INTERNATIONAL STANDARD

ISO 2453

Second edition
1991-07-01

Rubber, raw styrene-butadiene, emulsion-polymerized — Determination of bound styrene content — Refractive index method

Caoutchouc butadiène-styrène brut polymérisé en émulsion — Détermination de la teneur en styrène lié — Méthode par l'indice de réfraction

Reference number
ISO 2453:1991(E)

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 2453 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

This second edition cancels and replaces the first edition (ISO 2453:1975), clauses 1 and 7 and sub-clause 5.3 of which have been technically revised.

Annex A of this International Standard is for information only.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

Rubber, raw styrene-butadiene, emulsion-polymerized — Determination of bound styrene content — Refractive index method

1 Scope

This International Standard specifies a method for determining the bound styrene content of emulsion-polymerized styrene-butadiene (SBR) rubbers by correlation with the measured refractive index of an extracted sample according to a table of refractive indices versus percentages by mass of styrene.

The method is also applicable to extracted oil-extended emulsion-polymerized SBR as long as it produces a film suitable for refractive index measurements. It is not applicable to solution-polymerized SBR.

2 Significance of the test

The bound styrene test is a measure of the bound monomeric composition of the rubber. It is used as a check on the accuracy of monomer charging and also as a guide to the uniformity of the product, since the bound styrene content affects the physical properties.

3 Principle

Extraction of a test piece with ethanol-toluene azeotrope (ETA), followed by drying and pressing between sheets of aluminium foil to provide sheeted rubber having a thickness of not more than 0,50 mm. Calculation of the bound styrene content from the refractive index obtained at 25 °C on this thinly sheeted rubber.

4 Reagents

4.1 Ethanol-toluene azeotrope (ETA).

Mix 7 volumes of absolute ethanol with 3 volumes of toluene. Alternatively, mix 7 volumes of commercial grade ethanol with 3 volumes of toluene, and boil the mixture with anhydrous calcium oxide (quicklime) under reflux for 4 h. Then distil the azeotrope and collect the fraction with a boiling range not exceeding 1 °C, for use in the test.

4.2 Acidified ETA.

Add 10 cm^3 of concentrated hydrochloric acid [approximately 35 % (m/m)] to a portion of ETA (4.1) and make the solution up to 1 000 cm^3 with ETA.

NOTE 1 Acidified ETA is used for alum-coagulated polymers.

4.3 α-Bromonaphthalene.

5 Apparatus

5.1 Spiders, consisting of 13 mm squares of sheet aluminium or stainless steel having a nickel-chromium wire leg about 38 mm long attached to each corner. When the extracting solvent is ETA acidified with hydrochloric acid, the spider and the legs shall be made of tantalum.

5.2 Reflux condenser.

5.3 Abbe-type refractometer, having fourth-decimal-place accuracy and whose refracting prism can be placed in a nearly horizontal position for measurement of the refractive index of solids. An Amici-type compensating prism for achromatization is necessary unless a sodium-vapour lamp is used as a light source.

The refractometer shall be maintained at a temperature of 25 °C ± 0,1 °C, obtained by the use of a constant temperature room or by circulating constant temperature water through the instrument.

5.4 Vacuum oven, capable of being evacuated to a pressure of 1 300 Pa[1)] and of maintaining a temperature of 100 °C ± 5 °C.

5.5 Aluminium foil, between 0,025 mm and 0,08 mm thick, having good tear strength.

5.6 Glass reference, for checking adjustment of the refractometer. The glass reference shall be calibrated for use at 25 °C.

5.7 Hydraulic press, that can be maintained at a temperature of 100 °C and can attain a total force of up to 100 kN on the platens.

5.8 Pressing plates (optional apparatus), measuring 210 mm × 210 mm × 3 mm, with a wooden handle. One of the plates shall have a 150 mm square area in the centre milled out to a depth not to exceed 0,65 mm.

5.9 Scissors, small and sharp.

5.10 Light source, which shall be collimated to provide a beam at grazing incidence to the prism. If an incandescent light source is used, such as a flashlight bulb, it shall be of low intensity. A sodium-vapour lamp may also be used. The light source requirement is that a clear, sharp line with good contrast can be observed in the telescope of the refractometer. Attenuation or diffusion of the light for better viewing may be accomplished by placing crumpled tissue paper in the light path.

