INTERNATIONAL STANDARD

ISO 4659

Sixth edition
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Styrene-butadiene rubber (carbon black or carbon black and oil masterbatches) — Evaluation procedure

Caoutchouc butadiène-styrène (mélanges-maîtres avec du noir de carbone ou avec du noir de carbone et de l'huile) — Méthode d'évaluation

Reference number
ISO 4659:2014(E)

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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).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 45, Rubber and rubber products, Subcommittee SC 3, Raw materials (including latex) for use in the rubber industry.

This sixth edition cancels and replaces the fifth edition (ISO 4659:2003), which has been technically revised with the following changes:

— Clause 2 has been updated.

— In 4.2, the method given in ISO 248-2 is now allowed.

— In 5.2.2.1, addition of a statement that the mixing with a laboratory internal mixer is the preferred procedure. Method B becomes "Single stage mixing with a laboratory internal mixer".

— In 5.2.2.3, advice on mixing with various sizes of laboratory internal mixer is given along with a general mixing procedure.

Styrene-butadiene rubber (carbon black or carbon black and oil masterbatches) — Evaluation procedure

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard 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 and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies the following:

— physical and chemical tests on raw rubbers;

— standard materials, standard test formulations, equipment, and processing methods for evaluating the vulcanization characteristics of styrene-butadiene rubber masterbatches with carbon black or with carbon black and oil.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 37, *Rubber, vulcanized or thermoplastic — Determination of tensile stress-strain properties*

ISO 247, *Rubber — Determination of ash*

ISO 248-1, *Rubber, raw — Determination of volatile-matter content — Part 1: Hot-mill method and oven method*

ISO 248-2, *Rubber, raw — Determination of volatile-matter content — Part 2: Thermogravimetric methods using an automatic analyser with an infrared drying unit*

ISO 289-1, *Rubber, unvulcanized — Determinations using a shearing-disc viscometer — Part 1: Determination of Mooney viscosity*

ISO 1795, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

ISO 2393, *Rubber test mixes — Preparation, mixing and vulcanization — Equipment and procedures*

ISO 3417, *Rubber — Measurement of vulcanization characteristics with the oscillating disc curemeter*

ISO 6502, *Rubber — Guide to the use of curemeters*

ISO 11235, *Rubber compounding ingredients — Sulfenamide accelerators — Test methods*

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

3 Sampling and further preparative procedures

3.1 Selection of the sample from the lot shall be in accordance with ISO 1795.

3.2 Take a laboratory sample of approximately 1,5 kg by the method described in ISO 1795.

3.3 Prepare test samples in accordance with ISO 1795.

4 Physical and chemical tests on raw rubber

4.1 Mooney viscosity

Prepare a test sample in accordance with the preferred procedure in ISO 1795, i.e. without milling.

If massing is deemed necessary, use a mill with its roll surfaces maintained at a temperature of 35 °C ± 5 °C and record this fact in the test report.

Determine the Mooney viscosity in accordance with ISO 289-1. Record the result as ML(1 + 4) at 100 °C.

4.2 Volatile matter

Determine the volatile-matter content by the hot-mill method or by the oven method as specified in ISO 248-1 or by the method specified in ISO 248-2.

4.3 Ash

Determine the ash in accordance with ISO 247.

5 Preparation of test mixes for evaluation

5.1 Standard test formulation

The standard test formulation is given in Table 1.

The materials used shall be national or international standard reference materials. If no standard reference material is available, the materials to be used shall be agreed between the interested parties.

5.2 Procedure

5.2.1 Equipment and procedure

Equipment and procedure for the preparation, mixing, and vulcanization shall be in accordance with ISO 2393.

5.2.2 Mixing procedure

5.2.2.1 General

Two alternative mixing procedures are specified, but in accordance with ISO 2393, the laboratory internal mixer procedure is preferred:

— Method A: Mixing with a laboratory mill;

— Method B: Single-stage mixing using a laboratory internal mixer — the preferred method.

