revision.

This edition includes the following significant technical changes with respect to the previous edition:

a) Annex A (informative) has been added to provide a round robin test with a different polymer type – polybuthylene terephthalate (PBY) – as an additional use case of the method in accordance with IEC TS 60216-7-1;
b) Tables 3 to 11 have been corrected by adding units, and texts have been refined for more technical clarifications of the procedures and observations.

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

Draft	Report on voting
112/651/DTR	112/658/RVDTR

Full information on the voting for its approval can be found in the report on voting indicated in the above table.

The language used for the development of this Technical Report is English.

This document was drafted in accordance with ISO/IEC Directives, Part 2, and developed in accordance with ISO/IEC Directives, Part 1 and ISO/IEC Directives, IEC Supplement, available at www.iec.ch/members_experts/refdocs. The main document types developed by IEC are described in greater detail at www.iec.ch/publications.

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 document will remain unchanged until the stability date indicated on the IEC website under webstore.iec.ch in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn, or
- revised.

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INTRODUCTION

IEC technical committee 112, (IEC TC 112) has been working on the development of IEC TS 60216-7-1 [1][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 Underwriters Laboratories Long-Term Thermal Aging Forum (UL LTTA Forum) has been discussing alternative methods that ~~could~~ can speed up the determination of a thermal index. Members of the IEC TC 112 and of the UL LTTA Forum have made joint efforts to determine whether the Technical Specification developed by IEC TC 112 can be used to offer an alternative method of evaluating polymeric compounds for a thermal index.

Members of IEC TC 112 and the UL LTTA Forum decided to conduct a round robin test (RRT) using thermogravimetric analysis (TGA) according to ISO 11358-2 [3] 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~~ can 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.

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

ELECTRICAL INSULATING MATERIALS – THERMAL ENDURANCE PROPERTIES –

Part 7-2: Accelerated determination of relative thermal endurance using analytical test methods (RTEA) – 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

This part of IEC 60216 is intended 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.

The round robin test results do not provide statistical analysis for precision. 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 precision.

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.

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

- IEC Electropedia: available at https://www.electropedia.org/
- ISO Online browsing platform: available at https://www.iso.org/obp

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 [2], modified – ~~the two notes have been deleted and replaced by a new note~~ "characterizing the thermal capability of an insulating material or an insulation system" has been replaced with "derived from the thermal endurance relationship at a time of 20 000 h (or other specified time)" and the two notes to entry have been replaced by a new note to entry.]

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~~2021, 3.3 [3], modified – The symbol "*C*" has been replaced with "α" and the notes to entry have been deleted.]

4 Test specimens

For the round robin test, one generic type of polymer, liquid crystal polyester (LCP), was pre-selected. Although it is known that materials can undergo more than one transition, the round robin test verified the assumption that one single thermal degradation reaction is predominant and directly correlated to the end-point of dielectric strength as a diagnostic property.

NOTE Since different materials can undergo more than one transition, the validity of results obtained from the evaluation of thermal endurance properties using TGA are assessed for the different materials.

LCP originally has very little entwining of molecules exhibiting crystalline properties as a liquid. Hence, 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 ranges. 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 as 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 materials. Configurations of monomers are the only differences between the samples which influence the difference in thermal resistance, as shown in Table 1.

The samples were homogenized by freeze-pulverization from test plaques. 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 [4]

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
TI (°C)	250,0	241,5	249,1	246,2	249,1	234,7
E_a (kJ/mol)	130,6	142,3	165,2	145,9	134,5	102,9

5 Test apparatus

5.1 Thermogravimetric analyser (TGA)

A thermogravimetric analyser (TGA) in accordance with ISO 11358-1 [5] was used for the determination of RTE_A concerning the test samples. In fact, a number of commercial instruments suitable for the ~~document~~ measurement are available and various models of TGAs were used for evaluation of the test samples by the participating laboratories. 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[2]), but air supplied from the facility (compressed air with or without an air dryer) was used in a few laboratories.

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2 ppm = parts per million.

6 Test procedures

6.1 General

Thermal analysis with TGA of the test samples was evaluated with reference to ISO 11358-2 [3] and IEC TS 60216-7-1 in principle. A few modifications of test conditions and more detailed procedures were added as follows.

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 [3] 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 resulted in the lowest and highest heating rates differing by a factor of 8, in accordance with ISO 11358-2 [3]. 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 for given degrees of conversion in accordance with Equation (2) in ISO 11358-2:~~2014~~2021 [3]. 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~~ and a cubic curve fitting approximately was performed as shown in Figure 1. Equation (2) in ISO 11358-2:~~2014~~2021 [3] was used for the 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 [3] and had ~~another fitting curve of activation energy and~~ a similar degree of conversion versus the activation energy fitting curve for the candidate material.

All TGA raw data were submitted by eleven participating laboratories and analysis with ISO 11358-2 [3] was carried out by one of the laboratories with the analytical tool, to avoid any discrepancy among various software calculations.

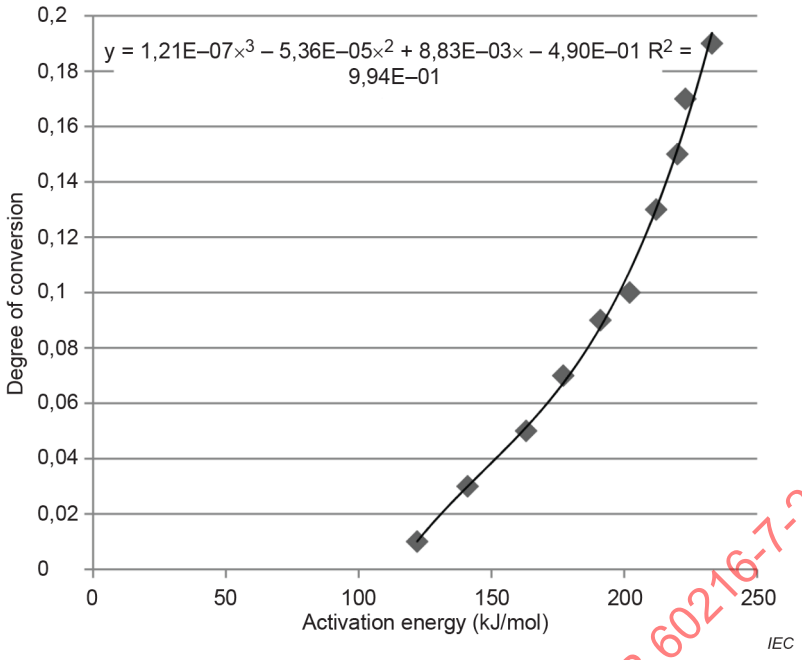

Figure 1 – Fitting curve of plots between degree of conversion and activation energy determined by ISO 11358-2 [3] (example)

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 [4], and procedures in accordance with IEC TS 60216-7-1.

In accordance with ISO 11358-2 [3], 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 activation energy are sometimes used experimentally for prediction of end-point of properties [6], [7], 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.

NOTE The assumption that the degree of conversion for the candidate material is the same as the given degree of conversion for the reference material, is validated since the candidate material can be of the same type of the reference material.

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 [7], [8]. 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 [3] 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 at multiple heating rates magnified to show the degrees of conversion between 0 and 0,02. Figure 5 provides typical examples of logarithm graphs between reciprocal temperatures and heating rates for 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 [3] 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 a 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 found to be higher than the ones determined by heat ageing in the considered 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 and 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 K	HIC_A of sample B K	HIC_A of sample A K	HIC_A of sample B K
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
	K	K	K	K
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
	K	K	K	K
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
	°C	°C	°C	°C
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
	°C	°C	°C	°C
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 °C	RTE_A of sample B °C	TI_A of sample A °C	TI_A of sample B °C
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 °C	RTE_A-TI of sample B °C	TI_A-TI of sample A °C	TI_A-TI of sample B °C
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 °C	RTE_A-TI of sample B °C	TI_A-TI of sample A °C	TI_A-TI of sample B °C
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 °C	RTE_A-TI of sample B °C	TI_A-TI of sample A °C	TI_A-TI of sample B °C
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 with a difference in 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 between laboratories.

It is noted, however, that results show differences between the laboratories, with differences in temperature exceeding 20 °C in some instances of the report.

In particular, the difference of 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 [9], 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 [10].

