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Raw rubber and rubber latex — Determination of the glass transition temperature by differential scanning calorimetry (DSC)

Caoutchouc et latex de caoutchouc brut — Détermination de la température de transition vitreuse par analyse calorimétrique différentielle (DSC)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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

This document was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

This third edition cancels and replaces the second edition (ISO 22768:2017), which has been technically revised.

The main changes compared to the previous edition are as follows:

— rubber latex has been added to the scope and to Clause 6 as 6.2;

— a new Annex B on the precision of rubber latex has been added.

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

Raw rubber and rubber latex — Determination of the glass transition temperature by differential scanning calorimetry (DSC)

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices.

1 Scope

This document specifies a method using a differential scanning calorimeter to determine the glass transition temperature of raw rubber and rubber latex.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 124:2014, *Latex, rubber — Determination of total solids content*

ISO 1407, *Rubber — Determination of solvent extract*

ISO 11357-1:2016, *Plastics — Differential scanning calorimetry (DSC) — Part 1: General principles*

ISO 23529, *Rubber — General procedures for preparing and conditioning test pieces for physical test methods*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11357-1 and the following apply.

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

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

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

3.1
glass transition
reversible change in an amorphous polymer, or in amorphous regions of a partially crystalline polymer, from (or to) a rubbery or viscous condition to (or from) a glassy or hard condition

3.2
glass transition temperature
T_g
approximate midpoint of the temperature range over which *glass transition* (3.1) takes place

Note 1 to entry: For the purposes of this document, the glass transition temperature is defined as the point of inflection of the DSC curve which has been obtained at a heating rate of 20 °C/min (see A.3).

4 Principle

The change in specific heat capacity of the test sample as a function of temperature under a specified inert atmosphere is measured using a differential scanning calorimeter (DSC). The glass transition temperature is determined from the curve thus produced.

5 Apparatus and materials

5.1 Differential scanning calorimeter, in accordance with ISO 11357-1:2016, 5.1.

The calorimeter should be operated in a room held at standard laboratory temperature. It should be protected from draughts, direct sunlight and sudden temperature changes.

5.2 Specimen pans (crucibles), in accordance with ISO 11357-1:2016, 5.2.

5.3 Gas supply, analytical grade, usually nitrogen or helium.

5.4 Balance, capable of measuring the specimen mass to an accuracy of ±0,1 mg.

5.5 Oven, capable of being maintained at 105 °C ± 5 °C.

6 Preparation of the test sample

6.1 Raw rubber

The test specimen shall be as representative as possible of the sample being examined and shall have a mass between 0,01 g and 0,02 g.

To determine T_g of polymers, extract raw rubber in accordance with ISO 1407.

6.2 Rubber latex

Dry rubber latex samples at 105 °C± 5 °C in accordance with ISO 124:2014, 6.2. Remove the rubber latex film and cut into pieces about 2 mm × 2 mm.

7 Conditioning

Condition the sample to be examined and the test specimen in accordance with ISO 23529.

8 Calibration

Calibrate the calorimeter according to the manufacturer's instructions.

The use of suitable analytical grade substances is recommended to check the accuracy of the temperature scale. Ideally, substances whose melting points bracket the temperature range of interest should be chosen. *n*-Octane, *n*-heptane and cyclohexane have been found to be useful. Indium should be used if a higher temperature calibrant is required.

9 Procedure

9.1 Gas flow rate

The same inert gas flow rate with a tolerance of ±10 %, shall be used throughout the procedure. Flow rates between 10 ml/min and 100 ml/min have been found to be suitable.

9.2 Loading the test specimen

Determine the mass of the test specimen to an accuracy of ±0,1 mg. Unless otherwise specified in the materials standard, use a mass between 5 mg and 20 mg. The same nominal mass shall be used for all determinations. If possible, the specimen shall have a flat surface so as to give good thermal contact with the bottom of the pan.

NOTE 1 Intimate thermal contact between the test specimen and the bottom of the pan is essential for good repeatability.