Table 1 — Standard test formulation for evaluation of masterbatches of styrene-butadiene rubbers

Material	Parts by mass
Masterbatch	$100 + x^{a} + y^{b}$
Zinc oxide	3,00
Sulfur	1,75
Stearic acid	1,50
TBBS [c]	1,25
Total	$107{,}50 + x + y$

[a] x is the number of parts of carbon black to 100 parts of rubber in the masterbatch.

[b] y is the number of parts of oil to 100 parts of rubber in the masterbatch.

[c] *N*-tert-butyl-benzothiazole-2-sulfenamide. This shall be supplied in powder form having an initial insoluble-matter content, determined in accordance with ISO 11235, of less than 0,3 %. The material shall be stored at room temperature in a closed container and the insoluble matter shall be checked every 6 months. If this is found to exceed 0,75 %, the TBBS shall be discarded or recrystallized.

5.2.2.2 Method A — Mixing with a laboratory mill

The standard laboratory mill batch mass factor shall be selected to the nearest 0,5 to give as large a total mass as possible that does not exceed 525 g. The surface temperature of the rolls shall be maintained at 50 °C ± 5 °C throughout the mixing.

A good rolling bank at the nip of the rolls shall be maintained during mixing. If this is not obtained with the nip settings specified hereunder, small adjustments to the mill openings may be necessary.

	Duration (min)	**Cumulative time** (min)
a) Band the masterbatch with the mill opening set at 1,4 mm.	2,0	2,0
b) Add the sulfur slowly and evenly across the masterbatch.	2,0	4,0
c) Add the stearic acid. Make one 3/4 cut from each side.	2,0	6,0
d) Add the zinc oxide and the TBBS.	3,0	9,0
e) Make three 3/4 cuts from each side.	2,0	11,0
f) Cut the batch from the mill. Set the mill opening to 0,8 mm and pass the rolled batch endwise between the rolls six times.	2,0	13,0
Total time	**13,0**	**13,0**

g) Sheet the batch to approximately 6 mm and determine the mass of the batch (see ISO 2393). If the mass of the batch differs from the theoretical value by more than $^{+\,0,5}_{-\,1,5}$ %, discard the batch and re-mix.

h) Remove sufficient material for curemeter testing.

i) Sheet the batch to approximately 2,2 mm for preparing test sheets or to the appropriate thickness for preparing ISO ring specimens in accordance with ISO 37.

j) Leave the batch for 2 h to 24 h after mixing, if possible at standard temperature and humidity as defined in ISO 23529.

5.2.2.3 Method B — Single stage mixing using a laboratory internal mixer

For laboratory internal mixers having nominal capacities of 65 cm^3 to about 2 000 cm^3, the batch mass shall be equal to the nominal mixer capacity, in cubic centimetres, multiplied by the density of the compound. For each batch mixed, the laboratory internal mixer conditions shall be the same during the preparation of a series of identical mixes. At the beginning of each series of test mixes, a machine-conditioning batch shall be mixed using the same formulation as the mixes under test. The laboratory internal mixer shall be allowed to cool down to 60 °C between the end of one test batch and the start of the next. The temperature control conditions shall not be altered during the mixing of a series of test batches.

The mixing technique shall be such as to obtain a good dispersion of all the ingredients.

The temperature of the batch discharged on completion of mixing shall not exceed 120 °C. If necessary, adjust the batch mass or the mixer starting temperature so that this condition is met

In the following procedure, compounding materials other than masterbatch, may be added to the batch more precisely and with greater ease if they are previously blended together in the proportions required by the formulation. Such blends may be made using one of the following:

— a mortar and pestle;

— a double-cone mixer (mix for 10 min with the intensifier bar turning);

— a blender (mix for five periods of 3 s each, scraping the inside of the blender to dislodge material stuck to the sides after each 3 s period) (a “Waring”-type blender has been found suitable for this method).

CAUTION — If the mixing periods are longer than 3 s, the stearic acid may melt, thus preventing good dispersion.

NOTE The following is a general mixing procedure for the laboratory internal mixer.