6 Preparation of test pieces

6.1 Sheet out the rubber to a thickness of no greater than 0,5 mm. Cut the sheeted rubber into strips approximately 13 mm wide and 25 mm long. Fasten one strip to each leg of the spider (5.1), thus allowing each portion of the rubber to be contacted on all sides by the solvent. Place the spider and strips in a 400 cm^3 flask into which 60 cm^3 of ETA have been placed (for alum-coagulated polymers, use acidified ETA and tantalum spiders). Fit the reflux condenser (5.2) in position.

Extract for 1 h at a temperature at which the solvent boils gently. Replace the solution with another 60 cm^3 of ETA or acidified ETA and extract for an additional hour, remove the spider from the flask and dry the rubber to constant mass in the vacuum oven (5.4), maintained at a pressure of about 1 300 Pa and a temperature of 100 °C ± 5 °C. It is important that the test pieces be extracted and dried thoroughly since either residual solvent or incompletely extracted materials will result in erroneous readings of the refractive index.

NOTE 2 Avoid plasticizing of the sample by overheating.

6.2 After the test pieces have been thoroughly dried, remove them from the spiders. At this point, more than one technique is suitable for pressing the test piece. The method of pressing may be modified to suit the type of rubber and the type of equipment available. The pressure and the time of pressing at 100 °C may be varied. The test piece may be cooled to room temperature under pressure, or removed from the press while hot. The time of hot pressing shall never exceed 10 min, and should preferably be 5 min.

The conditions shall be chosen so that the pressed test piece is homogeneous and so that a distinct line can be observed dividing the light and dark fields of the telescope field when the refractive index is determined. Two general techniques are given for the pressing operation, in 6.2.1 and 6.2.2.

6.2.1 If pressing plates (5.8) are used, proceed as follows.

Place approximately 0,3 g of the dry extracted polymer between two sheets of aluminium foil about 50 mm square and fold the corners over once. Place this test piece between the pressing plates and place the plates in the press held at 100 °C. Close the platens without applying pressure and preheat for 1 min. Several test pieces may be pressed at one time. Apply a force of about 100 kN for 3 min. Release the pressure, remove the test pieces from the press and allow them to cool.

6.2.2 If the pressing is to be done between flat platens without a cavity, proceed as follows, modifying the details of the procedure to suit the sample.

Prepare approximately 25 mm squares of the clean aluminium foil. Place a portion of one of the dried strips between two pieces of foil. Press the test piece between the foil squares with a force of between 2,2 kN and 6,6 kN at 100 °C for from 3 to 10 (preferably 3 to 5) min. If several test pieces are pressed at one time, increase the applied force proportionally so that the pressure on each test piece is between about 3,45 MPa and 10,35 MPa. Forces lower than the usual limit may be necessary for some polymers. It may also be necessary, with some polymers, to allow the pressed test pieces to cool under pressure while cooling the platens with cold water.

1) 10^3 Pa = 10^3 N/m^2 = 7,5 mmHg

6.3 The thickness of the final test piece to be measured shall not exceed 0,5 mm and may be much thinner. The ability to handle the pressed test piece and obtain a good refractive index reading are the only requirements with respect to test piece thickness.

6.4 Cut the prepared test piece in half with sharp scissors (5.9) and peel off one piece of the foil. Cut off a strip about 6 mm wide by 12 mm long with the scissors, in such a way that one of the narrower ends is freshly cut. The second piece of foil may be removed but it is frequently easier to handle the test piece with one foil piece left on the rubber.

7 Procedure

7.1 Check that the temperature of the refractometer has stabilized at 25 °C.

7.2 Check the adjustment of the refractometer by means of the glass reference (5.6) pressed firmly against the prism, using a drop of α-bromonaphthalene (4.3) as contact liquid. The small light source (5.10) shall be collimated and the best readings are obtained with the glass reference if the light is diffused through crumpled tissue paper. Move the hand control until the boundary line just reaches the cross-hairs (always moving from the light into the dark field). Make at least three readings. Adjust the instrument to give the reading of the glass reference.

After this adjustment, clean the prism well with ethanol and a lens paper.

