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Rubber, vulcanized — Determination of the glass transition temperature and enthalpy by differential scanning calorimetry

Caoutchouc vulcanisé — Détermination de la température de transition vitreuse et de l'enthalpie par analyse calorimétrique différentielle

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Foreword

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This document was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

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Rubber, vulcanized — Determination of the glass transition temperature and enthalpy by differential scanning calorimetry

WARNING — Persons using this document should be familiar with normal laboratory practice, if applicable. This document does not purport to address all of the safety concerns, 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 of thermal analysis of vulcanized rubber by differential scanning calorimetry (DSC). This method is intended for the observation and measurement of various properties and phenomena associated, such as physical transitions (glass transition, melting and crystallization, polymorphic transitions, etc.).

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 11357-1, *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 terminology databases for use in standardization at the following addresses:

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

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

3.1
glass transition temperature
T_g
temperature of change from a glassy or hard condition to a rubbery or viscous condition

3.2
melting
transition stage between a fully crystalline or partially crystalline solid state and an amorphous liquid of variable viscosity

Note 1 to entry: The transition, also referred to as “fusion”, is characterized by an endothermic peak in the DSC curve (see Figure 1).

3.3

crystallization

transition stage between an amorphous liquid state and a fully crystalline or partially crystalline solid state

Note 1 to entry: The transition is characterized by an exothermic peak in the DSC curve (see Figure 1).

3.4

enthalpy of fusion

heat required to melt a material at constant pressure

Note 1 to entry: It is expressed in kilojoules per kilogram (kJ/kg) or joules per gram (J/g).

3.5

enthalpy of crystallization

heat released by the *crystallization* (3.3) of a material at constant pressure

Note 1 to entry: It is expressed in kilojoules per kilogram (kJ/kg) or joules per gram (J/g).

3.6

reference crucible

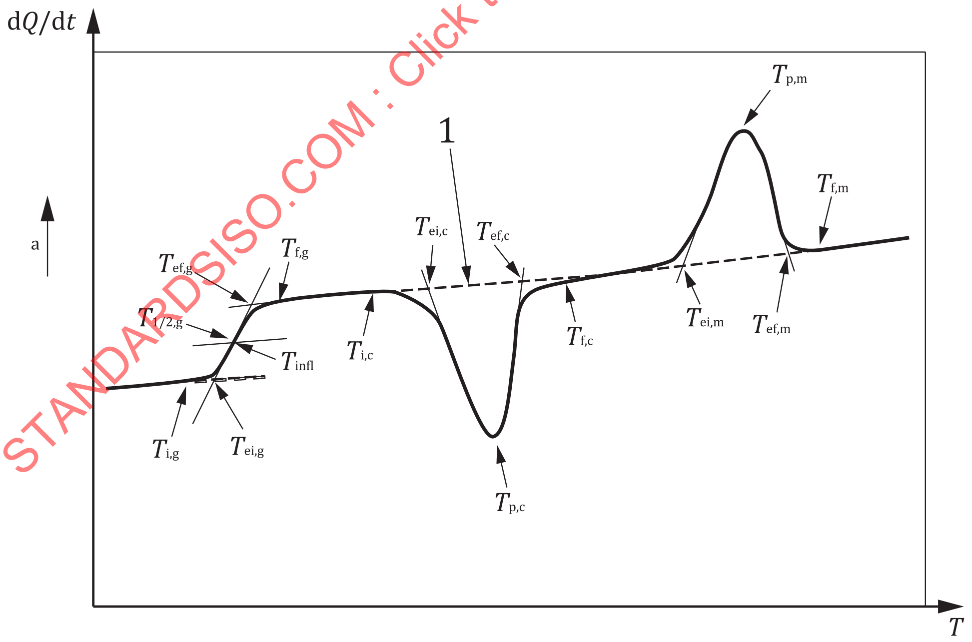
crucible used on the reference side of the symmetrical crucible holder assembly

Note 1 to entry: Normally, the reference crucible is empty.

Note 2 to entry: This reference material should be thermally inactive over the temperature and time range of interest.

4 Symbols

A typical DSC curve, with conventional temperatures, is shown in Figure 1 and explained in Table 1.



Key

dQ/dt	heat flow rate
T	temperature
T_i	onset temperature
T_{ei}	extrapolated onset temperature
$T_{1/2,g}$	midpoint temperature

T_{infl}	point of inflection temperature
T_p	peak temperature
T_{ef}	extrapolated end temperature
T_f	end temperature
1	virtual baseline
[a]	Endothermic direction.

NOTE All these thermal phenomena are not necessarily present for all rubbers.