	Duration (min)	**Cumulative time** (min)
a) Load the mixing chamber with the masterbatch, lower the ram and start the timer.		
b) Masticate the masterbatch.	0,5	0,5
c) Raise the ram and add the pre-blended zinc oxide, sulfur, stearic acid and TBBS. Sweep in any powder round the mouth of the mixing chamber, taking care to avoid any losses. Lower the ram.	0,5	1,0
d) Allow the batch to mix.	5,0	6,0
Total time	**6,0**	**6,0**

e) Turn off the rotors, raise the ram, open the mixing chamber and discharge the batch. Record the maximum batch temperature indicated, if desired.

f) Pass the batch through a laboratory mill set at 50 °C ± 5 °C, once with the mill opening set at 0,5 mm then twice with the mill opening set at 3 mm.

g) Check-weigh the batch and record the mass. If it differs from the theoretical value by more than $^{+0,5}_{-1,5}$ %, discard the batch.

h) Leave the batch for 2 h to 24 h after mixing and prior to vulcanizing, if possible at standard temperature and humidity as defined in ISO 23529.

For a laboratory internal mixer having a nominal mixing capacity of 65 cm^3, a batch mass corresponding to 0,47 times the formulation mass (i.e. 0,47 × 156,75 = 73,67 g) has been found to be suitable.

Prepare the masterbatch by passing it through a laboratory mill once with the roll temperature set at 50 °C ± 5 °C and with an opening that will give an approximately 5 mm thick sheet. Cut into strips approximately 25 mm wide.

Mix with the head temperature of the MIM maintained at 60 °C ± 3 °C and the rotor speed at 6,3 rad/s to 6,6 rad/s (60 r/min to 63 r/min).

For a laboratory internal mixer having a nominal capacity of 1170 cm^3 ± 40 cm^3, a batch mass corresponding to (8,5 × 156,75 g = 1 332 g) has been found to be suitable.

The speed of the fast rotor shall be set at 7 rad/s to 8 rad/s (67 rpm to 87 rpm).

6 Evaluation of vulcanization characteristics by a curemeter test

WARNING — Formation of nitrosamines is possible during the cure.

6.1 Using an oscillating-disc curemeter

Measure the following standard test parameters:

M_L, M_H at defined time, t_{s1}, $t'_c(50)$ and $t'_c(90)$

in accordance with ISO 3417, using the following test conditions:

— oscillation frequency: 1,7 Hz (100 cycles per minute);

— amplitude of oscillation: 1° of arc;

— selectivity: to be chosen to give at least 75 % of full-scale deflection at M_H;

NOTE With some rubbers, 75 % may not be attainable.

— die temperature: 160 °C ± 0,3 °C;

— pre-heat time: none.

6.2 Using a rotorless curemeter

Measure the following standard test parameters:

F_L, F_{max} at defined time, t_{s1}, $t'_c(50)$ and $t'_c(90)$

in accordance with ISO 6502, using the following test conditions:

— oscillation frequency: 1,7 Hz (100 cycles per minute);

— amplitude of oscillation: 0,5° of arc;

— selectivity: to be chosen to give at least 75 % of full-scale deflection at F_{max};

NOTE With some rubbers, 75 % may not be attainable.

— die temperature: 160 °C ± 0,3 °C;

— pre-heat time: none.

7 Evaluation of tensile stress-strain properties of vulcanized test mixes

WARNING — Formation of nitrosamines is possible during the cure.

Vulcanize sheets at 145 °C for 25 min, 35 min, and 50 min. Alternatively, vulcanize sheets at 150 °C for 20 min, 30 min, and 50 min. The three periods of cure shall be chosen to cover the undercure, optimum cure, and overcure of the material under test.

Condition the vulcanized sheets for 16 h to 96 h, if possible at standard temperature and humidity as defined in ISO 23529.

Measure the stress-strain properties in accordance with ISO 37.

8 Precision

See Annex A.

9 Test report

The test report shall include the following information:

a) a reference to this International Standard (i.e. ISO 4659:2014);

b) all details necessary for the identification of the sample;

c) the time and temperature used for the Mooney viscosity determination, and whether a massing procedure was used (and, if so, the parameters);

d) the method used for the volatile-matter content determination (ISO 248-1, mill or oven, or ISO 248-2);

e) the method used for the ash determination (method A or B of ISO 247);

f) the reference materials used;

g) the mixing procedure used;

h) the size (nominal mixer capacity) of the mixer used for Method B;

i) the conditioning times used in 5.2.2.2 or 5.2.2.3;

j) for Clause 6:

— the type of curemeter used,

— the time for M_H or F_{max};

k) any operation not included in this International Standard or in the International Standards to which reference is made, as well as any operation regarded as optional;

l) the results and the units in which they have been expressed;

m) the dates of the tests.

