INTERNATIONAL STANDARD

ISO 2322

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Styrene-butadiene rubber (SBR) — Emulsion- and solution-polymerized types — Evaluation procedures

Caoutchouc butadiène-styrène (SBR) — Types polymérisés en émulsion et en solution — Méthode d'évaluation

Reference number
ISO 2322:1996(E)

Foreword

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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 2322 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 2322:1985) which has been technically revised.

Annexes A, B and C of this International Standard are for information only.

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Styrene-butadiene rubber (SBR) — Emulsion- and solution-polymerized types — Evaluation procedures

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 emulsion- and solution-polymerized styrene-butadiene rubbers (SBR), including oil-extended rubbers.

It applies to those rubbers listed in table 1 which are normally used in vulcanized form.

Table 1 — Types of raw styrene-butadiene rubber

Rubber (oil-extended or non-oil-extended)	Styrene		
	Type of copolymer	Total content % (*m/m*)	Block content % (*m/m*)
Series A			
1) Emulsion SBR	random	< 50	0
2) Solution SBR	random	< 50	0
3) Solution SBR	partial block	< 50	< 30
Series B			
1) Emulsion SBR	random	> 50	0
2) Solution SBR	random	> 50	0
3) Solution SBR	partial block	< 50	> 30

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 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions.*

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.*

ISO 6502:—[1)], *Rubber — Introduction and guide to the use of curemeters.*

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

ISO 11235:—[2)], *Rubber compounding ingredients — Sulfenamide-type accelerators — Methods of test.*

ASTM D 412-92, *Test methods for vulcanized rubber and thermoplastic rubbers and thermoplastic elastomers — Tension.*

ASTM D 1646-95a, *Test methods for rubber — Viscosity, stress relaxation, and pre-vulcanization characteristics (Mooney viscometer).*

ASTM D 2084-93, *Test method for rubber property — Vulcanization characteristics using oscillating disk cure meter.*

ASTM D 3185-88(1994), *Test methods for rubber — Evaluation of SBR (styrene-butadiene rubber) including mixtures with oil.*

3 Sampling and further preparative procedures

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

3.2 Prepare test portions 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 in accordance with the preferred method of ISO 1795 (unmilled test portion).

Record the result as ML(1 + 4) at 100 °C.

NOTES

1 If ML(1 + 4) at 100 °C exceeds 100 MU, the small rotor may be used and the result reported as MS(1 + 4) at 100 °C.

2 Alternatively, the Mooney viscosity may be determined on a test portion prepared by the mill massing procedure of ISO 1795. This method will give poorer reproducibility, however, and the results may be different.

4.2 Volatile matter

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

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1) To be published. (Revision of ISO 6502:1991)

2) To be published.

4.3 Ash

Determine the ash in accordance with method A or method B of ISO 247:1990.

5 Preparation of the test mixes

5.1 Standard test formulations

The standard test formulations are given in table 2.

The materials shall be national or international standard reference materials.

If no standard reference material is available, the materials to be used shall be agreed by the parties concerned.

5.2 Alternative formulations for oil-extended types

ASTM D 3185 specifies the test formulations given in table 3 for evaluation of general-purpose, oil-extended SBR, according to the oil content of the rubber. These test formulations may be used as alternatives to the test formulations given in table 2.

5.3 Procedure

5.3.1 Equipment and procedure

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

Two alternative mixing procedures are specified:

Method A — Mill mixing

Method C — Miniature internal mixer mixing

NOTE — A method B using an internal mixer for initial mixing and a mill for final mixing is presented in annex A for information only since insufficient experience has been gained with this method and the absence of information on precision does not allow it to be included as an integral part of the standard.

Table 2 — Test formulations

Material	Parts by mass	
	Series A	Series B
Styrene-butadiene rubber (SBR) (including oil in oil-extended SBR)	100,00	—
Type 1500 SBR[1)]	—	65,00
Series B SBR	—	35,00
Sulfur	1,75	1,75
Stearic acid	1,00	1,00
Current industry reference black[2)]	50,00	35,00
Zinc oxide	3,00	3,00
TBBS[3)]	1,00	1,00
	156,75	141,75

1) SBR 1500 EST, supplied by Enichem Elastomeri, Strada 3, Palazzo B1, 20090 Assago, Milan, Italy, is an example of a suitable product available commercially. This information is given for convenience of users of this International Standard and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

2) Dried for 1 h at 125 °C ± 3 °C and stored in a tightly closed container.