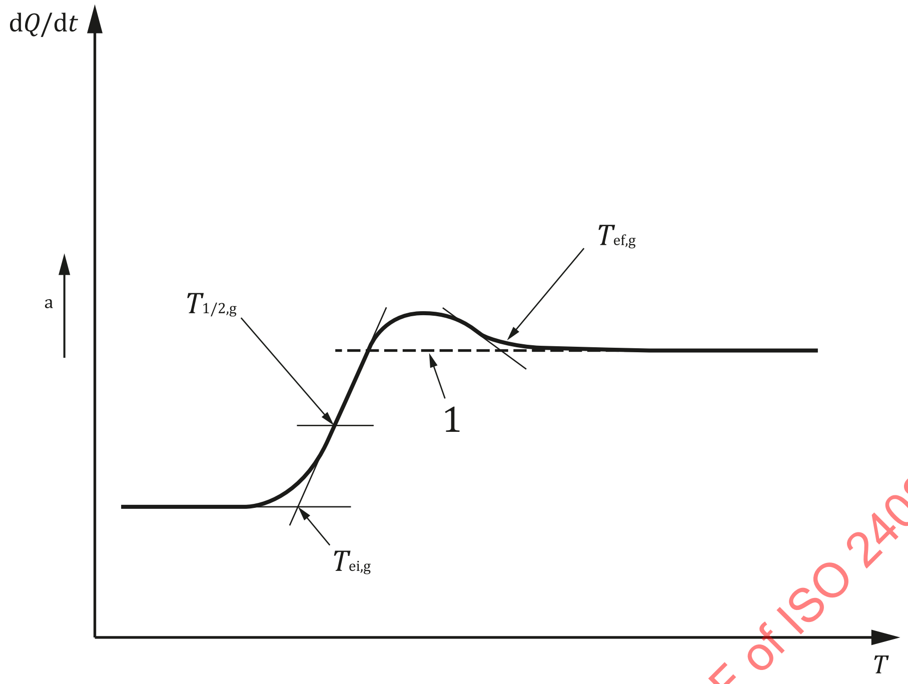
Figure 1 — Typical DSC curve

Table 1 — Symbols for conventionnal temperatures

Conventionnal temperatures	
The first subscript, or pair of subscripts, denotes the position on the DSC curve with respect to the step or peak:	
T_i	first detectable departure of DSC curve from extrapolated start baseline
T_{ei}	(for a peak) point of intersection of virtual baseline and tangent drawn at point of inflection of near side of peak or (for a step) point of intersection of start baseline and tangent drawn at point of inflection of step (onset)
$T_{1/2,g}$	half-height of a step
T_{infl}	point of inflection (maximum of the first-derivative curve) in the range of transition NOTE 1 For the purposes of this document, the glass transition temperature T_g corresponds to value of T_{infl}
T_p	greatest distance between DSC curve and virtual baseline during a peak
T_{ef}	(for a peak) point of intersection of interpolated virtual baseline and tangent drawn at point of inflection of far side of peak or (for a step) point of intersection of extrapolated end baseline and tangent drawn at point of inflection of step (offset)
T_f	last detectable deviation of DSC curve from extrapolated end baseline
The second subscript indicates the type of transition:	
g	glass transition
c	crystallization
m	melting

If a peak of internal relaxation appears on the high-temperature side of the glass-transition temperature, find the glass-transition end temperature ($T_{ef,g}$) from the intersection of the two straight lines according to Figure 2.

One is a straight line that extends the high-temperature side baseline to the low-temperature side. The other is the tangent line drawn at the point where the slope of the curve on the hot side of the peak is maximum.



Key

$\mathrm{d}Q/\mathrm{d}t$	heat flow rate
T	temperature
1	virtual baseline
[a]	Endothermic direction.

Figure 2 — Curve for the glass-transition temperature determination with enthalpy relaxation

5 Principle

The difference between the rate of heat flow into a specimen and that into a reference crucible is measured as a function of temperature and/or time while the specimen and the reference are subjected to the same temperature-control programme under a specified atmosphere.

Two types of DSC can be carried out: heat-flux DSC and power-compensation DSC.

— Heat-flux DSC: The specimen and reference positions are subjected to the same temperature-control programme by a single heater. A difference in temperature, ΔT, occurs between the specimen position and the reference position because of the difference in heat capacity between the specimen and the reference.

— Power-compensation DSC: The difference in electrical power required to maintain both the specimen position and the reference position at the same temperature is recorded against temperature or time, while each position is subjected to the same temperature-control programme;

6 Apparatus and materials

6.1 Differential scanning calorimeter, with the following features.

a) A symmetrical crucible holder assembly which has holders for the specimen and reference crucibles.

b) The capability to generate heating and cooling rates between 0,5 K/min and 50 K/min.

c) The capability to carry out step heating or step cooling.

d) The capability to cool the target temperature for measuring the T_g of the sample.

e) The capability to maintain a constant purge gas flow rate controllable to within 10 ml/min and 100 ml/min.

f) The capability to measure temperature signals with a resolution of 0,1 °C and an accuracy of ±0,5 °C or better.

g) For calibration and operation with a test portion of 1 mg minimum (or smaller quantities if required for specific applications).