Annex A
(informative)

Precision

A.1 General

The precision results for the internal mixer procedure are based on data from ASTM D 3186. The repeatability and reproducibility have been calculated in accordance with ISO/TR 9272.

A.2 Precision details

A.2.1 Mill mixing

The type 2 (interlaboratory) precision was determined. Two different types of SBR were used. These were tested in four laboratories during two different weeks. For each type of SBR, the number of replicates was five.

A.2.2 Laboratory internal mixer mixing

A laboratory internal mixer of nominal capacity 65 cm^3 was used.

The type 2 (interlaboratory) precision was determined. Two different types of SBR were used. These were tested in six laboratories on two different days.

A.3 Precision results

The calculated repeatability and reproducibility values are given in Tables A.1 and A.2.

The symbols used in Tables A.1 and A.2 are defined as follows:

r is the repeatability, in measurement units. This is the value below which the absolute difference between two "within-laboratory" test results can be expected to lie with a specified probability;

(*r*) is the repeatability, in percent (relative).

The two test results are obtained with the same method on nominally identical test materials under the same conditions (same operator, apparatus, and laboratory) and within a specified time period. Unless stated otherwise, the probability is 95 %.

R is the reproducibility, in measurement units. This is the value below which the absolute difference between two "between-laboratory" test results can be expected to lie with a specified probability.

(*R*) is the reproducibility, in percent (relative).

The two test results are obtained with the same method on nominally identical test materials under different conditions (different operators, apparatus, and laboratories) and within a specified time period. Unless stated otherwise, the probability is 95 %.

s_r is the repeatability standard deviation, in measurement units.

s_R is the reproducibility standard deviation, in measurement units.

Table A.1 — Mill mixing procedure — Type 2 precision for various parameters

Property	Units	Range of values[a]	Within laboratory			Between laboratories		
			s_r	r	(r)	s_R	R	(R)
M_L	dN·m	5,3 to 7,5	0,126	0,357	5,581	0,588	1,665	25,497
M_H	dN·m	25,6 to 38,2	0,202	0,572	1,745	0,781	2,211	7,050
t_{s1}	min	5,3 to 6,7	0,168	0,474	7,934	0,407	1,153	19,180
$t'_c(50)$	min	9,4 to 13,2	0,193	0,547	4,747	0,527	1,490	12,940
$t'_c(90)$	min	15,0 to 18,5	0,162	0,459	2,656	0,964	2,728	15,876

[a] Measured at 160 °C, 1,7 Hz, 1° of arc; midpoint of range used for (r) and (R) calculations.

Table A.2 — Laboratory internal mixer mixing procedure — Type 2 precision for various parameters

Property	Units	Range of values[a]	Within laboratory			Between laboratories		
			s_r	r	(r)	s_R	R	(R)
M_H	dN·m	6,4 to 8,2	0,17	0,48	6,6	0,92	2,60	35,6
t_{s1}	dN·m	24,2 to 42,7	0,69	1,95	5,8	2,69	7,61	22,7
$t'_c(50)$	min	5,8 to 6,8	0,19	0,54	8,6	0,89	2,52	40,0
$t'_c(90)$	min	9,3 to 9,9	0,28	0,79	8,2	0,73	2,07	21,6
M_H	min	15,0 to 15,1	0,40	1,13	7,5	0,86	2,43	16,2

[a] Measured at 160 °C, 1,7 Hz, 1° of arc; midpoint of range used for (r) and (R) calculations.

Bibliography

[1] ISO/TR 9272, *Rubber and rubber products — Determination of precision for test method standards*

[2] ASTM D 3186, *Standard Test Methods for Rubber — Evaluation of SBR (Styrene-Butadiene Rubber) Mixed with Carbon Black or Carbon Black and Oil*

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