INTERNATIONAL STANDARD

ISO 18852

First edition
2005-05-15

Rubber compounding ingredients — Determination of multipoint nitrogen surface area (NSA) and statistical thickness surface area (STSA)

Ingrédients de mélange du caoutchouc — Détermination de la surface par adsorption d'azote (NSA) et de la surface par épaisseur statistique (STSA) par méthode multipoints

Reference number
ISO 18852:2005(E)

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Published in Switzerland

Contents

Page

Foreword

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The main task of technical committees is to prepare International Standards. 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.

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.

ISO 18852 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*.

Rubber compounding ingredients — Determination of multipoint nitrogen surface area (NSA) and statistical thickness surface area (STSA)

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This 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 nitrogen surface area (NSA) of carbon blacks and other rubber compounding ingredients, like silicas and zinc oxides, based on the Brunauer, Emmett and Teller (BET) theory of gas adsorption using a multipoint determination. This test method specifies the sample preparation and treatment, instrument calibration, required accuracy and precision of the experimental data, and calculation of the surface area results from the data obtained. Also given is a procedure for calculating the statistical thickness surface area (STSA), otherwise known as the external surface area.

The test method specified uses an automatic volumetric static-vacuum apparatus, the surface area being calculated using the BET theory based on monolayer measurements.

The method can also be used for verifying "single-point" procedures described in ISO 4652-1 and other standards.

The automatic instruments described in these standards perform all the necessary computations, including that of the surface area based on statistical thickness. However, the automatic point-setting procedures used are not applicable to the STSA method.

NOTE Automatic instruments based on continuous flow using mixtures of nitrogen and helium gas in various ratios are also available. As good as they are, it is highly desirable to verify their accuracy of measurement against results obtained from static-vacuum-type instruments.

2 Normative references

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

ISO 4652-1:1994, *Rubber compounding ingredients — Carbon black — Determination of specific surface area by nitrogen adsorption methods — Part 1: Single-point procedures*

ISO 5794-1:2005, *Rubber compounding ingredients — Silica, precipitated, hydrated — Part 1: Non-rubber tests*

ISO 9298:1995, *Rubber compounding ingredients — Zinc oxide — Test methods*

3 Principle

A test portion of carbon black, silica, zinc oxide, etc, is placed in a cell of known volume and degassed. Using the ideal-gas equation, the volume of nitrogen required to give a predetermined relative pressure is calculated and dosed into the sample cell. Any additional nitrogen required to attain this relative pressure is due to adsorption by the test portion. The amounts of nitrogen adsorbed at different relative pressures are then used to calculate the specific surface area.

When analysing the various materials cited above, the following degassing conditions shall be used:

Material	Temperature °C	Time, minimum h	Reference
Carbon black	300 ± 10	0,5	ISO 4652-1:1994 3.6.1.2; 4.4; 5.5.6; 6.7.4 and 6.7.5
Hydrated silica	155 ± 5	1,0	ISO 5794-1:2005 Annex D, D.4.3
Zinc oxide (type A or B) [a]	300 ± 10	0,5	
Zinc oxide (type C)[a]	155 ± 5	1,0	ISO 5794-1:2005 Annex D, D.4.3

[a] The various zinc oxide grades are listed in ISO 9298:1995 in Annex D, Table D.1.

In the method described below, the degassing conditions indicated are those for carbon black, and have to be replaced by those indicated in the table for silica or zinc oxide.

4 Apparatus

4.1 Automatic static-volumetric vacuum apparatus for multipoint nitrogen surface area analysis, with vacuum system, Dewar flasks and all other accessories required for the analysis.

The instruments on the market are of two types: those in which the surface area of the empty sample tube is determined prior to the analysis of the test portion, thus allowing corrections for non-ideal gas behaviour to be made and sample tube correction factors to be applied, and those instruments with a reference tube, on which measurements are made in parallel with those on the sample tube, thus avoiding the need to calculate corrections of this type.

Either type of instrument may, additionally, use a different procedure to determine data points:

Procedure A: The points may be obtained by fully automatic metering of the injected-gas volume, the pressure equilibration parameters being chosen by the operator. The number of data points will thus be dependent on these parameters.

Procedure B: A limited number of points (usually 5 or 10) may be defined at specific p/p_0 values. The equilibration procedure will then aim to come as near as possible to these values. They may, for instance, be chosen to be equidistant from each other.