As TI of the two LCP materials evaluated in this document 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~~ were not able to 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~~ can 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 [3] 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~~ can be considered with respect to ISO 11358-2~~,~~ [3], but not as a significant factor with regard to the technical concerns of reproducibility in laboratories mentioned above.

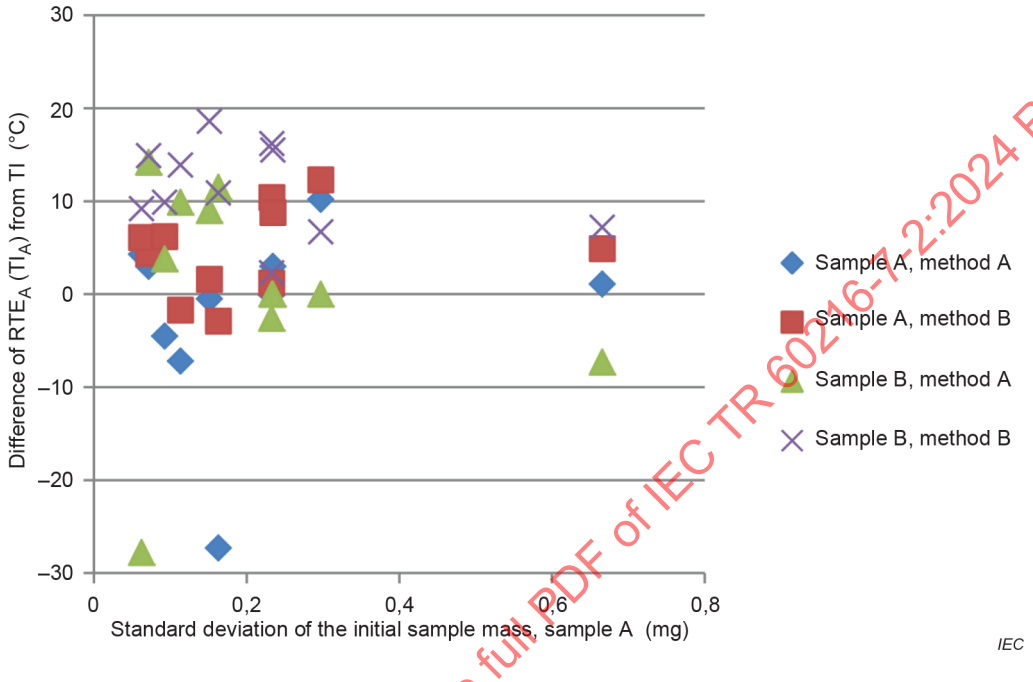

Figure 2 – Correlation between the initial sample mass of sample A and the difference of RTE_A (TI_A) from TI

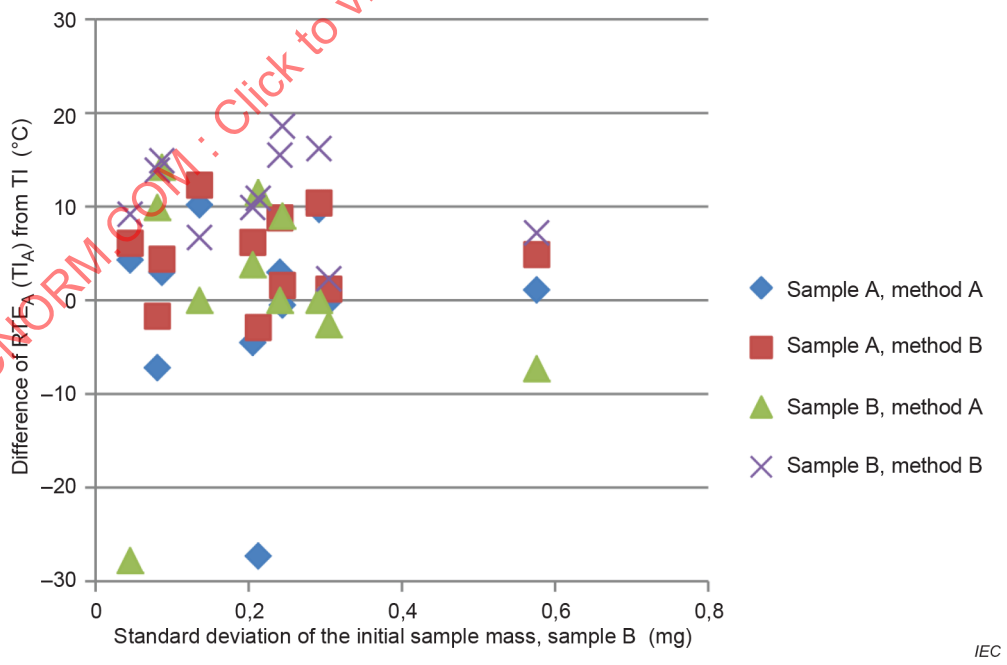

Figure 3 – Correlation between the initial sample mass of sample B and the difference of RTE_A (TI_A) from TI

8.3 Humidity and hydrolysis of the sample

The round robin test samples were liquid crystal polyesters, and since moisture ~~could~~ can accelerate the polymer degradation with hydrolysis, humidity and hydrolysis were therefore pointed out as the factors potentially influencing the reproducibility at specific laboratories.

At first, all of samples A and samples B provided to the laboratories were homogenized and pre-dried at 140 °C for 4 h to remove absorbed water during freeze-pulverization and then 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~~ can 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 each laboratory, 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 and the 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 Considerations on repeatability of TGA curves

In the round robin test based on IEC TS 60216-7-1 and ISO 11358-2 [3], 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~~ can 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 130,6 kJ/mol		Degree of conversion for E_a of sample B at 142,3 kJ/mol	
	Original data at 8 K/min	Rerun data at 8 K/min	Original data at 8 K/min	Rerun data at 8 K/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 a significant change in the given degree of conversion for sample A by rerun data at 8 K/min, which exceeded the degree of conversion at 0,05 (Method B). Another laboratory k ~~could~~ was not able to 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 (8 K/min) was retested for a preliminary review of repeatability check. It is suggested that 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 [3] is conducted in each laboratory, if repeatability and reproducibility improvements are necessary.

It is suggested that repeatability of the TGA curve is checked at all heating rates to decrease variations of the degree of conversion and the activation energy determined by TGA.

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 [3], and the fitting curve example given in Figure 1 were plotted 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.