6.2 Data acquisition and processing system.

6.3 Crucibles, for the specimen and reference positions.

They shall be of the same type, made of the same material and have similar masses (±0,5 mg). They shall be physically and chemically inert to the specimen, the calibration materials and the purge gas under the measurement conditions (see Table A.2).

Crucibles should preferably be made of a material with a high thermal conductivity, for example, aluminium. Crucibles shall be closed with lids or hermetically sealed depinding on the measurement.

6.4 Crucibles setting press.

6.5 Balance, capable of measuring the test portion mass with a resolution of 0,01 mg and an accuracy of ±0,1 mg or better.

6.6 Calibration materials (see Table A.2 for examples).

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

7 Calibration

7.1 General

Calibrate the calorimeter, both in energy and temperature, according to the manufacturer's instructions.

The calibration can be affected by the following:

- type of calorimeter used and its stability;
- type of purge gas used and its flow rate;
- type of crucible used, the crucible size and the positions of the crucibles in the crucible holder;
- mass and particle size of the test portion;
- heating and cooling rates;
- type of cooling system used;
- thermal contact between the specimen crucible and the crucible holder.

The conditions of the actual determination should therefore be defined as precisely as possible and the calibration carried out under these conditions as closely as possible. Computer-controlled DSC instruments can automatically correct for the effects of some of these sources of error.

7.2 Temperature calibration

The following procedure describes the minimum requirements for carrying out temperature calibration.

- weigh at least two calibration materials, indium and another material, covering the temperature range required;
- determine the transition temperatures for the calibration materials under the same conditions as those used with the test portion; the transition temperatures of the calibration materials being defined at the initial extrapolated temperature T_{ei};
- determine the temperature calibration function, either by comparing the nominal values with the recorded values or by entering the nominal values and the recorded values into a computer system associated with the calorimeter; in the last-mentioned case, the function is obtained automatically.

This calibration procedure is dependent on the heating rate and has to be performed for each heating rate. More frequent checks can be made if necessary. The repeatability of the temperature calibration shall be ±0,5 °C.

7.3 Heat calibration

NOTE Refer to the manufacturer' recommendation to choose the calibration method.

The following procedure describes the minimum requirements for carrying out heat calibration.

- for heat calibration, the same measurements can be made as those made for temperature calibration;
- carry out a heating run with one material, preferably indium;
- examine the calibration material under the same conditions as those used with the test portion;
- record the curve corresponding to the transition heat of the calibration material as a function of temperature;
- determine the heat calibration function, either by comparing the nominal values with the recorded values or by entering the nominal value and the recorded values into a computer system associated with the calorimeter; in the last-mentioned case, the function is obtained automatically.

Heat calibration checks shall be carried out regularly. The repeatability of the heat calibration shall be ±2 %.

8 Test portion

The test portion shall be representative of the sample being examined and shall be prepared and handled with care. If it has been cut from a sample, it will have at least one flat surface (to ensure good thermal contact) and be in one piece, if possible.

9 Conditioning

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

10 Procedure

10.1 General

10.1.1 Switching on

Switch the instrument on at least 1 h prior to any calibration or testing to allow it to reach steady-state conditions.

Adjust the baseline according to the instructions of the device manufacturer.

10.1.2 Baseline determination

Place empty crucibles of the same nominal mass at the specimen and reference positions in the crucible holder. Adjust the experimental conditions to those which will be used for the actual measurement run. The recorded DSC curve (i.e. the instrument baseline) should be close to a straight line over the required temperature range. If significant baseline curvature is observed, check the crucible holder for contamination.

NOTE With computer-controlled instruments, any remaining curvature can be corrected for by subtracting the instrument baseline from the DSC curve. When a reasonably straight line cannot be obtained, record the DSC curve after confirming its repeatability.

10.1.3 Test portion and crucible

Use crucible of volume recommended or specified by the equipment manufacturer. Select two identical crucibles for the intended measurements, one for the test portion and one (normally empty) as the reference crucible.

Load the test portion (10 mg to 20 mg) into the crucible.

If an enthalpy shall be measured (see 10.3), note the mass of this test portion with an accuracy of at least 0,1 mg.

Crimp the crucibles using the press. If necessary, drill the cover.

Place the crucibles on the calorimeter cells using pliers or any other appropriate tool.

Good thermal contact between the specimen and crucible and between the crucible and holder shall be ensured. Close the oven.

NOTE The accuracy of the result can be impacted by the mass of the sample, take the highest possible mass.

