



Standard Test Method for Rubber—Chemical Analysis for Polystyrene Blocks In SBR (Styrene-Butadiene Rubber) and Styrene-Reinforced Latices¹

This standard is issued under the fixed designation D 3314; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of long polystyrene blocks in SBR rubbers and styrene-reinforced latices.

1.2 Percent block styrene content may be determined in the range from 1 to 100 %.

1.3 This test method is intended for use on gel-free polymers, but it may be used on polymers containing gel, if it has been proven that gel does not interfere.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 7.

2. Referenced Documents

2.1 ASTM Standards:

D 1076 Specification for Rubber—Concentrated, Ammonia Preserved, Creamed, and Centrifuged Natural Latex²

D 1416 Test Methods for Rubber from Synthetic Sources—Chemical Analysis²

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries²

E 145 Specification for Gravity-Convection and Forced-Ventilation Ovens³

3. Summary of Test Method

3.1 The test method is based upon oxidative cleavage of the ethylenic bonds in the block copolymer by treating a 1,2-dichlorobenzene solution of the polymer with tertiary butyl hydroperoxide (2-methyl-2-hydroperoxypropane) with os-

mium tetroxide catalyst. The saturated portions of the polymer, which contain no ethylenic bonds, remain unattacked. The small fragments (low molecular weight aldehydes) and the low-molecular weight polystyrene fragments from scissions within the random copolymer block are soluble in methyl alcohol, whereas the detached high-molecular weight polystyrene from the styrene homopolymer block is insoluble in alcohol. It is therefore possible to separate the high-molecular weight polystyrene, which constitutes the homopolymer block, from the polymer solution.

4. Significance and Use

4.1 This test method is suitable for manufacturing control, development, and research studies.

5. Apparatus

5.1 *Erlenmeyer Flask*, or round-bottom flask for use with the heating mantle, of 250-cm³ capacity with ground-glass joint. An iodine flask is also satisfactory.

5.2 *Air Condenser*, for 5.1.

5.3 *Beaker*, 600-cm³.

5.4 *Graduated Cylinder*, 50-cm³.

5.5 *Pipet*, 1-cm³.

5.6 *Buret*, 100-cm³, for dispensing tertiary butyl hydroperoxide.

5.7 *Thermometer*, to 150°C range.

5.8 *Crucible*, Gooch-type, fritted-glass, medium-porosity, 25 to 50-cm³ size.

5.9 *Hot Plate*, capable of operating to provide 120 to 130°C to boiling solution, or heating mantle for round-bottom flasks operating in the same temperature range.

5.10 *Drying Oven*, capable of controlling at 100°C Type 1B oven in accordance with Specification E 145.

¹ This test method is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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² *Annual Book of ASTM Standards*, Vol 09.01.

³ *Annual Book of ASTM Standards*, Vol 14.04.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *1,2-Dichlorobenzene.*

6.3 *Methanol.*

6.4 *Osmium Tetroxide (0.004 M Solution in Toluene 1 kg/m³ (0.1 g/100 cm³))*—Protect the solution from light. Decomposition is indicated by formation of a black precipitate. *The vapors are highly toxic.* Therefore, use due precaution in reagent preparation, use, and disposal. One cubic centimetre of this stock solution is needed for each analysis. In view of the toxicity of the reagent, the amount of solution prepared should not greatly exceed the number of determinations to be made over a reasonable period of time, depending on the stability of the solution and the work load.

6.5 *Sulfuric Acid (density 1.84 Mg/m³)*—(H₂SO₄).

6.6 *Tertiary Butyl Hydroperoxide (2-Methyl-2-Hydroperoxypropane)*, approximately 70 % purity assay is typical.

6.7 *Toluene.*

7. Use of Osmium Tetroxide

7.1 *Precautions:*

7.1.1 Store osmium tetroxide ampules (maximum total of 3 g) inside capped pipe or its equivalent.

7.1.2 Persons working with osmium tetroxide or its solutions should wear rubber gloves, a rubber apron, and a face shield or goggles.

7.1.3 Keep solutions of osmium tetroxide (maximum of 0.5 g) in unbreakable containers and store and use in the hood. The volume of air mechanically exhausted should be such that the hood-face velocities are within acceptable limits (a recommended minimum of (0.5 m/s) 100 ft/min).

7.1.4 Mark all containers of osmium tetroxide, whether concentrated or diluted with “DANGER” labels.

7.1.5 Transfer all osmium tetroxide or its solutions to be disposed of, to polyethylene bottles and incinerate. Filtrates are collected in a dump-can set aside for chlorinated solvents, and the contents are also incinerated. Do not accumulate waste solutions.

7.2 *Hazards:*

7.2.1 Osmium tetroxide is a yellow crystalline mass at room temperature. It can be hazardous in either its crystalline or vapor form. On contact with the skin or eyes, it produces irritation and if not removed immediately, may cause dermatitis and ulceration of the skin and intense conjunctivitis and

corneal ulceration to the eye. Inhalation of osmium tetroxide may cause capillary bronchitis and dermatitis. Even small amounts, if inhaled over a considerable period, cause headache, insomnia, pharyngeal and laryngeal distress, and digestive disturbance.

7.2.2 **Warning**—Analysts must thoroughly familiarize themselves with a current Material safety data Sheet (MSDS) for osmium tetroxide.

7.2.3 The vapor has a pronounced acrid, chlorine-like odor, which should be taken as a warning of the toxic concentration in the atmosphere, and personnel should immediately remove to an area of fresh air. The minimum perceptible concentration is 0.02 g/m³ of air. The threshold safety limit is 0.002 mg/m³ of air. Therefore, it cannot be detected by odor at the threshold safety limit. The melting point of the crystals is 56°C and the boiling point at 100 kPa is 130°C. However, it begins to sublime and distill well below the boiling point.