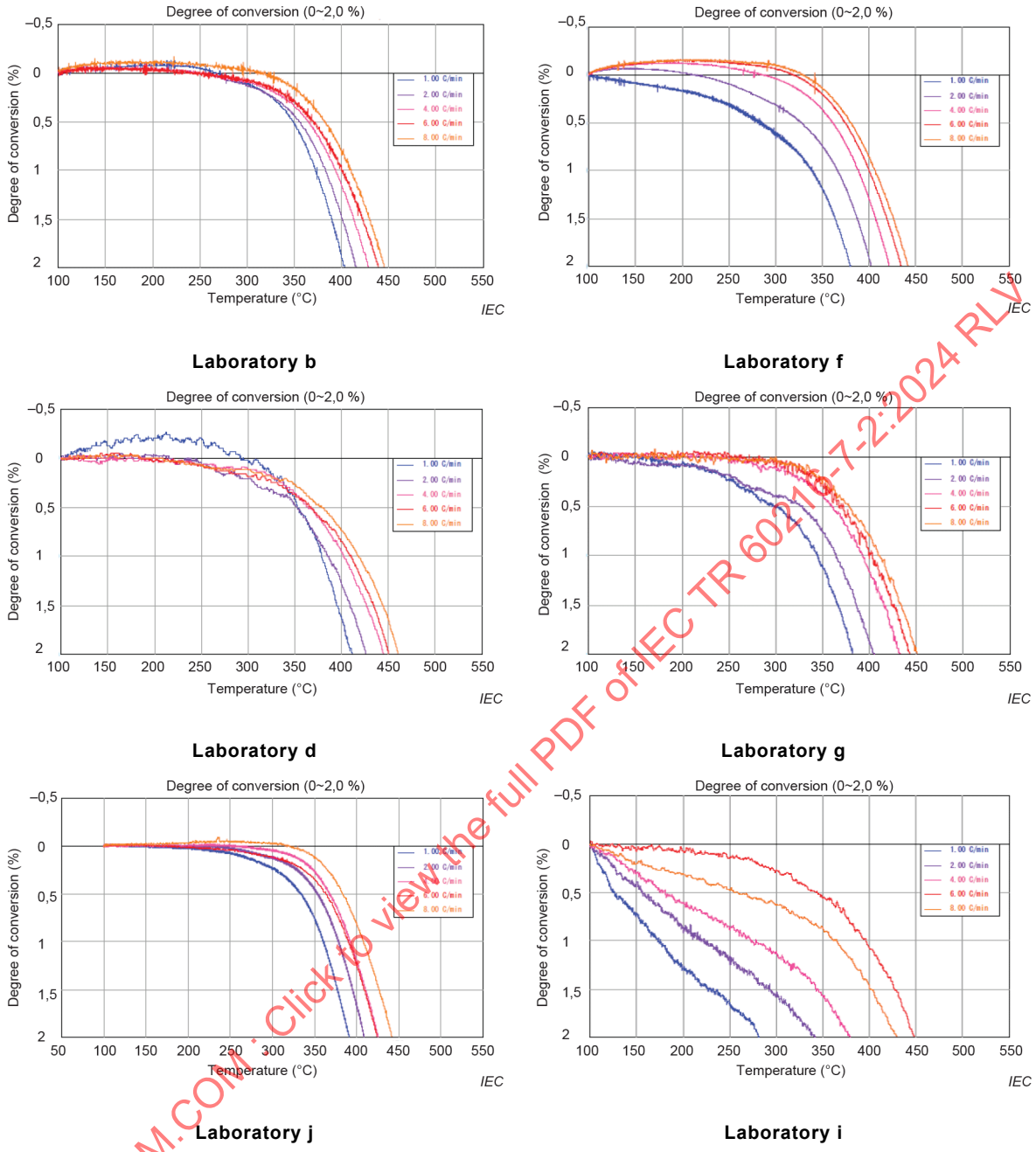

Figure 4 – Overlay charts of TGA curves in multiple heating rates in multiple laboratories (enlarged)

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 between multiple heating rates (narrower range in temperature among the curves) than that of 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 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.

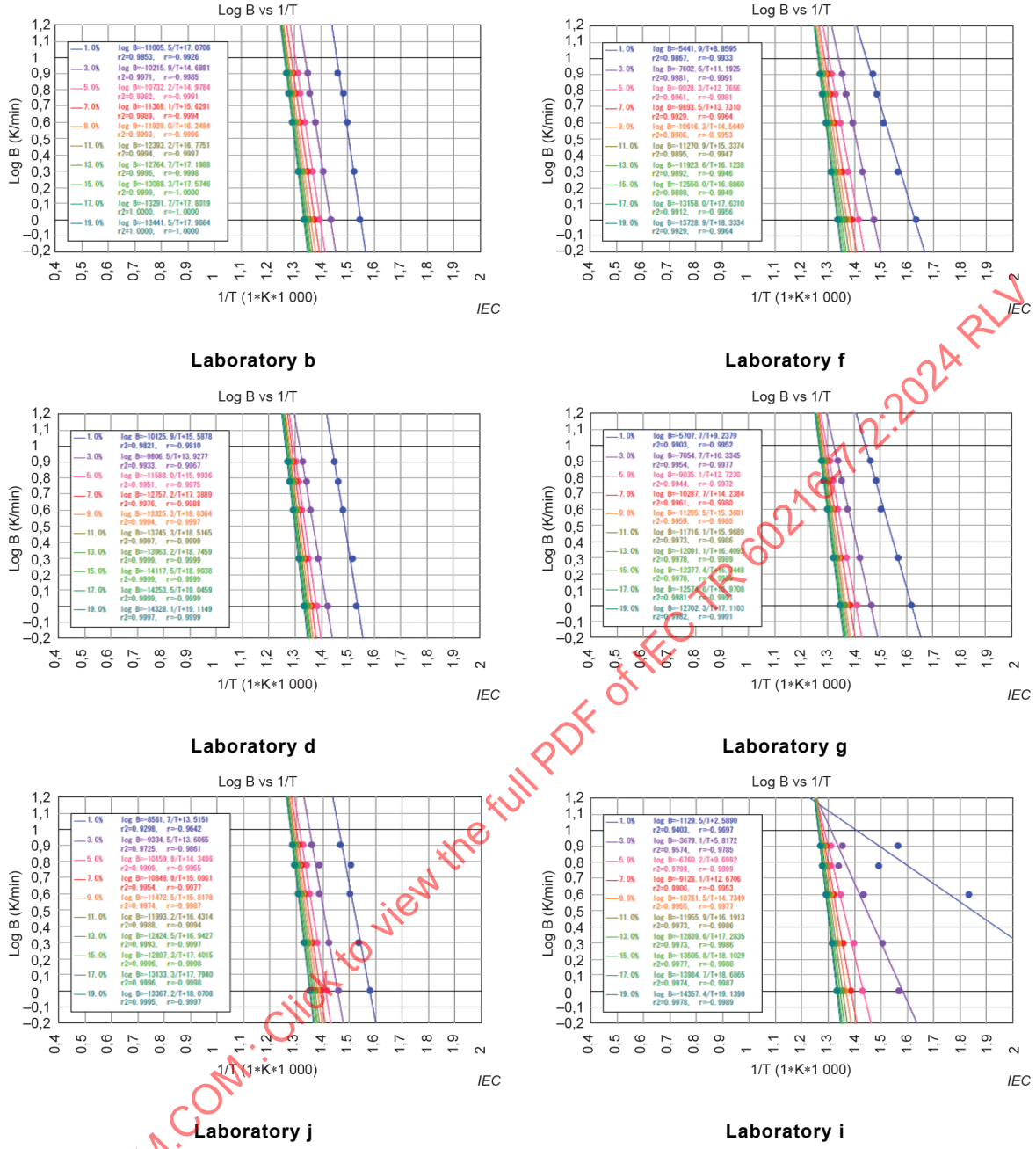

Figure 5 – Logarithm plots for activation energy calculation

It was not clarified why laboratories b, d, and j obtained lower differences between TGA curves in multiple heating rates, but it is suggested that repeatability of TGA curves in the same heating rate ~~could affect~~ possibly affected the results as observed in 8.3. It was indeed confirmed that laboratory d and laboratory f in Figure 4 and Figure 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 it is suggested that the same approach of repeatability check ~~would~~ be ~~recommended~~ followed 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 cancellation of the baseline ~~may~~ can 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~~ are considered outside the scope of this document until additional information on apparatus and conditions during test is provided by the laboratory.