Place the specimen in the pan, using tweezers and seal with a lid. Place the sealed pan in the calorimeter using tweezers.

Do not handle the test specimen or the pan with bare hands.

NOTE 2 Placing an empty pan with a lid as a reference helps to obtain stable DSC thermograms.

9.3 Temperature scan

9.3.1 Cool the test specimen to a temperature of approximately −140 °C at a rate of 10 °C/min or 20 °C/min and hold at this temperature for 1 min to 10 min until the baseline becomes stable.

A starting temperature of −140 °C is required for the determination of rubbers and rubber latices with very low glass transition temperatures, e.g. high-cis polybutadiene. For rubbers and rubber latices with higher glass transitions, this temperature is not necessary.

A starting temperature should be chosen so that a stable base line is achieved before the glass transition region, e.g. about 30 °C to 40 °C below the expected glass transition temperature.

If the apparatus is not capable of maintaining the specified cooling rate, it should be adjusted to give a rate as close as possible to that specified.

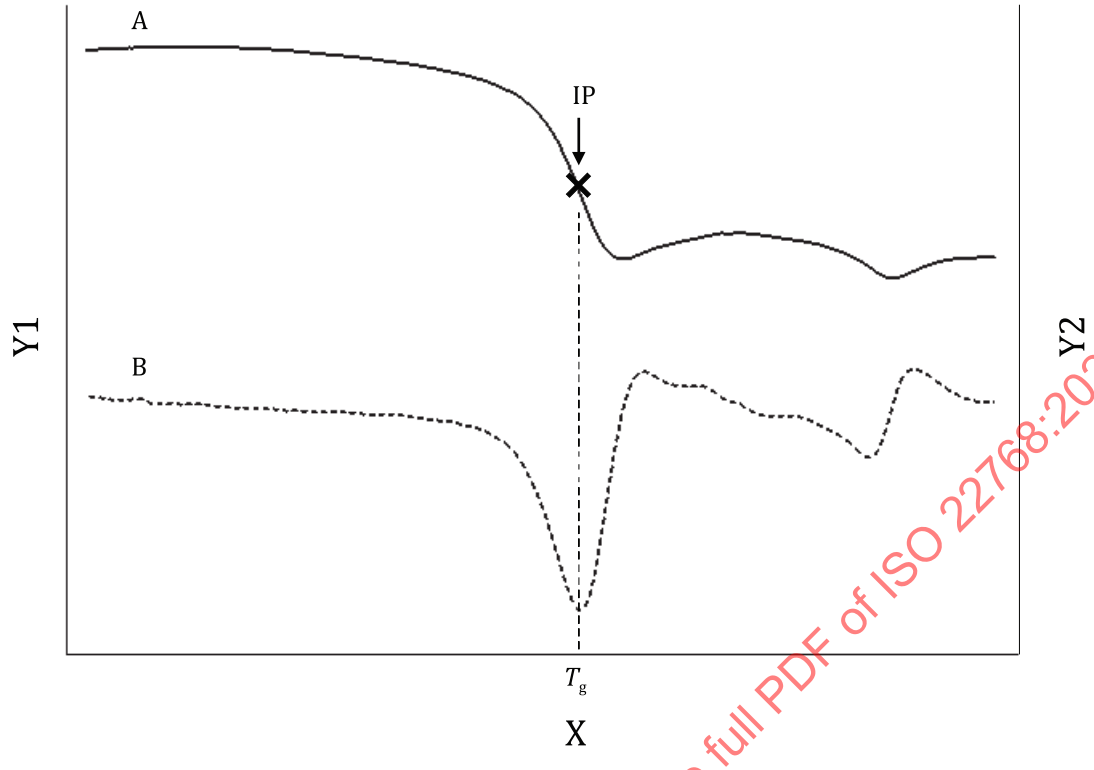
9.3.2 Perform the temperature scan at a heating rate of 20 °C/min, heating until a temperature about 30 °C above the upper limit of the glass transition range is reached.

NOTE Most instruments can be programmed to carry out the required thermal cycle automatically.