8. Sampling

8.1 If the sample is latex, prepare a dried film in accordance with Specification D 1076.

8.2 If the sample is an oil-extended rubber, conduct an ETA extraction in accordance with Test Methods D 1416.

8.3 In all cases, use a random unhomogenized sample.

9. Procedure

9.1 For a sample containing less than 30 % block styrene, cut approximately 0.5 g of rubber weighed to the nearest 0.1 mg into small pieces. Add the pieces to a 250-cm³ Erlenmeyer flask (or round-bottom flask), to which 35 cm³ of 1,2-dichlorobenzene has been previously added. For rubbers containing more than 30 % block styrene, use a 0.3-g specimen.

9.2 Fit an air condenser to the flask and heat it and its contents to 120 ± 5°C, until the rubber dissolves.

9.3 Remove the flask from the hot plate or heating mantle and cool it just enough to stop refluxing. Separate the air condenser from the flask, add 10 cm³ of the tertiary butyl hydroperoxide solution (see 6.6) and 1 cm³ of the osmium tetroxide solution (see 6.4). Replace the air condenser and continue heating the resulting solution at 100 to 120°C for 12 to 15 min. (Polystyrene is itself slowly degraded in this process, therefore digestion time should be constant and not lengthy.)

9.4 Remove the flask from the hot plate or heating mantle. When it has cooled so that it can be held without discomfort, pour the solution slowly and with constant stirring into a 600-cm³ beaker containing 350 cm³ of methanol to which 5 drops of concentrated H₂SO₄ has been added. Agitate the resulting mixture with a magnetic stirrer for 1 to 2 h, to flocculate the insoluble polystyrene.

9.5 Quantitatively transfer, with the aid of a rubber “policeman,” the precipitated polystyrene to a tared, medium-fritted Gooch crucible. Wash the precipitated polystyrene copiously with methanol to remove all the 1,2-dichlorobenzene, then with 100 cm³ of hot water to remove surfactants and electrolytes. Finally, wash with 100 cm³ of methanol again.

9.6 Dry the precipitate for 2 h at 100°C, cool in a desiccator, and weigh.

⁴ “Reagent Chemicals, American Chemical Society Specifications,” Am. Chem. Soc., Washington, DC. For suggestions on the testing of reagents not tested by the American Chemical Society, see “Reagent Chemicals and Standards,” by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the “United States Pharmacopeia.”

TABLE 1 Type 1 Precision

NOTE 1—

- S_r = within laboratory standard deviation.
 r = repeatability (in measurement units).
 (r) = repeatability (in percent).
 S_R = between laboratory standard.
 R = reproducibility (in measurement units).
 (R) = reproducibility (in percent).

Material	Mean Value, %	Within Laboratories			Between Laboratories		
		S_r	r	$(r)^A$	S_R	R	$(R)^A$
1	2.85	0.509	1.44	50.5	0.320	0.906	31.7
2	5.03	0.498	1.41	28.0	0.553	1.56	31.0
3	16.54	0.650	1.84	11.1	0.720	2.04	12.4
4	29.81	0.707	2.00	6.71	0.550	1.56	5.2
5	37.78	1.64	4.64	12.3	2.75	7.78	20.6

^ARelative precision, that is, for this test method a percent of a percentage.

10. Calculation

10.1 Calculate the percent block styrene as follows:

$$\text{Block styrene, \%} = [(W_A - W_B)/W_C] \times 100 \quad (1)$$

where:

- W_A = mass of crucible + polystyrene precipitate, g,
 W_B = mass of crucible, g, and
 W_C = mass of sample, g.

10.2 A test result is the average of two test determinations.

11. Precision and Bias ⁵

11.1 This precision and bias section has been prepared in accordance with Practice D 4483. Refer to Practice D 4483 for terminology and other statistical calculation details.

11.2 A Type 1 (interlaboratory) precision was evaluated. Both repeatability and reproducibility are short term, a period of a few days separates replicate test results. A test result is the average value as specified by this test method, obtained on two determinations or measurements of the property or parameter in question.

11.3 Five different materials were used in the interlaboratory program, these were tested in two laboratories on four different days.

11.4 The results of the precision calculations for repeatability and reproducibility are given in Table 1, in ascending order of material average or level, for each of the materials evaluated.

11.5 The precision of this test method may be expressed in the format of the following statements which use what is called an “appropriate value” of r , R , (r) , or (R) , that is, that value to

be used in decisions about test results (obtained with this test method). The appropriate value is that value of r or R associated with a mean level in Table 1 closest to the mean level under consideration at any given time, for any given material in routine testing operations.

11.6 *Repeatability*—The repeatability, r , of this test method has been established as the appropriate value for any parameter tabulated in Table 1. Two single test results, obtained under normal test method procedures, that differ by more than this tabulated r (for any given level) must be considered as derived from different or nonidentical sample populations.

11.7 *Reproducibility*—The reproducibility, R , of this test method has been established as the appropriate value tabulated in Table 1. Two single test results obtained in two different laboratories, under normal test method procedures, that differ by more than the tabulated R (for any given level) must be considered to have come from different or nonidentical sample populations.

11.8 Repeatability and reproducibility expressed as a percentage of the mean level, (r) and (R) , have equivalent application statements as above for r and R . For the (r) and (R) statements, the difference in the two single test results is expressed as a percentage of the arithmetic mean of the two test results.

11.9 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values do not exist for this test method since the value (of the test property) is exclusively defined by the test method. Bias, therefore, cannot be determined.

12. Keywords

12.1 polystyrene; SBR; styrene-butadiene rubber

⁵ Supporting data are available from ASTM Headquarters. Request RR: D11-1001.

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