INTERNATIONAL STANDARD

ISO 6235

Third edition
2016-09-15

Rubber, raw — Determination of block polystyrene content — Ozonolysis method

Caoutchouc brut — Dosage du polystyrène séquencé — Méthode de l'ozonolyse

Reference number
ISO 6235:2016(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

The committee responsible for this document is ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

This third edition cancels and replaces the second edition (ISO 6235:1995), of which it constitutes a minor revision with the following changes.

— the Normative References have been updated;

— in 7.2, the text in ISO 4655:1985, 4.4 has been included, because this International Standard has been withdrawn;

— a Bibliography has been added.

Rubber, raw — Determination of block polystyrene content — Ozonolysis method

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International 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 a method for the determination of the long polystyrene block content of raw uncompounded styrene-butadiene rubber (SBR) and raw uncompounded blends of block SBR.

It is not applicable to blends of block SBR with EPDM, IIR, CSM and other halogenated rubbers.

The method is applicable to raw, uncompounded latices of the above compositions and is suitable for rubbers having block polystyrene contents in the range from 5 % (by weight) to 100 % (by weight).

Rubbers having block polystyrene contents of less than 5 % (by weight) may yield incorrect results unless a correction factor, based on information gained by working with such rubbers, is applied.

The method is intended for use on gel-free rubbers, but it may be used on rubbers containing gel if it has been proved that the gel does not interfere.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1407, *Rubber — Determination of solvent extract*

ISO 4793, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*

3 Principle

A test portion is dissolved in dichloromethane and the ethylenic bonds in the rubber ruptured by reaction with ozone. The ozonides thus formed are subsequently decomposed by methanolic sulfuric acid solution.

4 Reactions

The reactions upon which the method is based are as follows.

a) Long, saturated, polystyrene blocks are not attacked by ozone, but small fragments (aldehydes and carboxylic acids) produced by the ozonolysis and the relatively low molecular mass polystyrene fragments from scission within the random copolymer blocks are soluble in methanolic sulfuric acid solution.

b) Relatively high molecular mass polystyrene blocks are insoluble in methanolic sulfuric acid solution.

c) It is possible to separate the relatively high molecular mass polystyrene blocks, which constitute the homopolymer blocks, from other soluble products, using methanolic sulfuric acid solution.

5 Reagents

During the analysis, use only reagents of recognized analytical quality and only distilled water or water of equivalent purity.

5.1 Dichloromethane.

It is essential that this reagent does not contain any impurities which could react with ozone to form an explosive mixture.

5.2 Methanol.

5.3 Potassium iodide, 3 % (by mass) solution.

5.4 Sulfuric acid, concentrated, ρ = 1,84 Mg/m^3.

5.5 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.

5.6 2-Propanol.

6 Apparatus

Use ordinary laboratory apparatus and the following.

6.1 Gooch crucibles, of fritted glass, having fine porosity, and of capacity 20 cm^3 to 25 cm^3, complying with the requirements of ISO 4793.

6.2 Drechsel (gas-washing) bottles.

6.3 Ozone generator, capable of delivering about 2 % (by volume) of ozone.

NOTE The actual ozone concentration depends on the type of generator used.

IMPORTANT — To minimize health hazards due to ozone, locate the ozone generator in a fume cupboard.

6.4 Magnetic stirrer.

6.5 Air condenser, if necessary (see 8.8).

7 Sample preparation

7.1 General

In all cases, use random, unhomogenized test samples.

Do not mill the test samples before analysis.

7.2 Latex

If the sample is latex, prepare a dried film as follows.

Dilute 5 g of latex with 2 cm^3 to 3 cm^3 of water. Using a dropping tube, add the diluted latex to 100 cm^3 of the vigorously stirred 2-propanol (5.6) at approximately 23 °C. Allow to settle and decant the supernatant liquid. Stir vigorously with water to wash the coagulum and drain thoroughly on a Büchner funnel. Wash copiously with water.

Steep overnight in cold water, drain off the water, rinse well with 2-propanol, shred and then dry in an open dish under vacuum at approximately 50 °C to constant mass. All handling shall be carried out in such a way as to avoid contamination.

Use part of this film as the test portion.

If the test portion cannot be used immediately, store it under nitrogen in a cool, dark place.

7.3 Oil-extended solid rubber

For oil-extended solid rubbers, extract with ETA (5.5) using the apparatus specified in ISO 1407, dry and use part of this as the test portion.