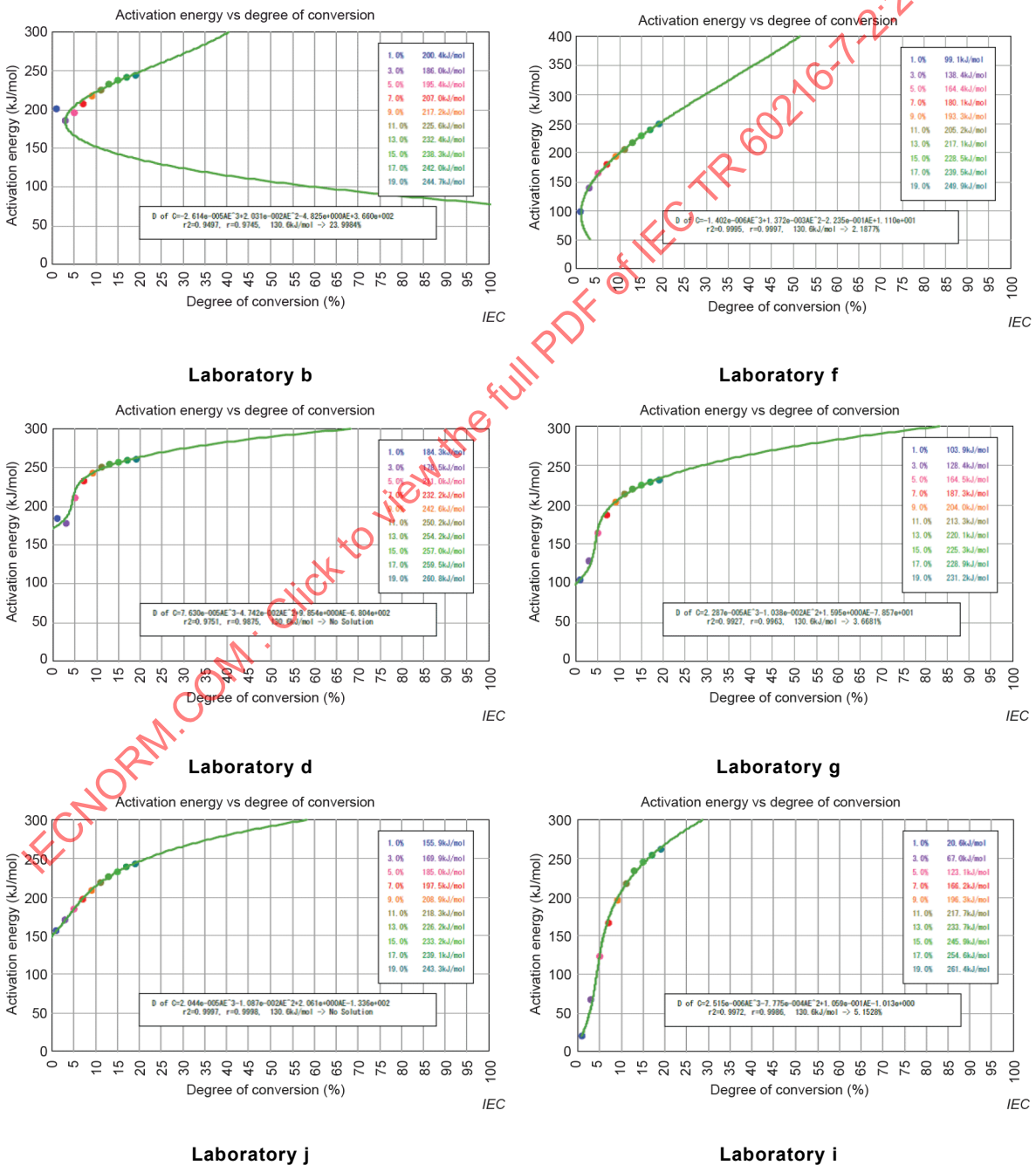

Figure 6 – Fitting curves of degree of conversion versus activation energy by TGA

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~~ will not always be repeatable in the same material and at the same heating rates with the same test conditions, depending on the 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 [3] and IEC TS 60216-7-1. Confirmation of TGA curves per heating rate ~~would~~ are therefore ~~be recommended~~ suggested 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 cancellation of the base line drift of the TGA curves ~~may~~ can be further considered as ~~questionable~~ potential factors which ~~may~~ can 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.

– While the difference with TI and E_a from heat ageing was not very significant between the two LCP materials given by one laboratory, the difference of RTI_A or TI_A between laboratories was significant in some instances (which possibly led to differences in excess of 20 °C between laboratories).

Additional round robin studies using polybuthylene terephthalate are provided in Annex A.

Annex A
(informative)

Additional round robin studies with polybuthylene terephthalate

A.1 Objectives

The additional study preselected a generic polymer type of polybuthylene terephthalate (PBT) materials having a lower TI than LCP, to validate the procedure of IEC TS 60216-7-1 and enhance data consistency based on the findings of necessary improvements in the round robin using LCP as follows:

– compensation of equipment baseline drift for TGA measurement;
– water content of purge air or nitrogen gas less than 0,001 % by mass;
– mass and temperature calibrations in accordance with ISO 11358-1; and
– heavier samples amount and smaller tolerance of 10 mg ± 0,1 mg.

A.2 Test specimens

Two powdered materials of unfilled PBT (PBT) and 30 % glass fibre reinforced PBT (PBT-GF30) were tested. The samples were powdered by cryogenic grinder with 0,5 mm mesh and then the homogeneous samples were delivered to 10 laboratories (A, B, C, D, E, F, G, H, I and J). The TI and HIC of the two materials in accordance with the conventional heat ageing are shown in Table A.1.

Table A.1 – Heat ageing properties of the PBT test specimens by the conventional procedure in accordance with IEC 60216-5 [4]

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	PBT	PBT-GF30	PBT	PBT-GF30	PBT	PBT-GF30
180	686	850		881		
170	1 433	194		2 431		
160	3 043	4 190		4 516		
150	6 113	7 877	418	7 362		2 032
140			3 506		458	
130						
120						
TI (°C)	116,6	118,6	209,7	111,0	140,9	78,7
E_a (kJ/mol)	135,7	139,4	125,7	138,7	104,8	111,2

A.3 Test apparatus

The same apparatus as used for TGA (see 5.1) was used for the evaluations. In addition to the conditions specified in 5.1, all the laboratories for this additional study did compensation of the equipment baseline drift. For the purge gas (see 5.2), all the laboratories selected dry air (water content less than 0,001 % by mass).

A.4 Test procedures

For pre-conditioning (see 6.2), this study used 10 mg ± 0,1 mg of the test sample which was 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 50 °C for 5 min until heating tests were started at 50 °C. Other procedures after stating the TGA measurement followed the round robin with LCPs (see 6.3, 6.4 and 6.5).

A.5 Test results

Degrees of conversion at the activation energy identical to those from conventional heat ageing (see 7.2) are shown in Table A.2.

NOTE The two studies using reported LCP materials and PBT materials specified in this Annex A were analysed by different software, even though both followed the same analytical methodology in accordance with IEC TS 60216-7-1. Software algorithms are minor but it is possible they will not provide identical values depending on significant figures of raw data values.

It was observed that both sample PBT and sample PBT-GF30 had a higher degree of conversion under TGA (around 5 % to 20 % mass loss) correlating to thermal degradation of the dielectric strength under a heating oven in terms of the identical activation energies.

Table A.2 – Degrees of conversion at the activation energy identical to that from conventional heat ageing

Laboratory	Degree of conversion identical to activation energy of the conventional heating, sample PBT	Degree of version identical to activation energy to the conventional heating, sample PBT-GF30
A	0,0506	0,2831
B	0,0817	0,1816
C	0,0648	0,3360
D	0,0525	0,1927
E	0,0505	0,3030
F	0,0783	0,0057
G	0,1961	0,2262
H	0,2720	0,4496
I	0,0506	0,0763
J	0,0517	0,3559
Average	**0,0949**	**0,2410**
Standard deviation	**0,0764**	**0,1333**

HIC_A of the PBT materials determined by Method A and Method B according to IEC TS 60216-7-1 (see 7.3) are shown in Table A.3, Table A.4, Table A.5 for dielectric strength, tensile strength, and impact strength, respectively.

Table A.3 – HIC_A determined by Method A and Method B for dielectric strength

Laboratory	Method A		Method B	
	HIC_A of sample PBT	HIC_A of sample PBT-GF30	HIC_A of sample PBT	HIC_A of sample PBT-GF30
A	6,2	12,0	8,0	12,3
B	7,4	10,6	9,4	11,5
C	6,1	12,5	9,1	12,3
D	5,9	11,4	7,6	11,4
E	6,1	12,1	8,1	12,3
F	N/A	7,0	9,6	7,4
G	8,0	8,9	10,9	12,5
H	7,4	10,3	13,6	15,4
I	7,4	9,7	8,4	9,9
J	6,4	12,5	8,5	12,6
Average	**6,8**	**10,7**	**9,3**	**11,8**
Standard deviation	**0,8**	**1,8**	**1,8**	**2,1**
NOTE N/A means that in the cubic approximation of activation energy versus the degree of conversion equation did not provide a solution.				

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

Laboratory	Method A		Method B	
	HIC_A of sample PBT	HIC_A of sample PBT-GF30	HIC_A of sample PBT	HIC_A of sample PBT-GF30
A	5,7	N/A	7,4	11,3
B	6,9	N/A	8,8	10,7
C	5,7	N/A	8,4	11,4
D	5,3	N/A	7,0	10,5
E	5,7	N/A	7,5	11,4
F	N/A	N/A	9,0	6,8
G	7,8	N/A	10,3	11,5
H	7,0	N/A	13,1	14,3
I	7,1	N/A	7,8	9,1
J	5,9	N/A	7,9	11,7
Average	**6,3**	**N/A**	**8,7**	**10,9**
Standard deviation	**0,9**	**N/A**	**1,8**	**1,9**
NOTE N/A means that in the cubic approximation of activation energy versus the degree of conversion equation did not provide a solution.				