7.3 Place the test piece on the prism with the cut edge toward the light source approximately where the glass reference was positioned. Remove the tissue paper from the light source. Press the test piece firmly on the prism with a finger and wait 1 min for temperature equilibrium. It is also permissible to close the upper prism on the test piece lightly if adequate light can still be focused on the end of the test piece, but unless the test piece is very thin this operation can damage the prism or its mounting. Adjust the compensating prism until a sharp dividing line between the light and dark fields, with minimum colour, is obtained. Test the contact between rubber and prism by pressing the test piece against the prism. There shall be no change in the position of the boundary line during this test.

7.4 Make at least three readings. If the readings differ by more than 0,000 1, further readings are necessary.

7.5 Repeat the process of obtaining readings with another portion of the test piece having a freshly cut edge. Average the mean values of the two sets of readings thus obtained. If the two mean values do not differ by more than 0,000 2, use this average for the calculation in accordance with clause 8. If the difference is more than 0,000 2, the procedure shall be repeated. If necessary, correct the refractive index measurement to 25 °C using the following equation:

$$n_{25} = n_\theta + 0{,}00037(\theta - 25)$$

where

n_{25} is the refractive index at 25 °C;

n_θ is the refractive index at temperature of measurement θ;

θ is the temperature of measurement, in degrees Celsius.

8 Expression of results

8.1 Method of calculation

The bound styrene content, w_s, of the styrene-butadiene rubber, expressed as a percentage by mass, is determined from the refractive index, corrected to 25 °C, by using table 1 or the following equation:

$$w_s = 23{,}50 + 1164(n_{25} - 1{,}53456) - 3497(n_{25} - 1{,}53456)^2$$

8.2 Precision

8.2.1 Repeatability

95 % of the results shall not differ from the mean by more than 0,5 % (*m*/*m*) when the bound styrene content is in the range of 20 % (*m*/*m*) to 30 % (*m*/*m*).

8.2.2 Reproducibility

The reproducibility is of the same order of magnitude as the repeatability for SBR polymerized at 50 °C. The reproducibility for SBR polymerized at 5 °C is not known exactly, but it is thought to be within the above repeatability limits, when testing polymers in the 20 % (*m*/*m*) to 30 % (*m*/*m*) styrene region.

9 Test report

The test report shall include the following particulars:

a) a reference to this International Standard;

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

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard, or any operation regarded as optional.

Table 1 — Values of refractive index at 25 °C and percentage, by mass, of bound styrene