8 Procedure

WARNING — Ozone reacts with unsaturated compounds to yield ozonides. Ozonides are stable in dilute solutions and these solutions are not hazardous. However, when concentrated and/or dried, the ozonides quickly decompose and may, in some cases, explode. Concentrated solutions of ozonides are also explosive.

8.1 Cut the test sample into small pieces and weigh out, to the nearest 0,1 mg, 0,5 g to 1,0 g of the test sample thus prepared. Choose the mass of the test portion as a function of the expected block polystyrene content.

8.2 Place the test portion in a Drechsel bottle (6.2) and add 50 cm^3 of dichloromethane (5.1).

8.3 Dissolve the test portion at about 25 °C with occasional stirring and connect the Drechsel bottle inlet to the ozone generator (6.3), which is connected to the oxygen tank. Connect the Drechsel bottle outlet to the inlet of another Drechsel bottle containing 100 cm^3 of potassium iodide solution (5.3).

When performing this analysis, avoid decreasing the volume of solvent in the reaction vessel.

If the level of solvent decreases, immediately stop the flow of ozone and carefully add fresh solvent to the original solvent level.

8.4 Allow a flow of about 100 cm^3/min of oxygen, containing about 2 % (by volume) of ozone, to pass through the Drechsel bottle (6.2). Stop the gas flow 15 min after the yellow colour, due to free iodine freed from the potassium iodide, appears.

Prolonged reaction with ozone could produce cleavage of the saturated carbon chains. Therefore, adherence to the reaction time with ozone, as outlined in this International Standard, is mandatory. The use of di-n-butyl sulfide, which reacts with excess ozone, and a temperature of −25°C for the ozonolysis, has been used to reduce cleavage of the saturated carbon chains.[1]

8.5 Disconnect the Drechsel bottle (6.2) containing the dichloromethane solution from the ozone generator (6.3) and the Drechsel bottle containing the potassium iodide solution (5.3).

8.6 Transfer the dichloromethane solution, slowly and with constant stirring, into a 600 cm^3 beaker containing 350 cm^3 of methanol (5.2) to which five drops of concentrated sulfuric acid (5.4) have been added. Wash the Drechsel bottle with a few cubic centimetres of dichloromethane and transfer the washings into the beaker.

8.7 In most cases, the insoluble polystyrene settles to the bottom of the beaker after standing overnight.

8.8 In some cases, the insoluble polystyrene does not settle so easily. When this occurs, agitate overnight the solution, using the magnetic stirrer (6.4). To ensure that dichloromethane does not evaporate excessively, place the solution in a flask fitted with an air condenser (6.5).

8.9 If, after 24 h, the insoluble polystyrene has still not settled to the bottom of the beaker, the solution may be centrifuged, after transferring to a suitable centrifuge container.

8.10 Transfer the precipitated polystyrene to a tared Gooch crucible (6.1) with the aid of a rubber "policeman". Wash the precipitate copiously with methanol (5.2) to remove the dichloromethane, then with 100 cm^3 of hot water to remove surfactants and electrolytes, and finally again with methanol.

8.11 Dry the precipitate for 2 h at 100 °C, allow cooling in a desiccator and weigh. Repeat the drying and weighing operations until the mass is constant.

8.12 Carry out two determinations on each test sample. The test result is the average of the two determinations.

9 Expression of results

Calculate the block styrene content, C, as a percentage by mass, to the nearest 0,2 %, from the following formula:

$$C = \frac{m_1 - m_2}{m_0} \times 100$$

where

m_0 is the mass of the test portion, in grams;

m_1 is the mass of the Gooch crucible and block polystyrene precipitate, in grams;

m_2 is the mass of the Gooch crucible, in grams.

10 Test report

The test report shall include the following information:

a) a reference to this International Standard, i.e. ISO 6235:2016;

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

c) the individual results and the mean of the two results from each determination, as well as the units in which they are expressed;

d) any unusual features noted during the determination;

e) 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;

f) the date of the test.

Bibliography

[1] BARNARD D. Ozonolytic degradation of interpolymers of natural rubber with methyl methacrylate and styrene. *J. Polym. Sci., Polym. Phys. Ed.* 1956, **22** pp. 213–216. Available at: http://onlinelibrary.wiley.com/doi/10.1002/pol.1956.1202210103/full