

INTERNATIONAL STANDARD

ISO
4659

Fifth edition
2003-01-15

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*

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Reference number
ISO 4659:2003(E)

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Published in Switzerland

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 4659 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 fifth edition cancels and replaces the fourth edition (ISO 4659:1997), which has been technically revised.

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 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

- 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 referenced documents are indispensable for the application 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 37:1994, *Rubber, vulcanized or thermoplastic — Determination of tensile stress-strain properties*

ISO 247:1990, *Rubber — Determination of ash*

ISO 248:1991, *Rubbers, raw — Determination of volatile-matter content*

ISO 289-1:1994, *Rubber, unvulcanized — Determinations using a shearing-disc viscometer — Part 1: Determination of Mooney viscosity*

ISO 471:1995, *Rubber — Temperatures, humidities and times for conditioning and testing*

ISO 1795:2000, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

ISO 2393:1994, *Rubber test mixes — Preparation, mixing and vulcanization — Equipment and procedures*

ISO 3417:1991, *Rubber — Measurement of vulcanization characteristics with the oscillating disc curemeter*

ISO 6502:1999, *Rubber — Guide to the use of curemeters*

ISO/TR 9272:1986, *Rubber and rubber products — Determination of precision for test method standards*

ISO 11235:1999, *Rubber compounding ingredients — Sulfenamide accelerators — Test methods*

3 Sampling and sample preparation

3.1 A laboratory sample of approximately 1,5 kg shall be taken by the method described in ISO 1795.

3.2 Preparation of the test portions shall be in accordance with ISO 1795.

4 Physical and chemical tests on raw rubber

4.1 Mooney viscosity

Determine the Mooney viscosity in accordance with ISO 289-1 on a test portion prepared as indicated in ISO 1795 (without massing).

If massing is necessary, use a mill with its roll surfaces maintained at a temperature of $35^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and record this fact in the test report.

Record the result as $\text{ML}(1 + 4)$ at 100°C .

4.2 Volatile matter

Determine the volatile-matter content in accordance with ISO 248.

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:

- Method A: Mixing with a laboratory mill;
- Method B: Mixing with a miniature internal mixer (MIM).

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 $50\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ 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	Cumulative time
	(min)	(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
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 $^{+0,5}_{-1,5}\text{ %}$, 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 471.		

5.2.2.3 Method B — Mixing with a miniature internal mixer (MIM)

Mix with the head temperature of the MIM maintained at $60\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ and the rotor speed at 6,3 rad/s to 6,6 rad/s (60 r/min to 63 r/min).

Prepare the masterbatch by passing it through a laboratory mill once with the roll temperature set at $50\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ and with an opening that will give an approximately 5 mm thick sheet. Cut into strips approximately 25 mm wide.

	Duration (min)	Cumulative time (min)
a) Load the mixing chamber with the masterbatch strips, 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.	8,0	9,0
	Total time	9,0
		9,0
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 $50\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$, 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 $^{+0,5}_{-1,5}\text{ %}$, 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 471.		

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: $160\text{ }^{\circ}\text{C} \pm 0,3\text{ }^{\circ}\text{C}$

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: $160\text{ }^{\circ}\text{C} \pm 0,3\text{ }^{\circ}\text{C}$

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 $145\text{ }^{\circ}\text{C}$ for 25 min, 35 min and 50 min. Alternatively, vulcanize sheets at $150\text{ }^{\circ}\text{C}$ 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 471.

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

8 Precision

8.1 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.

8.2 Precision details

8.2.1 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.

8.2.2 MIM mixing

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

8.3 Precision results

The calculated repeatability and reproducibility values are given in Tables 2 and 3.

The symbols used in Tables 2 and 3 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 may be expected to lie, with a specified probability.

(r) is the repeatability, in per cent (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 may 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 %.

Table 2 — 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
s_r is the repeatability standard deviation, in measurement units;								
s_R is the reproducibility standard deviation, in measurement units.								
^a Measured at 160 °C, 1,7 Hz, 1° of arc; midpoint of range used for (r) and (R) calculations.								

Table 3 — MIM 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	6,4 to 8,2	0,17	0,48	6,6	0,92	2,60	35,6
M_H	dN·m	24,2 to 42,7	0,69	1,95	5,8	2,69	7,61	22,7
t_{s1}	min	5,8 to 6,8	0,19	0,54	8,6	0,89	2,52	40,0
$t'_c(50)$	min	9,3 to 9,9	0,28	0,79	8,2	0,73	2,07	21,6
$t'_c(90)$	min	15,0 to 15,1	0,40	1,13	7,5	0,86	2,43	16,2
s_r is the repeatability standard deviation, in measurement units; s_R is the reproducibility standard deviation, in measurement units.								
^a Measured at 160 °C, 1,7 Hz, 1° of arc; midpoint of range used for (r) and (R) calculations.								

9 Test report

The test report shall include the following information:

- a) a reference to this International Standard;
- 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 (mill or oven);
- e) the method used for the ash determination (method A or B of ISO 247:1990);
- f) the reference materials used;
- g) the mixing procedure used, i.e. method A (5.2.2.2) or method B (5.2.2.3);
- h) the conditioning times used in 5.2.2.2 or 5.2.2.3;
- i) for clause 6:
 - the type of curemeter used,
 - the time for M_H or F_{max} ;
- j) 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;
- k) the results and the units in which they have been expressed;
- l) the dates of the tests.