Refractive index n_{25}	0	1	2	3	4	5	6	7	8	9
1,515						0,05	0,18	0,31	0,44	0,57
1,516	0,70	0,83	0,96	1,09	1,22	1,34	1,47	1,60	1,73	1,86
1,517	1,99	2,12	2,25	2,37	2,50	2,63	2,76	2,89	3,02	1,14
1,518	3,27	3,40	3,53	3,66	3,78	3,91	4,04	4,17	4,29	4,42
1,519	4,55	4,67	4,80	4,93	5,06	5,18	5,31	5,44	5,56	5,69
1,520	5,82	5,94	6,07	6,20	6,32	6,45	6,57	6,70	6,83	6,95
1,521	7,08	7,20	7,33	7,46	7,58	7,71	7,83	7,96	8,08	8,21
1,522	8,33	8,46	8,58	8,71	8,83	8,96	9,08	9,21	9,33	9,46
1,523	9,58	9,71	9,83	9,95	10,08	10,20	10,33	10,45	10,57	10,70
1,524	10,82	10,95	11,07	11,19	11,32	11,44	11,56	11,69	11,81	11,93
1,525	12,06	12,18	12,30	12,43	12,55	12,67	12,79	12,92	13,04	13,16
1,526	13,28	13,41	13,53	13,65	13,77	13,89	14,02	14,14	14,26	14,38
1,527	14,50	14,62	14,75	14,87	14,99	15,11	15,23	15,35	15,47	15,60
1,528	15,72	15,84	15,96	16,08	16,20	16,32	16,44	16,56	16,68	16,80
1,529	16,92	17,04	17,16	17,28	17,40	17,52	17,64	17,76	17,88	18,00
1,530	18,12	18,24	18,36	18,48	18,60	18,72	18,84	18,96	19,08	19,19
1,531	19,31	19,43	19,55	19,67	19,79	19,91	20,03	20,14	20,26	20,38
1,532	20,50	20,62	20,73	20,85	20,97	21,09	21,21	21,32	21,44	21,56
1,533	21,68	21,79	21,91	22,03	22,15	22,26	22,38	22,50	22,61	22,73
1,534	22,85	22,96	23,08	23,20	23,31	23,43	23,55	23,66	23,78	23,90
1,535	24,01	24,13	24,24	24,36	24,47	24,59	24,71	24,82	24,94	25,05
1,536	25,17	25,28	25,40	25,51	25,63	25,74	25,86	25,97	26,09	26,20
1,537	26,32	26,43	26,55	26,66	26,78	26,89	27,00	27,12	27,23	27,35
1,538	27,46	27,58	27,69	27,80	27,92	28,03	28,14	28,26	28,37	28,48
1,539	28,60	28,71	28,82	28,94	29,05	29,16	29,28	29,39	29,50	29,61
1,540	29,73	29,84	29,95	30,06	30,18	30,29	30,40	30,51	30,62	30,74
1,541	30,85	30,96	31,07	31,18	31,30	31,41	31,52	31,63	31,74	31,85
1,542	31,96	32,07	32,19	32,30	32,41	32,52	32,63	32,74	32,85	32,96
1,543	33,07	33,18	33,29	33,40	33,51	33,62	33,73	33,84	33,95	34,06
1,544	34,17	34,28	34,39	34,50	34,61	34,72	34,83	34,94	35,05	35,16
1,545	35,27	35,38	35,48	35,59	35,70	35,81	35,92	36,03	36,14	36,25
1,546	36,35	35,46	36,57	36,68	36,79	36,89	37,00	37,11	37,22	37,33
1,547	37,43	37,54	37,65	37,76	37,86	37,97	38,08	38,19	38,29	38,40
1,548	38,51	38,61	38,72	38,83	38,93	39,04	39,15	39,25	39,36	39,47
1,549	39,57	39,68	39,79	39,89	40,00	40,10	40,21	40,32	30,42	40,53
1,550	40,63	40,74	40,84	40,95	41,05	41,16	41,26	41,37	41,47	41,58
1,551	41,68	41,79	41,89	42,00	42,10	42,21	42,31	42,42	42,52	42,63
1,552	42,73	42,83	42,94	43,04	43,15	43,25	43,35	43,46	43,56	43,66
1,553	43,77	43,87	43,97	44,08	44,18	44,28	44,39	44,49	44,59	44,70
1,554	44,80	44,90	45,00	45,11	45,21	45,31	45,41	45,52	45,62	45,72
1,555	45,82	45,92	46,03	46,13	46,23	46,33	46,43	46,54	46,64	46,74
1,556	46,84	46,94	47,04	47,14	47,25	47,35	47,45	47,55	47,65	47,75
1,557	47,85	47,95	48,05	48,15	48,25	48,35	48,45	48,55	48,65	48,75
1,558	48,85	48,95	49,05	49,15	49,25	49,35	49,45	49,55	49,65	49,75
1,559	49,85	49,95	50,05	50,15	50,25	50,35	50,44	50,54	50,64	50,74
1,560	50,84	50,94	51,04	51,13	51,23	51,33	51,43	51,53	51,63	51,72
1,561	51,82	51,92	52,02	52,11	52,21	52,31	52,41	52,50	52,60	52,70
1,562	52,80	52,89	52,99	53,09	53,18	53,28	53,38	53,47	53,57	53,67
1,563	53,76	53,86	53,96	54,05	54,15	54,25	54,34	54,44	54,53	54,63
1,564	54,73	54,82	54,92	55,01	55,11	55,20	55,30	55,39	55,49	55,58

Annex A
(informative)

Other international standards relating to the styrene content of styrene-butadiene rubbers

ISO 3136:1983, *Rubber latex — Styrene-butadiene — Determination of bound styrene content.*

ISO 4655:1985, *Rubber — Reinforced styrene-butadiene latex — Determination of total bound styrene content.*

ISO 5478:1990, *Rubber — Determination of styrene content — Nitration method.*

ISO 6235:1982, *Rubber, raw — Determination of block polystyrene content — Ozonolysis method.*

This page intentionally left blank

This page intentionally left blank

This page intentionally left blank

UDC 678.746.22-136.22

Descriptors: rubber, raw materials, styrene-butadiene rubber, copolymers, chemical analysis, determination of content, styrene, refractometric analysis.

Price based on 6 pages