10 Expression of results

Determine the glass transition temperature as the inflection point of the transition curve using the instrument software. General DSC endothermogram and inflection point are given in Figure 1.

NOTE If the glass transition temperature has to be determined directly from the curve, a better indication of the position of the inflection point is obtained by studying the first derivative of the curve (DDSC thermogram). In the case of the representation of the exotherm curve, this is the peak minimum.



Key

X temperature, in °C
Y1 DSC (exothermic direction)
Y2 DDSC
A DSC thermogram
B DDSC thermogram
IP inflection point

Figure 1 — General thermogram and inflection point

11 Test report

The test report shall include the following:

a) a reference to this document, i.e. ISO 22768:2020;

b) identification of the sample;

c) the mass of the specimen, in grams;

d) the type of DSC instrument used;

e) the type of inert gas and the flow rate;

f) the calibrants used;

g) the thermal cycle used;

h) the T_g value in degrees Celsius, together with the DSC curve;

i) the date of the test.

12 Precision

Precision data on raw rubber are given in Annex A.

Precision data on rubber latex are given in Annex B.

Annex A
(informative)

Precision on raw rubber

A.1 General

A.1.1 The interlaboratory test programme (ITP) for precision evaluation for T_g was conducted in 2004, using the precision procedures and guidelines as described in ISO/TR 9272. See ISO/TR 9272 for other details and terminology on precision evaluation.

A.1.2 The ITP was conducted using four rubbers, NdBR (neodymium-catalysed high-*cis* BR), SBR 1502, SBR 1721 and OESSBR. These represent a range of T_g values from about −100 °C to −20 °C. Thirty laboratories participated in the ITP and a Type 1 precision was evaluated. A test result represents a single determination or measurement of T_g using the DSC procedure as specified in this document. Two measurements of T_g were conducted on two test days, one week apart. Measurements were conducted at both 10 °C/min and at 20 °C/min on each test day. For precision analysis, all T_g values were converted to Kelvin. This avoids negative values in the calculation algorithms and, more importantly, it provides mean values (for T_g) that are not near zero and thus permits relative precision (in percent) to be more meaningful for all materials, i.e. it avoids large percent values.

A.1.3 The precision results as determined by this ITP may not be applied to acceptance or rejection testing for any group of materials or products without documentation that the results of this precision evaluation actually apply to the products or materials tested.

A.2 Precision results

A.2.1 General

Precision results are given in Table A.1 for each of the four materials for both 10 °C/min and 20 °C/min. The precision results were obtained using the outlier deletion procedures as described in ISO/TR 9272. Table A.1 lists the number of laboratories remaining in the database for the precision evaluation after the deletion of laboratories that had outlier values. General statements for the use of the precision results are cited in A.2.2. These are given in terms of both the absolute precision, r and R, and also for relative precision (r) and (R).

A.2.2 Repeatability and reproducibility statements

A.2.2.1 Repeatability

The repeatability, or local domain precision, for each of the materials (rubbers) has been established by the values found in Table A.1, for each of the materials as listed in Table A.1. Two single test results (obtained by the proper use of the method of this document) that differ by more than the tabulated values for r in measurement units, and (r) in percent, shall be considered as suspect, i.e. to have come from different populations. Such a decision suggests that some appropriate investigative action be taken.

A.2.2.2 Reproducibility

The reproducibility, or global domain precision, for each of the materials has been established by the values found in Table A.1, for each of the materials as listed in Table A.1. Two single test results obtained in different laboratories (by the proper use of the method of this document) that differ by more than

the tabulated values for R in measurement units, and (R) in percent, shall be considered as suspect, i.e. to have come from different populations. Such a decision suggests that some appropriate investigative action be taken.

