INTERNATIONAL STANDARD

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Rubber, butadiene (BR) — Solution-polymerized types — Evaluation procedures

Caoutchouc butadiène (BR) — Types polymérisés en solution — Méthode d'évaluation

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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.

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.

International Standard ISO 2476 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 fourth edition cancels and replaces the third edition (ISO 2476:1988), which has been technically revised.

Annex A of this International Standard is for information only.

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Rubber, butadiene (BR) — Solution-polymerized types — Evaluation procedures

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 solution-polymerized butadiene rubbers (BR), including oil-extended types (OEBR), and the tensile stress-strain properties of vulcanized mixes.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

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 1795:1992, *Rubber, raw, natural and 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 6502:1991, *Rubber — Measurement of vulcanization characteristics with rotorless curemeters.*

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

3 Sampling and preparation of test portion

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 portion 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 (preferably without milling). If milling is necessary, maintain the mill roll surface temperature at 35 °C ± 5 °C.

Record the result as 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 of butadiene rubbers

5.1 Standard test formulations

Two standard test formulations are given in table 1.

The materials used shall be national or international standard reference materials (or, if no standard reference material is available, as agreed by the interested parties).

Table 1 — Standard test formulations

Material	Parts by mass	
	Non-oil-extended	Oil-extended
Butadiene rubber	100,00	100,00 [1]
Zinc oxide	3,00	3,00
Current industry reference black	60,00	60,00
Stearic acid	2,00	2,00
ASTM 103 oil [2]	15,00	—
Sulfur	1,50	1,50
TBBS [3]	0,90	0,90
Total	182,40	167,40
Calculated density, g/cm³	1,11	1,14 to 1,16 [4]

1) 100 parts of oil-extended rubber means 100 parts of the rubber including the extender oil.

2) This oil, density = 0,92 g/cm³, is available in 3,8 litre and 19 litre quantities from Sun Oil, Industrial products Dept., 1608 Walnut Street, Philadelphia, PA 19103, USA. Alternative oils, such as Circosol 4240, R.E. Caroll IRM 43 or Shellflex 724, are suitable but may give slightly different results.

ASTM 103 oil has the following characteristics:

Kinematic viscosity at 100 °C: 16,8 mm²/s ± 1,2 mm²/s
Viscosity gravity constant: 0,889 ± 0,002

The viscosity gravity constant (VGC) is calculated from the Saybolt universal viscosity at 37,8 °C and the relative density (specific gravity) at 15,5/15,5 °C. Use the following equation to calculate the VGC from the measured properties:

$$VGC = \frac{10d - 1{,}075\ 2 \log_{10}(v - 38)}{10 - \log_{10}(v - 38)}$$

where

d is the relative density (specific gravity) at 15,5/15,5 °C;

v is the Saybolt universal viscosity at 37,8 °C.

3) *N-tert*-butylbenzothiazole-2-sulfenamide. This shall be obtained in powder form with an initial methanol-insoluble-matter content of less than 0,3 %. The material shall be stored at room temperature in a closed container and the methanol-insoluble matter shall be checked every 6 months. If this is found to exceed 0,75 %, the material shall be discarded or recrystallized.

4) Based on 37,5 % oil-extended BR.

5.2 Procedure

5.2.1 General

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

5.2.2 Mixing procedures

Four mixing procedures are specified:

Method A — Internal mixer for initial and final mixing

Method B — Internal mixer for initial and mill for final mixing

Methods C1 and C2 — Mill mixing.

NOTES

1 These procedures may give different results.

2 The mill handling of solution-polymerized butadiene rubbers is more difficult than for other rubbers, and mixing is best accomplished by using an internal mixer. With some types of butadiene rubber, it is not possible to get a satisfactory mix using the mill mixing procedure.