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

Laboratory	Method A		Method B	
	HIC_A of sample PBT	HIC_A of sample PBT-GF30	HIC_A of sample PBT	HIC_A of sample PBT-GF30
A	5,4	12,0	6,6	11,3
B	8,0	7,0	7,8	10,7
C	5,5	11,6	7,5	11,4
D	6,0	10,6	6,3	10,5
E	5,5	11,7	6,7	11,4
F	N/A	5,8	8,0	6,8
G	8,4	6,6	9,0	11,5
H	7,3	7,7	11,3	14,3
I	8,6	7,5	7,0	9,1
J	5,6	11,1	7,0	11,7
Average	**6,7**	**9,2**	**7,7**	**10,9**
Standard deviation	**1,4**	**2,4**	**1,5**	**1,9**
NOTE N/A means that in the cubic approximation of activation energy versus the degree of conversion equation did not provide a solution.				

RTE_A determined by Method A and TI_A by Method B (see 7.4) are shown in Table A.6, Table A.7 and Table A.8 for dielectric strength, tensile strength, and impact strength, respectively.

Table A.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 PBT	RTE_A of sample PBT-GF30	TI_A of sample PBT	TI_A of sample PBT-GF30
A	144,9	125,0	137,2	124,0
B	140,0	131,0	130,6	127,0
C	145,3	123,0	132,3	123,9
D	146,4	127,7	138,9	127,5
E	145,3	124,5	136,5	123,6
F	N/A	145,2	129,8	143,7
G	137,3	137,6	123,7	123,1
H	139,7	132,0	110,3	109,9
I	139,9	134,7	135,3	133,9
J	144,1	123,0	134,9	122,5
Average	**142,5**	**130,4**	**130,9**	**125,9**
Standard deviation	**3,3**	**7,2**	**8,5**	**8,6**
NOTE N/A means that in the cubic approximation of activation energy versus the degree of conversion equation did not provide a solution.				

Table A.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 PBT	RTE_A of sample PBT-GF30	TI_A of sample PBT	TI_A of sample PBT-GF30
A	125,2	N/A	120,6	128,0
B	121,9	N/A	116,6	130,8
C	125,2	N/A	117,6	127,9
D	126,2	N/A	121,6	131,3
E	125,2	N/A	120,2	127,6
F	N/A	N/A	116,1	146,1
G	119,5	N/A	112,3	127,2
H	121,6	N/A	103,8	115,0
I	121,3	N/A	119,5	137,1
J	124,6	N/A	119,2	126,6
Average	**123,4**	**N/A**	**116,7**	**129,7**
Standard deviation	**2,4**	**N/A**	**5.3**	**8,0**
NOTE N/A means that in the cubic approximation of activation energy versus the degree of conversion equation did not provide a solution.				

Table A.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 PBT	RTE_A of sample PBT-GF30	TI_A of sample PBT	TI_A of sample PBT-GF30
A	106,0	105,8	100,3	108,6
B	93,4	125,3	94,3	111,3
C	105,8	107,5	95,9	108,5
D	103,4	111,4	101,9	111,8
E	105,9	107,0	99,7	108,2
F	N/A	129,9	93,6	126,4
G	91,3	126,8	88,1	107,8
H	97,0	122,8	75,9	95,8
I	90,3	123,4	98,6	117,5
J	105,1	109,4	98,3	107,2
Average	**99,8**	**116,9**	**94,7**	**110,3**
Standard deviation	**6,7**	**9,5**	**7,7**	**7,8**
NOTE N/A means that in the cubic approximation of activation energy versus the degree of conversion equation did not provide a solution.				

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 (see 7.5), are shown in Table A.9, Table A.10, and Table A.11 for dielectric strength, tensile strength, and impact strength, respectively.

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

Laboratory	Method A		Method B	
	RTE_A-TI of sample PBT	RTE_A-TI of sample PBT-GF30	TI_A-TI of sample PBT	TI_A-TI of sample PBT-GF30
A	9,2	-14,4	1,5	-15,4
B	4,3	-8,4	-5,1	-12,4
C	9,6	-16,4	-3,4	-15,5
D	10,7	-11,7	3,2	-11,9
E	9,6	-14,9	0,8	-15,8
F	N/A	5,8	-5,9	4,3
G	1,6	-1,8	-12,0	-16,3
H	4,0	-7,4	-25,4	-29,5
I	4,2	-4,7	-0,4	-5,5
J	8,4	-16,4	-0,8	-16,9
Average	**6,8**	**-9,0**	**-4,7**	**-13,5**
Mean	**8,4**	**-10,1**	**-2,1**	**-15,5**
Standard deviation	**3,3**	**7,2**	**8,5**	**8,6**
NOTE N/A means that in the cubic approximation of activation energy versus the degree of conversion equation did not provide a solution.				

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

Laboratory	Method A		Method B	
	RTE_A-TI of sample PBT	RTE_A-TI of sample PBT-GF30	TI_A-TI of sample PBT	TI_A-TI of sample PBT-GF30
A	-0,5	N/A	-5,1	-10,7
B	-3,8	N/A	-9,1	-7,9
C	-0,5	N/A	-8,1	-10,8
D	0,5	N/A	-4,1	-7,4
E	-0,5	N/A	-5,5	-11,1
F	N/A	N/A	-9,6	7,4
G	-6,2	N/A	-13,4	-11,5
H	-4,1	N/A	-21,9	-23,7
I	-4,4	N/A	-6,2	-1,6
J	-1,1	N/A	-6,5	-12,1
Average	**-2,3**	**-**	**-9,0**	**-8,9**
Mean	**-1,1**	**-**	**-7,3**	**-10,8**
Standard deviation	**2,3**	**-**	**5,3**	**8,0**
NOTE N/A means that in the cubic approximation of activation energy versus the degree of conversion equation did not provide a solution.				

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

Laboratory	Method A		Method B	
	RTE_A-TI of sample PBT	RTE_A-TI of sample PBT-GF30	TI_A-TI of sample PBT	TI_A-TI of sample PBT-GF30
A	1,2	-5,4	-4,5	-2,6
B	-11,4	14,1	-10,5	0,1
C	1,0	-3,7	-8,9	-2,7
D	-1,4	0,2	-29	0,6
E	1,1	-4,2	-5,1	-3,0
F	N/A	18,7	-11,2	15,2
G	-13,5	15,6	-16,7	-8,4
H	-7,8	11,6	-28,9	-15,4
I	-14,5	12,2	-6,2	6,3
J	0,3	-1,8	-6,5	-4,0
Average	**-5,0**	**5,7**	**-10,1**	**-0,9**
Mean	**-1,4**	**5,9**	**-7,7**	**-2,7**
Standard deviation	**6,7**	**9,5**	**7,7**	**7,8**
NOTE N/A means that in the cubic approximation of activation energy versus the degree of conversion equation did not provide a solution.				

A.6 Observations

The RRT results revealed that the decomposition E_a of PBT can be higher than that of PBT-GF30 by using the TGA test in most laboratories. The results are similar to the data obtained from the conventional ageing test for mechanical properties (impact and strength).

Data in PBT revealed the same or lower variations than those in PBT-GF30, probably because of the difference in PBT amount in a TGA sample and the side effect of the surface area of glass fibres which can affect the decomposition speed of PBT.

A sample amount change from 5 mg to 10 mg can, not only contribute to the decrement of variations, but also to the increment of approximately 20 kJ/mol to 40 kJ/mol in the activation energy obtained under the same degree of conversion. In fact, laboratory E carried out an additional test of PBT and PBT-GF30 with a sample amount of 5 mg, as shown in Figure A.1. As a result, unreinforced PBT samples provided different activation energy by changing the sample amount, whereas 30 % glass fibre reinforced PBT provided similar activation energy between the different sample amounts. These results suggested that the volatilization speed of decomposed PBT would be different with or without glass fibres, depending on the heating rate of the TGA furnace.

