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Styrene-butadiene copolymers — Determination of bound styrene content

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FOREWORD

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Styrene-butadiene copolymers — Determination of bound styrene content

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method for determining the bound styrene content of a styrene-butadiene (SBR) copolymer by calculation from the measured refractive index of an extracted sample.

The method is applicable to hot (approximately 50 °C) emulsion-polymerized SBR (0 to 55 % bound styrene) and the same formula has been found suitable for use with cold (approximately 5 °C) emulsion-polymerized SBR (18 to 40 % bound styrene). It is applicable neither to solution-polmerized SBR nor to SBR in which the proportion of molecular configurations (i.e. *cis, trans* or vinyl) are different from those of current SBR production.

2 SIGNIFICANCE OF THE TEST

The bound styrene test is a measure of the bound monomeric composition of the polymer. 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 — 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.

5.4 Vacuum oven capable of being evacuated to a pressure of 1 300 N/m^2 (10 mmHg) and of maintaining a temperature of 100 ± 5 °C.

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

5.6 Glass standard for checking adjustment of the refractometer.

5.7 Hydraulic press that can be maintained at a temperature of 100 °C and can attain a total force up to 100 kN (22 000 lbf) on the platens.

* The term millilitre (ml) is commonly used as a special name for the cubic centimetre (cm^3), in accordance with a decision of the Twelfth Conférence Générale des Poids et Mesures. The term millilitre is acceptable, in general, for references in International Standards to capacities of volumetric glassware and to liquid volumes.

5.8 Pressing plate (optional apparatus), 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 polymer to a thickness of 0,5 mm. Cut the sheeted polymer 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 N/m^2 (10 mmHg) and a temperature of 100 ± 5 °C.

NOTES

1 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.

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 polymer 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.

6.2.1 If pressing plates (5 %) 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 (22 000 lbf) 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 and 6,6 kN (500 and 1 500 lbf) 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 and 10,35 MN/m^2 (500 and 1 500 lbf/in^2). 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.

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 the adjustment of the refractometer by means of the glass standard (5.6) pressed firmly against the prism, using a drop of α-bromonaphthalene (4.3) for contact liquid. The small light source (5.10) shall be collimated and the best readings are obtained with the glass standard 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 standard.

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

7.2 Place the test piece on the prism with the cut edge toward the light source approximately where the glass standard was positioned. Remove the tissue paper from the light source. Press the test piece firmly on the prism by means of the 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 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.

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

7.4 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 :

$$n_{25} = n_\theta + 0{,}000\,37\,(\theta - 25)$$

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

The bound styrene content, S, of the styrene-butadiene copolymer, expressed as a percentage by mass, is determined from the refractive index, corrected to 25 °C, by using the following equation or the table on page 4.

$$S = 23{,}50 + 1\,164\,(n_{25} - 1{,}534\,56) - 3\,497\,(n_{25} - 1{,}534\,56)^2$$

NOTES

1 REPRODUCIBILITY

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

2 ACCURACY

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

9 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

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

TABLE – **Values of refractive index and percentage 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	44,62	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