5.2.2.1 Method A — Internal mixer for initial and final mixing

5.2.2.1.1 Stage 1 — Initial mixing procedure

		Duration (min)	Cumulative time (min)
a)	Adjust the temperature (50 °C ± 5 °C is recommended), rotor speed and ram pressure of the internal mixer to achieve the conditions outlined in 5.2.2.1.1e). Close the discharge gate, start the motor and raise the ram.	—	—
b)	Load one-half of the rubber, the zinc oxide, the carbon black, the oil (omit from oil-extended BR), the stearic acid and the balance of the rubber. Lower the ram.	0,5	0,5
c)	Allow the batch to mix.	3,0	3,5
d)	Raise the ram and clean the mixer throat and the top of the ram. Lower the ram.	0,5	4,0
e)	Discharge the batch at a temperature of 170 °C or after a total time of 6 min, whichever occurs first.	2,0	6,0

f) Immediately pass the batch three times through a laboratory mill with a mill opening of 5,0 mm and a temperature of 50 °C ± 5 °C. Check-weigh the batch (see ISO 2393). If the mass of the batch differs from the theoretical value by more than + 0,5 % or – 1,5 %, discard the batch and re-mix.

5.2.2.1.2 Stage 2 — Final mixing procedure

		Duration (min)	Cumulative time (min)
a)	Cool the internal mixer to a temperature of 40 °C ± 5 °C with full cooling water on the rotors. Start the motor and raise the ram.	—	—
b)	Leave the cooling water on and the steam off. Roll all the sulfur and the TBBS into one-half of the masterbatch and load into the mixer. Add the remaining portion of the masterbatch. Lower the ram.	0,5	0,5
c)	Allow the batch to mix until a temperature of 110 °C or a total time of 3 min is reached, whichever occurs first.	2,5	3,0

d) Immediately pass the batch through a laboratory mill with a mill opening set at 0,8 mm and at a temperature of 50 °C ± 5 °C.

e) Pass the rolled batch endwise through the rolls six times.

f) Sheet the batch to approximately 6 mm. Check-weigh the batch (see ISO 2393). If the mass of the batch differs from the theoretical value by more than + 0,5 % or – 1,5 %, discard the batch and re-mix. Remove sufficient material for cure-meter testing.

g) 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.

5.2.2.2 Method B — Internal mixer for initial and mill for final mixing

5.2.2.2.1 Stage 1 — Initial mixing procedure

Proceed in accordance with 5.2.2.1.1.

5.2.2.2.2 Stage 2 — Final mill mixing procedure

Cut 720,0 g (in the case of non-oil-extended rubber) or 660,0 g (in the case of oil-extended rubber containing 37,5 % oil) from the masterbatch. Weigh out four times the formula mass of the curatives (i.e. 6,0 g of sulfur, 3,6 g of TBBS, etc.).

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, make small adjustments to the mill openings.

	Duration (min)	Cumulative time (min)
a) Set and maintain the mill roll temperature at 35 °C ± 5 °C and the mill opening at 1,5 mm. Band the masterbatch around the front roll.	1,0	1,0
b) Add the sulfur and the TBBS slowly to the batch. Sweep up any material which has fallen into the mill pan and add it to the mix.	1,0	2,0
c) Make six 3/4 cuts from each side.	1,5	3,5
d) Cut the batch from the mill. Set the mill opening to 0,8 mm and pass the rolled batch endwise through the rolls six times.	1,5	5,0

e) Sheet the batch to approximately 6 mm. Check-weigh the batch (see ISO 2393). If the mass of the batch differs from the theoretical value by more than + 0,5 % or −1,5 %, discard the batch and re-mix. Remove sufficient material for curemeter testing.

f) 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.

5.2.2.3 Methods C1 and C2 — Mill mixing procedures

Solution-polymerized butadiene rubbers are difficult to process on a mill. Methods A and B, which give better dispersion of the ingredients, are preferred if an internal mixer is available. If this is not the case, two mill mixing procedures may be used:

— method C1, which may be used for solution-polymerized butadiene rubbers, whether oil-extended or not;

— method C2, which is limited to non-oil-extended rubbers but gives easier mixing and leads to better dispersion of the ingredients.

Methods C1 and C2 will not necessarily give identical results for non-oil-extended solution-polymerized butadiene rubbers. In laboratory cross-checks or in a series of evaluations, the same procedure shall therefore be used in all cases.