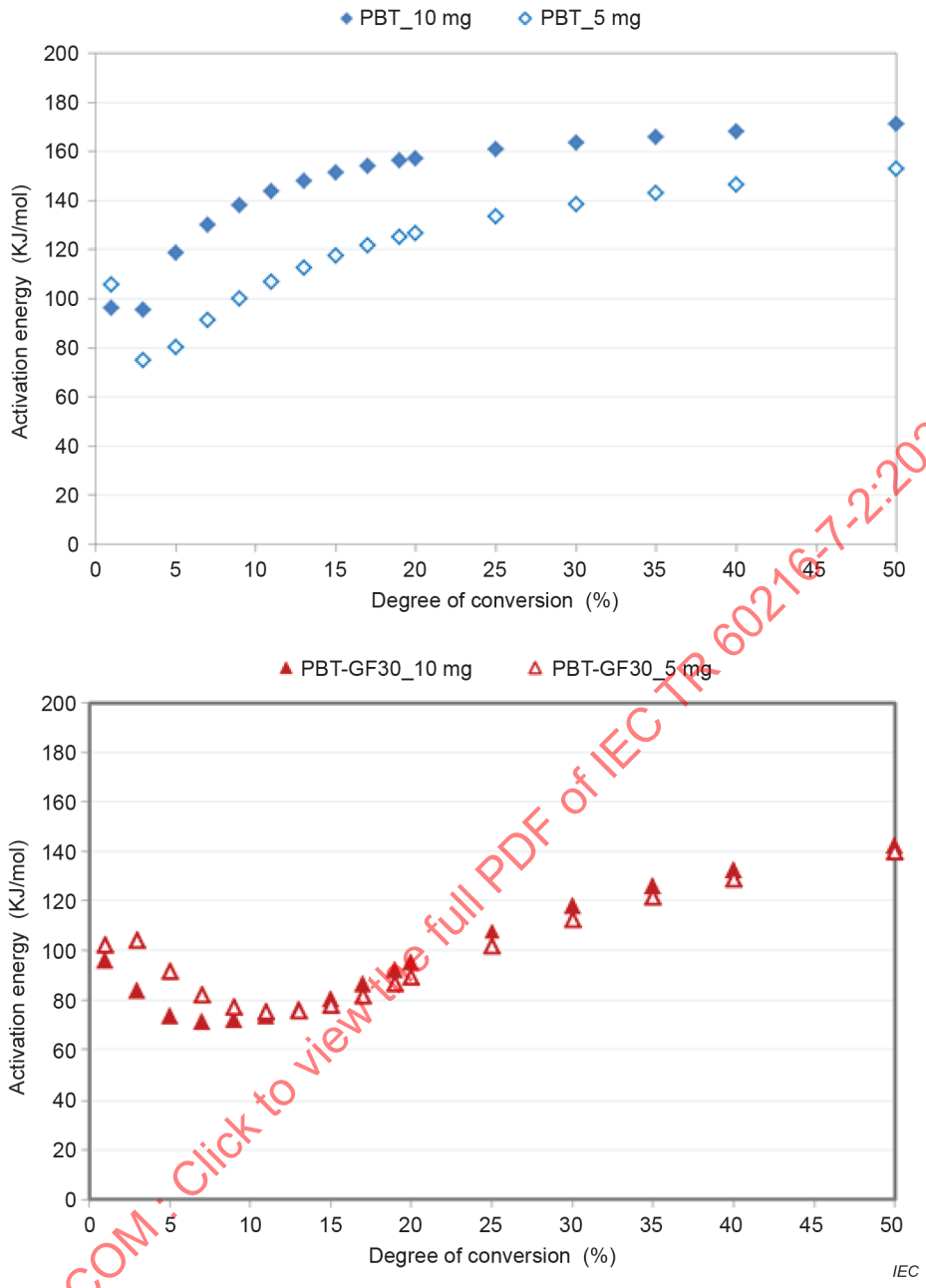

Figure A.1 – Effect of sample amount on E_a (data provided by laboratory E)

Differences between RTE_A (or TI_A) and the TI at 20 000 h from the conventional heat ageing programme of PBT materials are observed to be similar or larger than those of LCP materials. This is probably because the LCP round robin study used both 30 % glass filled materials whose TGA data showed no variations with or without the side effect of glass fibres on TGA data. The PBT study used unreinforced and 30 % glass filled materials for comparison, and it appears that this difference in material composition resulted in more variation factors than the TGA measurement conditions.

In conclusion, of the two studies using LCP and PBT, it is suggested that the analytical testing procedure be carried out carefully to ensure an accurate estimation of thermal endurance from the kinetic study. A validation test can be required to verify the appropriate test set-up before carrying out the kinetics study by using TGA. Factors affecting the kinetic study are summarized in Figure A.2.

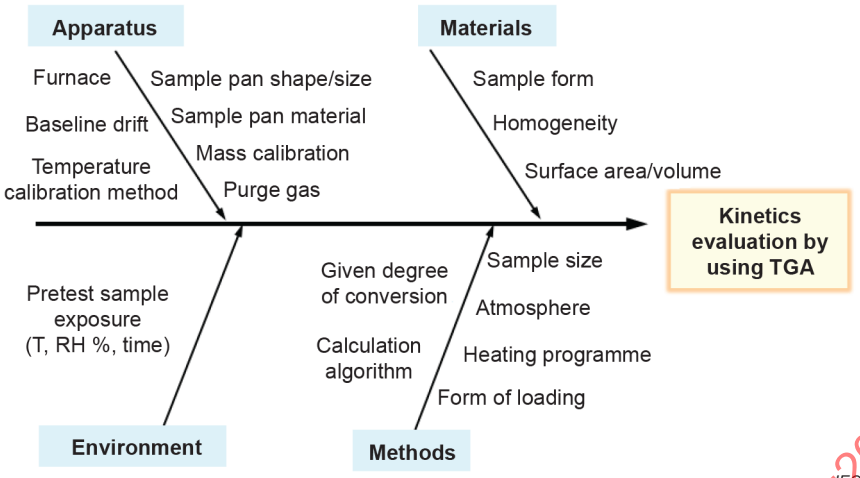

Figure A.2 – Summary of factors affecting the TGA kinetic study for determination of RTE_A and TI_A

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[9] IEC 60216-8, *Electrical insulating materials – Thermal endurance properties – Part 8: Instructions for calculating thermal endurance characteristics using simplified procedures*

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

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

IEC TR 60216-7-2

Edition 2.0 2024-09

TECHNICAL REPORT

colour inside

Electrical insulating materials – Thermal endurance properties – Part 7-2: Accelerated determination of relative thermal endurance using analytical test methods (RTEA) – Results of the round robin tests to validate procedures of IEC TS 60216-7-1 by non-isothermal kinetic analysis of thermogravimetric data

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CONTENTS

INTERNATIONAL ELECTROTECHNICAL COMMISSION

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ELECTRICAL INSULATING MATERIALS – THERMAL ENDURANCE PROPERTIES –

Part 7-2: Accelerated determination of relative thermal endurance using analytical test methods (RTEA) – Results of the round robin tests to validate procedures of IEC TS 60216-7-1 by non-isothermal kinetic analysis of thermogravimetric data

FOREWORD

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

This second edition cancels and replaces the first edition published in 2016. This edition constitutes a technical revision.

This edition includes the following significant technical changes with respect to the previous edition:

a) Annex A (informative) has been added to provide a round robin test with a different polymer type – polybuthylene terephthalate (PBY) – as an additional use case of the method in accordance with IEC TS 60216-7-1;

b) Tables 3 to 11 have been corrected by adding units, and texts have been refined for more technical clarifications of the procedures and observations.

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

Draft	Report on voting
112/651/DTR	112/658/RVDTR

Full information on the voting for its approval can be found in the report on voting indicated in the above table.

The language used for the development of this Technical Report is English.

This document was drafted in accordance with ISO/IEC Directives, Part 2, and developed in accordance with ISO/IEC Directives, Part 1 and ISO/IEC Directives, IEC Supplement, available at www.iec.ch/members_experts/refdocs. The main document types developed by IEC are described in greater detail at www.iec.ch/publications.

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 document will remain unchanged until the stability date indicated on the IEC website under webstore.iec.ch in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn, or
- revised.

IMPORTANT – The "colour inside" logo on the cover page of this document 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 TC 112) has been working on the development of IEC TS 60216-7-1 [1][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 Underwriters Laboratories Long-Term Thermal Aging Forum (UL LTTA Forum) has been discussing alternative methods that can speed up the determination of a thermal index. Members of the IEC TC 112 and of the UL LTTA Forum have made joint efforts to determine whether the Technical Specification developed by IEC TC 112 can be used to offer an alternative method of evaluating polymeric compounds for a thermal index.

Members of IEC TC 112 and the UL LTTA Forum decided to conduct a round robin test (RRT) using thermogravimetric analysis (TGA) according to ISO 11358-2 [3] 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 can 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.

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

ELECTRICAL INSULATING MATERIALS – THERMAL ENDURANCE PROPERTIES –

Part 7-2: Accelerated determination of relative thermal endurance using analytical test methods (RTEA) – 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

This part of IEC 60216 is intended 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.

The round robin test results do not provide statistical analysis for precision. 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 precision.

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.