3) *N-tert*-butylbenzothiazole-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 material shall be discarded or recrystallized.

Table 3 — Alternative test formulations for oil-extended types

Formulation No.	Quantity (parts by mass)					
	1B	2B	3B	4B	5B	6B
Parts oil	25	37,5	50	62,5	75	Y[1]
Oil-extended rubber	125,00	137,50	150,00	162,50	175,00	100 + Y
Zinc oxide	3,00	3,00	3,00	3,00	3,00	3,00
Sulfur	1,75	1,75	1,75	1,75	1,75	1,75
Stearic acid	1,00	1,00	1,00	1,00	1,00	1,00
Current industry reference black[2]	62,50	68,75	75,00	81,25	87,50	(100 + Y)/2
TBBS[3]	1,25	1,38	1,50	1,63	1,75	(100 + Y)/100
	194,50	213,38	232,25	251,13	270,00	
Batch factor for mill mix	2,4	2,2	2,0	1,9	1,7	
Batch factor for miniature internal mixer mix						
Cam head	0,37	0,34	0,31	0,29	0,27	
Banbury head	0,328	0,298	0,273	0,252	0,234	

1) Y = parts oil by mass per 100 parts base polymer in oil-extended rubber.

2) Dried for 1 h at 125 °C ± 3 °C and stored in a tightly closed container.

3) *N-tert*-butylbenzothiazole-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 material shall be discarded or recrystallized.

5.3.2 Method A — Mill mixing procedure

The standard laboratory mill batch mass, in grams, shall be based on four times the formulation mass (i.e. 4 × 156,75 g = 627 g or 4 × 141,75 g = 567 g). Maintain the surface temperature of the rolls at 50 °C ± 5 °C. Maintain a good rolling bank at the nip of the rolls during mixing. If this is not obtained with the nip settings specified hereunder, small adjustments to the mill openings may be necessary.

	Series A		Series B	
	Duration	Cumulative time	Duration	Cumulative time
	(min)	(min)	(min)	(min)
a) Homogenize series B rubbers with the mill opening set at 1,1 mm at a temperature of 100 °C ± 5 °C.	—	—	1,0	—
b) Band the rubber with the mill opening set at 1,1 mm and make 3/4 cuts every 30 s from alternate sides.	7,0	7,0	—	—
After banding SBR 1500, add the rubber [homogenized as in 5.3.2 a)] and make 3/4 cuts from both sides every 30 s.	—	—	8,0	9,0
c) Add the sulfur slowly and evenly across the rubber.	2,0	9,0	2,0	11,0
d) Add the stearic acid. Make one 3/4 cut from each side.	2,0	11,0	2,0	13,0
e) Add the carbon black evenly across the mill at a uniform rate. When about half the black has been incorporated, open the mill to 1,4 mm and make one 3/4 cut from each side. Then add the remainder of the carbon black. Be certain to add the black that has dropped into the mill pan. When all the black has been incorporated, open the mill to 1,8 mm and make one 3/4 cut from each side.	12,0	23,0	12,0	25,0

	Series A		Series B	
	Duration	Cumulative time	Duration	Cumulative time
	(min)	(min)	(min)	(min)
f) Add the zinc oxide and the TBBS with the mill opening still at 1,8 mm.	3,0	26,0	3,0	28,0
g) Make three 3/4 cuts from each side.	2,0	28,0	2,0	30,0
h) 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	30,0	2,0	32,0

i) Sheet the batch to an approximate thickness of 6 mm by opening the mill and passing the stock through the mill four times, folding it back on itself each time. 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 %, discard the batch and remix. Remove sufficient material for curemeter testing.

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

k) Condition 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.