A.2.3 Additional analysis comments

The last column of Table A.1 (the number of laboratories that were included in the database used for the final calculations for precision) indicates that a substantial number of laboratory data values were deleted as outliers. The final number of laboratories for NdBR is low because several laboratories did not submit data. There was some variation in precision improvement among the materials with outlier deletion but, on an overall basis (mean for all four materials), the repeatability limit, r, was reduced by a reduction factor (r_{final}/r_{orig}) of 0,56 for 10 °C/min and 0,46 for 20 °C/min, after all repeatability outlier data were deleted. On the same overall basis, the reproducibility limit, R, was reduced by a reduction factor of 0,71 for both 10 °C/min and 20 °C/min procedures, after all reproducibility data outliers were deleted. Individual laboratories may show poor agreement in repeatability or poor agreement in reproducibility, or both.

There does not appear to be any substantial overall difference in the precision for 10 °C/min versus 20 °C/min. The repeatability r for 10 °C/min is 9 % greater than for 20 °C/min, while the reproducibility R for 10 °C/min is 3 % less than for 20 °C/min.

The final precision, as expressed in Table A.1, represents the precision for the majority of laboratories in the ITP; these may be considered as a core group of high quality testing laboratories that constitute a benchmark level of performance for this particular property measurement.

A.2.4 Bias

Bias is the difference between a measured average test result and a reference or true value for the measurement in question. Reference values do not exist for this test method and therefore bias cannot be evaluated.

Table A.1 — Precision data for glass transition temperature

Material	Mean level		Within laboratory			Between laboratories			Number of laboratories[a]
	°C	K	s_r	r	(r)	s_R	R	(R)	
Measurements at 10 °C/min									
1 — NdBR	−106,3	166,7	0,379	1,06	0,64	1,531	4,29	2,57	20
2 — SBR 1502	−54,5	218,5	0,382	1,07	0,49	1,160	3,25	1,49	25
3 — SBR 1721	−34,3	238,7	0,408	1,14	0,48	1,417	3,97	1,66	24
4 — OESSBR	−24,3	248,7	0,245	0,69	0,28	1,449	4,06	1,63	23
Pooled or average value[b]			0,354	0,990	0,473	1,39	3,89	1,84	
Measurements at 20 °C/min									

NOTE 1 Notation used:

s_r = within-laboratory standard deviation (in measurement units)

r = repeatability (in measurement units)

(r) = relative repeatability (in percent of mean level)

s_R = between-laboratory standard deviation (for total between-laboratory variation in measurement units)

R = reproducibility (in measurement units)

(R)= relative reproducibility (in percent of mean level)

NOTE 2 The relative precision parameters, (r) and (R), are calculated using values of T_g in K.

[a] Number of laboratories after outliers deleted; 3-step analysis; total of 30 laboratories participated.

[b] Simple averages calculated.

Table A.1 *(continued)*

Material	Mean level		Within laboratory			Between laboratories			Number of laboratories[a]
	°C	K	s_r	r	(r)	s_R	R	(R)	
1 — NdBR	−104,8	168,2	0,273	0,76	0,45	1,418	3,97	2,36	19
2 — SBR 1502	−52,7	220,3	0,462	1,29	0,59	1,431	4,01	1,82	27
3 — SBR 1721	−32,2	240,8	0,372	1,04	0,43	1,164	3,26	1,35	22
4 — OESSBR	−21,9	251,1	0,190	0,53	0,21	1,724	4,83	1,92	24
Pooled or average value[b]			0,324	0,908	0,420	1,43	4,02	1,86	

NOTE 1 Notation used:

s_r = within-laboratory standard deviation (in measurement units)

r = repeatability (in measurement units)

(r) = relative repeatability (in percent of mean level)

s_R = between-laboratory standard deviation (for total between-laboratory variation in measurement units)

R = reproducibility (in measurement units)

(R)= relative reproducibility (in percent of mean level)

NOTE 2 The relative precision parameters, (r) and (R), are calculated using values of T_g in K.

[a] Number of laboratories after outliers deleted; 3-step analysis; total of 30 laboratories participated.

[b] Simple averages calculated.

A.3 Conclusions

The glass transition temperature determined at a heating rate of 20 °C/min is about 2 °C higher than with a heating rate of 10 °C/min. The heating rate of 10 °C/min or 20 °C/min makes no significant difference to the precision. Therefore, in the interests of convenience, the faster rate has been chosen.