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

- IEC Electropedia: available at https://www.electropedia.org/
- ISO Online browsing platform: available at https://www.iso.org/obp

3.1
activation energy
Arrhenius activation energy
E_a
empirical parameter characterizing the exponential temperature dependence of the reaction rate constant

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 [2], modified – "characterizing the thermal capability of an insulating material or an insulation system" has been replaced with "derived from the thermal endurance relationship at a time of 20 000 h (or other specified time)" and the two notes to entry have been replaced by a new note to entry.]

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 11358-2:2021, 3.3 [3], modified – The symbol "*C*" has been replaced with "α" and the notes to entry have been deleted.]

4 Test specimens

For the round robin test, one generic type of polymer, liquid crystal polyester (LCP), was pre-selected. Although it is known that materials can undergo more than one transition, the round robin test verified the assumption that one single thermal degradation reaction is predominant and directly correlated to the end-point of dielectric strength as a diagnostic property.

NOTE Since different materials can undergo more than one transition, the validity of results obtained from the evaluation of thermal endurance properties using TGA are assessed for the different materials.

LCP originally has very little entwining of molecules exhibiting crystalline properties as a liquid. Hence, 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 ranges. 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 as 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 materials. Configurations of monomers are the only differences between the samples which influence the difference in thermal resistance, as shown in Table 1.

The samples were homogenized by freeze-pulverization from test plaques. 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 [4]

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
TI (°C)	250,0	241,5	249,1	246,2	249,1	234,7
E_a (kJ/mol)	130,6	142,3	165,2	145,9	134,5	102,9

5 Test apparatus

5.1 Thermogravimetric analyser (TGA)

A thermogravimetric analyser (TGA) in accordance with ISO 11358-1 [5] was used for the determination of RTE_A concerning the test samples. In fact, a number of commercial instruments suitable for the measurement are available and various models of TGAs were used for evaluation of the test samples by the participating laboratories. 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[2]), but air supplied from the facility (compressed air with or without an air dryer) was used in a few laboratories.

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2 ppm = parts per million.

6 Test procedures

6.1 General

Thermal analysis with TGA of the test samples was evaluated with reference to ISO 11358-2 [3] and IEC TS 60216-7-1 in principle. A few modifications of test conditions and more detailed procedures were added as follows.

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 [3] 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 resulted in the lowest and highest heating rates differing by a factor of 8, in accordance with ISO 11358-2 [3]. 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 for given degrees of conversion in accordance with Equation (2) in ISO 11358-2:2021 [3]. Then, both values of degree of conversion and the activation energies were plotted between 1 % and 19 % with 2 % interval of degree of conversion and a cubic curve fitting approximately was performed as shown in Figure 1. Equation (2) in ISO 11358-2:2021 [3] was used for the 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 [3] and had a similar degree of conversion versus the activation energy fitting curve for the candidate material.

All TGA raw data were submitted by eleven participating laboratories and analysis with ISO 11358-2 [3] was carried out by one of the laboratories with the analytical tool, to avoid any discrepancy among various software calculations.

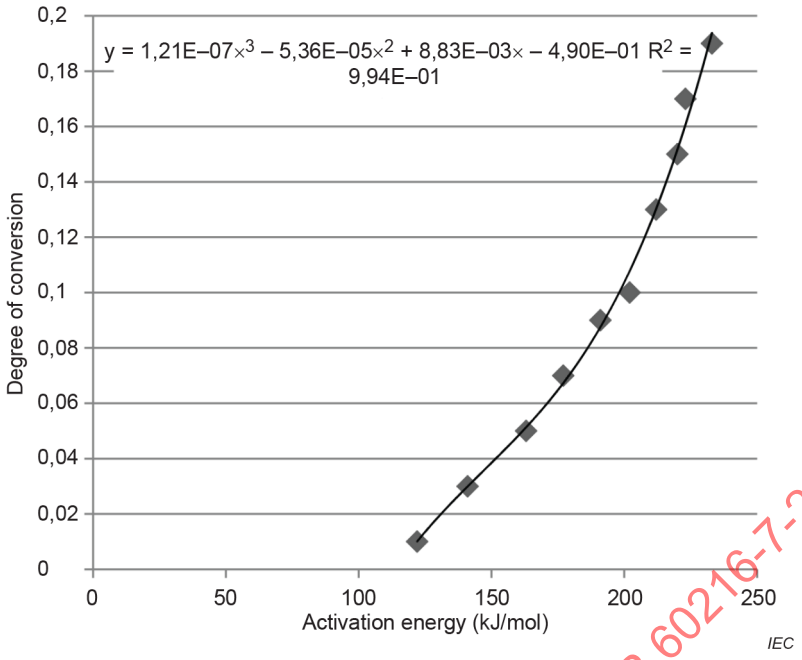

Figure 1 – Fitting curve of plots between degree of conversion and activation energy determined by ISO 11358-2 [3] (example)

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 [4], and procedures in accordance with IEC TS 60216-7-1.

In accordance with ISO 11358-2 [3], 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 activation energy are sometimes used experimentally for prediction of end-point of properties [6], [7], 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.

NOTE The assumption that the degree of conversion for the candidate material is the same as the given degree of conversion for the reference material, is validated since the candidate material can be of the same type of the reference material.

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 [7], [8]. 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 [3] 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 at multiple heating rates magnified to show the degrees of conversion between 0 and 0,02. Figure 5 provides typical examples of logarithm graphs between reciprocal temperatures and heating rates for 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 [3] 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 a 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 found to be higher than the ones determined by heat ageing in the considered 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 and 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 K	HIC_A of sample B K	HIC_A of sample A K	HIC_A of sample B K
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
	K	K	K	K
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
	K	K	K	K
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 °C	RTE_A of sample B °C	TI_A of sample A °C	TI_A of sample B °C
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 °C	RTE_A of sample B °C	TI_A of sample A °C	TI_A of sample B °C
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 °C	RTE_A of sample B °C	TI_A of sample A °C	TI_A of sample B °C
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 °C	RTE_A-TI of sample B °C	TI_A-TI of sample A °C	TI_A-TI of sample B °C
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 °C	RTE_A-TI of sample B °C	TI_A-TI of sample A °C	TI_A-TI of sample B °C
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 °C	RTE_A-TI of sample B °C	TI_A-TI of sample A °C	TI_A-TI of sample B °C
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 with a difference in 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 between laboratories.

It is noted, however, that results show differences between the laboratories, with differences in temperature exceeding 20 °C in some instances of the report.

In particular, the difference of 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 [9], 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 [10].

As TI of the two LCP materials evaluated in this document 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 were not able to 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 can 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 [3] 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 can be considered with respect to ISO 11358-2 [3], but not as a significant factor with regard to the technical concerns of reproducibility in laboratories mentioned above.

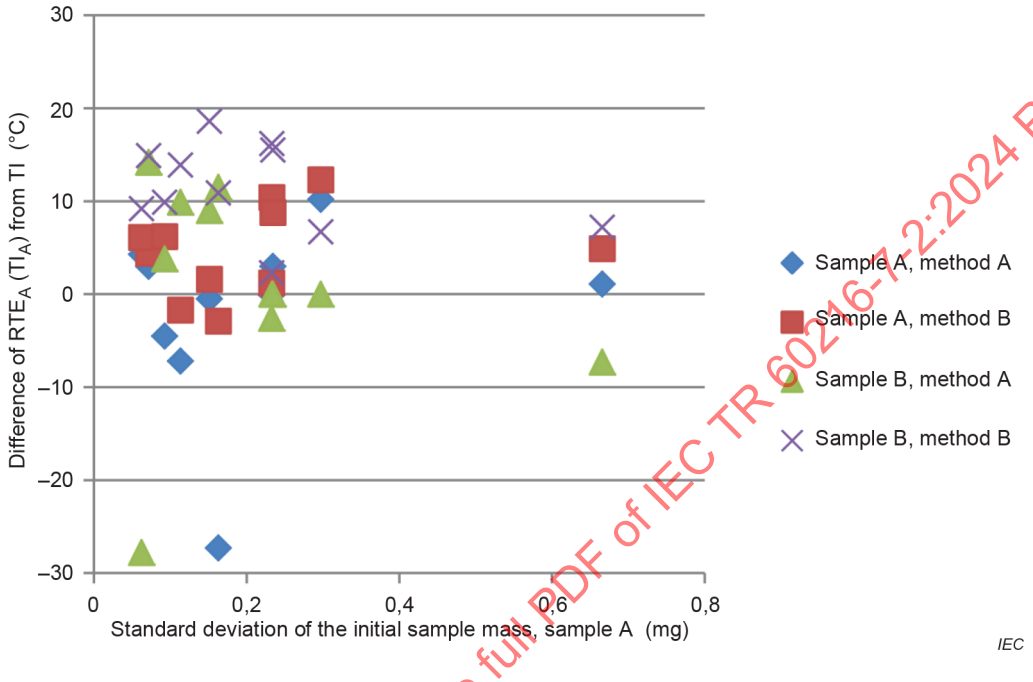

Figure 2 – Correlation between the initial sample mass of sample A and the difference of RTE_A (TI_A) from TI