10.1.4 Performing measurements

Programme the instrument and set the experimental parameters to carry out the required thermal cycle(s). Two types of programme can be used: continuous or stepwise heating or cooling.

Carry out the test according to 10.2 (glass transition) or 10.3 (other thermal phenomena).

After finishing the measurement run, bring the crucible holder back to the loading temperature and take out the crucible containing the specimen.

Repeat the test in case of overflow of the crucible contents.

Clean the equipment regularly according to the manufacturer's instructions. Check that the calibration is still valid using at least one calibration material for temperature and heat.

10.2 Determination of the glass transition temperature, T_g

10.2.1 Test performance

Define the test program:

- the sweeping gas (the use of nitrogen is recommended, helium being recommended with some calorimeters at very low temperatures) and its flow rate;
- cooling rate of 10 K/min, to reach the initial temperature;
- the initial temperature shall be at least 30 °C lower than the expected T_g;
- isothermal: until T_i stabilizes (°C) (5 min minimum);
- heating rate to reach the final temperature, choose one of the following two rates:
  - 10 K/min (Method 1);
  - 20 K/min (Method 2);
- the final temperature shall be at least 30 °C higher than the expected T_g;
- temperature rise conditions for stepwise.

Start the test after preparing the test sample in accordance with 10.1.3.

10.2.2 Use and expression of results

Check the curve for the existence of a glass transition in the temperature range considered.

By default, determine the temperature T_g at the inflection point (T_{infl}, extremum of the first derivative).

The median temperature ($T_{1/2,g}$, half-height of the step) may also be used. In this case, this shall be specified in the test report. Express the value obtained in degrees Celsius or Kelvin.

10.3 Determination of the transition temperature and enthalpy of other thermal phenomena

10.3.1 General

Other thermal phenomena may be detected: melting, crystallization, etc. The characteristics that can be determined are as follows (see Figure 1): peak temperature, initial temperature, final temperature, energy.

10.3.2 Test performance

Define the test program:

- the sweeping gas and its flow rate;
- cooling rate at temperature of 10 K/min, to reach the initial temperature;
- the initial temperature shall be at least 30 °C lower than the expected temperature $T_{i;}$
- heating rate to reach the final temperature, choose one of the following two rates:
  - 10 K/min (Method 1);
  - 20 K/min (Method 2).
- the final temperature shall be at least 30 °C higher than the expected temperature T_f.

Start the test after preparing the test portion and crucible in accordance with 10.1.3.

10.3.3 Use and expression of results

Construct the peak baseline (see Figure 1) by connecting the onset temperature T_i and the final temperature T_f ($T_{i,m}$ and $T_{f,m}$ for an endothermic melting peak, $T_{i,c}$ and $T_{f,c}$ for an exothermic crystallization peak), with T_i and T_f corresponding to the first and last detectable deviation between the DSC curve and the virtual baseline, respectively.

To determine the enthalpies of fusion and crystallization, integrate the area between the peak and the baseline constructed according to the paragraph above. Express the value obtained in J/g, after division of the enthalpy by the mass of the test portion.

The temperature of the measured thermal phenomenon corresponds to the temperature of the peak. The initial temperature T_i (onset) can also be taken. Express the value obtained in degrees Celsius or Kelvin.

11 Precision

See Annex B.

12 Test report

The test report shall include the following:

a) reference to this document;

b) and the method used depending on the scanning rate (method 1 or 2);

c) identification of the sample;

d) the mass of the test portion, in grams;

e) the type of DSC instrument used;

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

g) the type of crucibles used;

h) the calibrants used;

i) the thermal cycle used;

j) the T_g value in degrees Celsius or Kelvin, or enthalpy in J/g and the temperature value in degrees Celsius or Kelvin corresponding to other thermal phenomena;

k) the DSC curve;

l) the date of the test.

Annex A
(informative)

Recommended calibration materials

Table A.1 — Transition temperature, heat of transition and type of transition for various recommended calibration materials

Calibration materials	Point or heat of transition n[a] (extrapoled onset temperature) °C	Heat of transition J.g^{-1}
Cyclohexane (cristalline transition)	−87,00	80
Carbon dioxide snow (sublimation)	−78,48	—
Tricyclo[3.3.1.13,7]décane (adamantane) (crystalline transition)	−65,15	−22,0
n-Octane (melting)	−56,80	—
n-Decane (melting)	−29,70	202
Water (melting)	0,00	334
Cyclohexane (melting)	6,47	31
Potassium nitrate (transition)	128,80	—
Indium (melting)	156,60	28
Tin (melting)	231,93	60
Bismuth (melting)	271,40	53
Zinc (melting)	419,53	107
Caesium chloride (transition)	476,00	17

[a] The transition or melting points are given as an indication, they can vary according to the purity of the calibration materials.