5.2.2.3.1 Method C1

The standard laboratory batch mass, in grams, shall be based on three times the formulation mass (i.e. $3 \times 182{,}40$ g $= 547{,}20$ g or $3 \times 167{,}40$ g $= 502{,}20$ g). Adjust the mill roll cooling conditions to maintain a temperature of 35 °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, make small adjustments to the mill openings.

	Duration (min)	Cumulative time (min)
a) Band the rubber with the mill opening set at 1,3 mm.	1,0	1,0
NOTE 3 Non-oil-extended rubbers may require longer milling to achieve a good band.		
b) Add the zinc oxide and the stearic acid evenly across the rolls. Make two 3/4 cuts from each side	2,0	3,0
c) Add the carbon black evenly across the rolls at a uniform rate. When about half the black has been incorporated, open the rolls to 1,8 mm and then add the remainder of the black. Make two 3/4 cuts from each side, allowing 30 s between each cut. Be certain to add the black that has dropped into the mill pan.	15,0 to 18,0	18,0 to 21,0
d) Add the oil (omit from oil-extended BR) very slowly drop by drop.	8,0 to 10,0	26,0 to 31,0
e) Add the sulfur and the TBBS. Sweep up any material which has fallen into the mill pan and add it to the mix.	2,0	28,0 to 33,0

f)	Make six successive 3/4 cuts from each side.	2,0	30,0 to 35,0
g)	Cut the batch from the mill. Set the mill opening to 0,8 mm and pass the rolled batch endwise through the rolls six times.	2,0	32,0 to 37,0
h)	Sheet the batch to approximately 6 mm. Check-weigh the batch (see ISO 2393). If the mass of the batch differs from the theoretical value by more than + 0,5 % or − 1,5 %, discard the batch and re-mix. Remove sufficient material for cure-meter 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.		

5.2.2.3.2 Method C2

The standard laboratory batch mass, in grams, shall be based on two times the formulation mass (i.e. 2 × 182,40 g = 364,80 g). Adjust the mill roll cooling conditions to maintain a temperature of 35 °C ± 5 °C throughout the mixing. Add the ingredients to the batch slowly and evenly across the rolls. Do not cut the batch before all the ingredients have been incorporated.

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, make small adjustments to the mill openings.

		Duration	Cumulative time
		(min)	(min)
a)	Pass the rubber twice through the rolls with the mill opening set at 0,45 mm ± 0,01 mm and then band it. Make two successive 3/4 cuts from each side.	2,0	2,0
b)	Add the stearic acid and the zinc oxide. Make three successive 3/4 cuts from each side.	2,0	4,0
c)	Add successively half of the oil and half of the carbon black. Make seven successive 3/4 cuts from each side.	12,0	16,0
d)	Add successively the remainder of the oil and the remainder of the carbon black. Add any black that has dropped into the mill pan. Make seven 3/4 cuts from each side.	12,0	28,0
e)	Add the TBBS and the sulfur. Make six 3/4 cuts from each side.	4,0	32,0
f)	Cut the batch from the mill. Set the mill opening to 0,7 mm to 0,8 mm and pass the rolled batch endwise through the rolls six times.	3,0	35,0
g)	Sheet the batch to approximately 6 mm and check-weigh the batch (see ISO 2393). If the mass of the batch differs from the theoretical value by more than + 0,5 % or − 1,5 %, discard the batch and re-mix. Remove sufficient material for curemeter testing.		
h)	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.		

6 Conditioning of batches

Condition all batches produced by method A, B, C1 or C2 for 2 h to 24 h after mixing and prior to vulcanizing, if possible at standard temperature and humidity as defined in ISO 471.

7 Evaluation of vulcanization characteristics

7.1 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° arc

selectivity: To be chosen to give at least 75 % of full-scale deflection.