5.3.3 Method C — Miniature internal mixer procedure

For a miniature internal mixer having a nominal mixing capacity of 64 cm^3, a batch mass corresponding to 0,47 times the formulation mass (i.e. 0,47 × 156,75 g = 73,67 g) for series A rubbers or to 0,49 times the formulation mass (i.e. 0,49 × 141,75 g = 69,46 g) for series B rubbers has been found to be suitable.

Mix with the head temperature of the miniature internal mixer maintained at 60 °C ± 3 °C and the unloaded-rotor speed at 6,3 rad/s to 6,6 rad/s (60 rpm to 63 rpm).

Prepare the rubber by passing it once through a mill with the temperature set at 50 °C ± 5 °C and an opening of 0,5 mm. Cut the sheet into strips that are 25 mm wide.

NOTE — Compounding materials other than rubber, carbon black and oil may be added to miniature internal mixer batches 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 a mortar and pestle, by mixing for 10 min in a biconical blender with intensifier bar turning, or by mixing in a blender for five 3 s periods and scraping the inside of the blender to dislodge materials stuck to the sides after each 3 s mix. A Waring blender has been found suitable for this method. Caution: if mixed longer than 3 s, the stearic acid may melt and prevent good dispersion.

	Duration	Cumulative time
	(min)	(min)
a) Load the rubber, lower the ram and allow the rubber to be masticated.	1,0	1,0
b) Raise the ram and add the preblended zinc oxide, sulfur, stearic acid and TBBS, taking care to avoid any loss. Then add the carbon black, sweep the orifice and lower the ram.	1,0	2,0
c) Allow the batch to mix.	7,0	9,0

d) Turn off the motor, raise the ram, remove the mixing chamber and discharge the batch. Record the maximum batch temperature. The final temperature of the batch discharged after 9 min shall not exceed 120 °C. If necessary, adjust the batch mass or the head temperature so that this condition is met.

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

f) Determine the batch mass and record. If it differs from the theoretical value by more than 0,5 %, discard the batch.

g) Cut a test piece for testing vulcanization characteristics in accordance with ISO 3417 if required. Condition the specimen for 2 h to 24 h at 23 °C ± 3 °C before testing.

h) If required, sheet the batch to approximately 2,2 mm for preparing test sheets or to the appropriate thickness for preparing ring test pieces in accordance with ISO 37. To obtain the effects of mill direction, pass the folded batch four times between mill rolls set at 50 °C ± 5 °C and the appropriate mill opening. Cool on a flat, dry surface.

i) Condition 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

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
	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}
	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

Vulcanize sheets at 145 °C for three periods selected from a cure series of 15 min, 25 min, 35 min, 50 min and 75 min.

Alternatively, vulcanize sheets at 150 °C for three periods selected from a cure series of 10 min, 15 min, 20 min, 25 min, 30 min, 35 min and 50 min. These conditions will give results different from the ones obtained by the recommended standard vulcanization conditions.

The three periods of cure selected shall cover the undercure, optimum cure and overcure of the rubber under test.

Condition the vulcanized sheets for 16 h to 96 h, at a standard temperature and, if possible, at a standard humidity as defined in ISO 471.

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

NOTE — Method C provides sufficient compounded material for evaluation of the stress-strain properties of one vulcanized sheet.

8 Precision

8.1 Method A — Mill mixing

8.1.1 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 B gives guidance on the use of repeatability and reproducibility.

8.1.2 Precision details

8.1.2.1 An interlaboratory test programme (ITP) was organized in 1986. Two formulations with series A SBRs were selected:

A-1 with an oil-extended SBR, type 1712, and

A-2 with a non-oil-extended SBR, type 1500.

One formulation with a series B SBR was selected:

A-3 with a high-styrene SBR rubber.

Mixes of these formulations were made in each of the 13 laboratories participating in the ITP, on each of two days approximately one week apart. 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.

8.1.2.2 The modulus (stress at 300 %), tensile strength and percent elongation were determined on dumb-bell test pieces in accordance with ISO 37 and taking as the test result the median of five individual test determinations. The precision thus calculated is a type 2 precision, and the time period for repeatability and reproducibility is on a scale of days.

See annex C for comments on the precision results.

8.1.3 Precision results

The precision results are given in table 4. The symbols used in table 4 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 using 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 = 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 using 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 %.