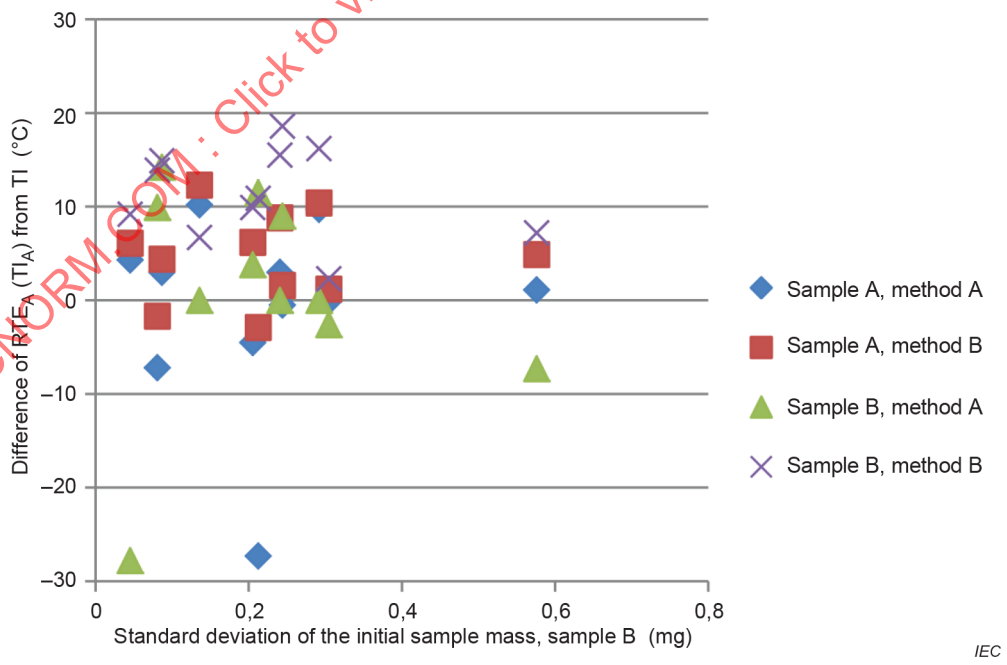

Figure 3 – Correlation between the initial sample mass of sample B and the difference of RTE_A (TI_A) from TI

8.3 Humidity and hydrolysis of the sample

The round robin test samples were liquid crystal polyesters, and since moisture can accelerate the polymer degradation with hydrolysis, humidity and hydrolysis were therefore pointed out as the factors potentially influencing the reproducibility at specific laboratories.

At first, all of samples A and samples B provided to the laboratories were homogenized and pre-dried at 140 °C for 4 h to remove absorbed water during freeze-pulverization and then 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 can 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 each laboratory, 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 and the 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 Considerations on repeatability of TGA curves

In the round robin test based on IEC TS 60216-7-1 and ISO 11358-2 [3], 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 can 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 130,6 kJ/mol		Degree of conversion for E_a of sample B at 142,3 kJ/mol	
	Original data at 8 K/min	Rerun data at 8 K/min	Original data at 8 K/min	Rerun data at 8 K/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 a significant change in the given degree of conversion for sample A by rerun data at 8 K/min, which exceeded the degree of conversion at 0,05 (Method B). Another laboratory k was not able to 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 (8 K/min) was retested for a preliminary review of repeatability check. It is suggested that the repeatability 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 [3] is conducted in each laboratory, if repeatability and reproducibility improvements are necessary.

It is suggested that repeatability of the TGA curve is checked at all heating rates to decrease variations of the degree of conversion and the activation energy determined by TGA.

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 [3], and the fitting curve example given in Figure 1 were plotted 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.

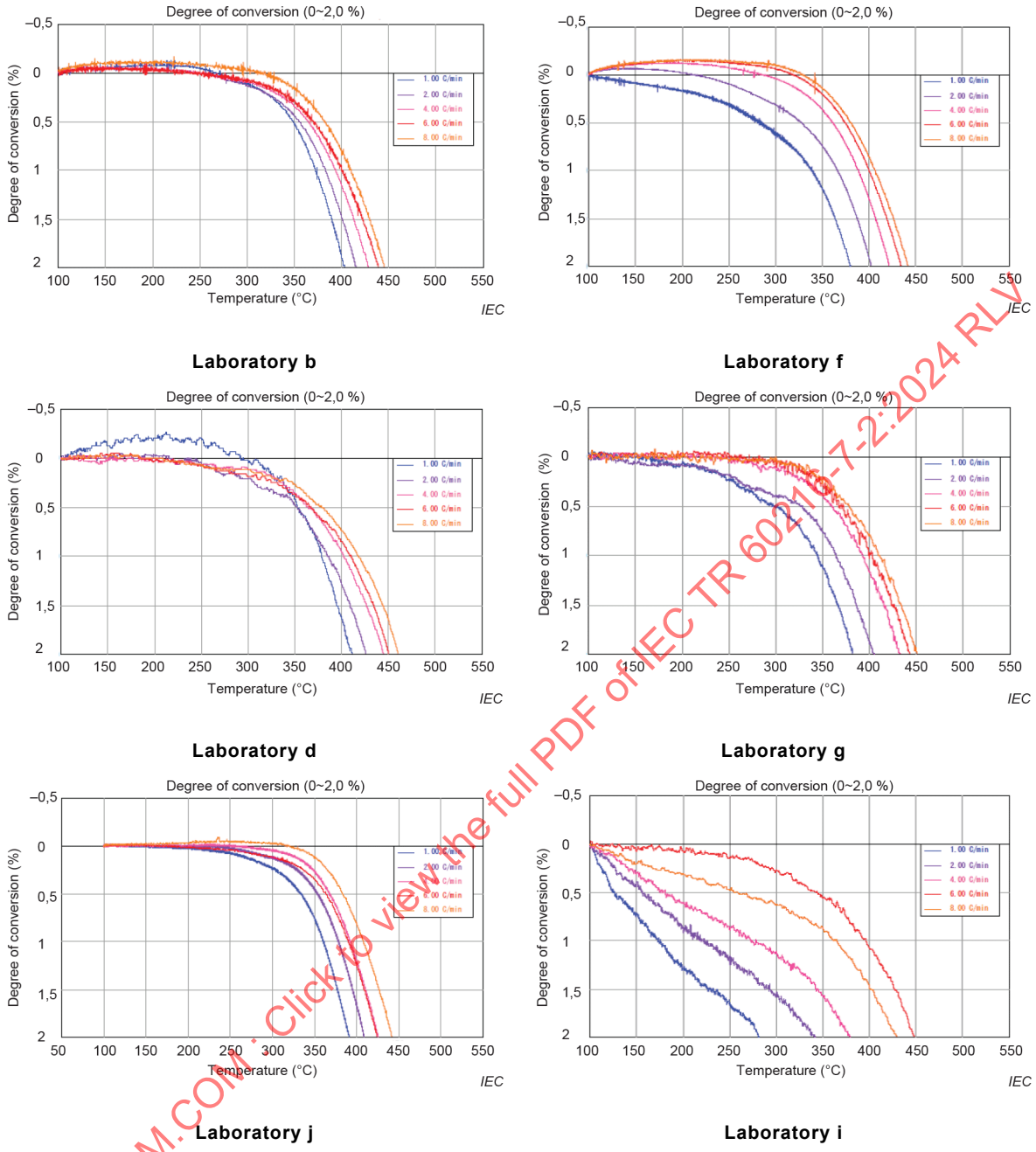

Figure 4 – Overlay charts of TGA curves in multiple heating rates in multiple laboratories (enlarged)

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 between multiple heating rates (narrower range in temperature among the curves) than that of 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 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.