NOTE 4 With some rubbers, 75 % may not be attainable.

die temperature: 160 °C ± 0,3 °C

pre-heat time: None

7.2 Using a rotorless curemeter

Measure the following standard test parameters:

F_L, F_{max} at defined time, t_{s1}, $t'_{0,50}$ and $t'_{0,90}$

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

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

amplitude of oscillation: 0,5° arc

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

NOTE 5 With some rubbers, 75 % may not be attainable.

die temperature: 160 °C ± 0,3 °C

pre-heat time: None

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

Vulcanize sheets at 145 °C for 25 min, 35 min and 50 min or, alternatively, 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 471.

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

9 Precision

9.1 General

The precision calculations to express repeatability and reproducibility were performed in accordance with ISO/TR 9272. Consult this for precision concepts and nomenclature. Annex A of this International Standard gives guidance on the use of repeatability and reproducibility.

9.2 Interlaboratory test programme

9.2.1 An interlaboratory test programme was organized in 1987. Formulations containing two types of BR were selected and mixes were prepared in each of the 17 laboratories that participated in the programme, on each of two days approximately one week apart. Formula 1 contained a non-oil-extended BR, while formula 2 contained an oil-extended BR.

Only method C1 of this International Standard (mill mixing) was used for preparing the mixes.

The mixes were prepared from special samples of all the necessary materials, sent to each laboratory prior to the actual testing. For each material, the samples were drawn from a uniform and homogeneous lot. Stress-strain tests were conducted on cured sheets of each of the mixes or compounds as specified by the test programme.

9.2.2 Determinations of modulus (stress at 300 %), tensile strength and percent elongation were made, taking as the result the median of five individual determinations, as specified in ISO 37. All 17 laboratories performed the test using dumb-bell test pieces. Five of the laboratories also performed the test using ring test pieces. The precision thus evaluated is a type 2 precision, and the time period for repeatability and reproducibility is on a scale of days.

9.3 Precision results

9.3.1 The precision results are given in table 2 for dumb-bell test pieces and in table 3 for ring test pieces.

The symbols used in tables 2 and 3 are defined as follows:

r = 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) = repeatability, in percent (relative).

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

R = 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) = reproducibility, in percent (relative).

The two test results are obtained with the same method on nominally identical test material under different conditions (different laboratories, operators and

apparatus) and within a specified time period; unless stated otherwise, the probability is 95 %.

9.3.2 It shall be borne in mind that these precision results apply to the mill mixing procedure of ISO 2476:1988, *Rubber, butadiene (BR) — Solution-polymerized types — Evaluation procedure*, only (method C1 of this International Standard)

NOTE 6 For the general procedure for using precision results, and their interpretation, see ISO/TR 9272.

10 Test report

The test report shall include the following:

a) a reference to this International Standard;

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

c) the standard test formula used;

d) the reference materials used;

e) the method used for the volatile-matter determination (mill or oven);

f) the mixing procedure used in 5.2.2;

g) the vulcanizing temperature and times used in clause 8;

h) any unusual features noted during the determination;

i) 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;

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

k) the date of the test.

Table 2 — Type 2 precision for dumb-bell test pieces

Formulation	Average value	Within lab		Between labs	
		r	(r)	R	(R)
1) Modulus (300 %), MPa					
Formula 1	10,9	1,37	12,6	2,61	23,8
Formula 2	13,0	1,66	12,8	2,90	22,3
2) Tensile strength, MPa					
Formula 1	16,5	1,23	7,47	3,13	18,9
Formula 2	17,7	1,82	10,3	3,93	22,3
3) Percent elongation					
Formula 1	367	35,1	9,55	76,6	20,8
Formula 2	424	57,8	13,6	127	29,9

Table 3 — Type 2 precision for ring test pieces

Formulation	Average value	Within lab		Between labs	
		r	(r)	R	(R)
1) Modulus (300 %), MPa					
Formula 1	10,3	0,82	7,98	4,13	40,2
Formula 2	11,9	0,82	6,93	4,73	39,7
2) Tensile strength, MPa					
Formula 1	14,4	0,98	6,81	3,03	21,1
Formula 2	15,8	1,40	8,88	4,36	27,6
3) Percent elongation					
Formula 1	362	62,1	17,2	62,1	17,2
Formula 2	433	51,7	11,9	51,7	11,9