Irrespective of the way they are obtained, the data points used in the calculation of the regression line shall be selected from inside the p/p_0 range defined below. However, results obtained with one and the same test portion may be different when the data has been acquired using different equilibration procedures. Since procedure A is more accurate, it shall be used to verify all other methods.

4.2 Adsorption cells, which, when attached to the adsorption apparatus, can be maintained at a pressure below 1,35 mPa (10 nmHg).

4.3 **McLeod gauge**, or equivalent, capable of measuring the pressure of a high vacuum.

4.4 **Pressure gauge or transducer**, with a reading accuracy of ± 0,25 % or ± 70 Pa (± 0,5 mmHg), covering the range 0 kPa to 135 kPa (0 mmHg to 1 000 mmHg).

4.5 **Small glass vials with caps** (about 30 cm^3), for oven-drying samples.

4.6 **Analytical balance**, with 0,1 mg sensitivity.

4.7 **Heating mantle** or **degassing station**, capable of maintaining a temperature of 300 °C ± 10 °C.

4.8 **Calibration volume**, consisting of a cylindrical or spherical glass (or corrosion-resistant metal) reservoir, having an internal volume between 75 cm^3 and 500 cm^3, and with a valve or stopcock and a connector by which it can be connected to the sample port of the gas adsorption apparatus.

5 Reagents

5.1 Reagent-grade chemicals, conforming to the specified or recommended standards for laboratory chemicals, shall be used in all tests.

5.2 **Water**, distilled, or of equivalent purity.

5.3 **Liquid nitrogen**, 98 % or higher purity.

5.4 **Ultra-high-purity nitrogen gas**, from a cylinder or other suitable source.

5.5 **Ultra-high-purity helium gas**, from a cylinder or other suitable source.

5.6 **High-vacuum stopcock grease**.

6 Preparation and calibration of static-volumetric apparatus

6.1 This procedure shall be performed for the initial calibration, periodically as a quality control measure, and following repairs or adjustments. If a commercial apparatus is used, consult the user's manual for specific instructions in carrying out the steps which follow.

6.2 Attach the vacuum and pressure gauges or transducers (4.3 and 4.4) to the apparatus and evacuate it, the manifold and all internal pressure/vacuum sensors to 2,7 Pa (20 µmHg) or below.

6.3 Verify that the internal vacuum sensor(s) are reading correctly and that the internal pressure sensor(s) are reading correctly in the vicinity of zero pressure, taking into account the expected resolution and stability limits. Make adjustments as needed.

6.4 Close the vacuum path and admit nitrogen gas to build 100 kPa ± 1 % (750 mmHg ± 7,5 mmHg) of pressure. Verify that the pressure sensors read the correct pressure to within ± 0,25 %. Make adjustments as needed.

6.5 Thoroughly clean and dry an empty adsorption cell (4.2). Connect it to the apparatus and evacuate it to 2,7 Pa (20 µmHg). Apply a 300 °C heating mantle and continue evacuation for at least 1 h and until the rate of pressure rise upon temporarily closing the vacuum path is under 0,4 Pa (3 µmHg) per minute.

6.6 Perform a "blank analysis" on this clean empty cell at 0,05; 0,10; 0,15; 0,20 and 0,25p/p_0. Use a "p_0 value" of 101,325 kPa (760 mmHg) and a "test portion mass" of 1 g for the calculations.

6.7 Examine the mean value of the "adsorbed quantities" obtained. Ideally, this should be zero. A single reading exceeding 0,25 standard cm^3 makes the set-up unacceptable. As a rule, only readings below

0,125 standard cm^3 are acceptable although one of them may go as high as 0,25 standard cm^3. A parabolic error versus pressure profile may indicate failure to correct properly for non-ideal gas behaviour or transducer linearity problems. A linear error profile indicates failure to properly measure or account for unadsorbed gas (free-space error). Erratic variation of data points indicates leaks or noisy measurements.

6.8 Determine the internal volume of the calibration-volume reservoir (4.8) below the valve or stopcock by the difference in mass when empty and then when filled completely with distilled water (5.2). Measure the water temperature and use the correct water density to obtain the exact volume of water contained. It may be necessary to immerse the device in boiling water to ensure complete filling and degassing. Repeat the procedure until the calibration volume is known to better than 0,1 %. Empty the calibration volume and thoroughly dry it overnight in the vacuum oven at 70 °C ± 5 °C.

6.9 Connect the calibration-volume reservoir to a sample port of the gas adsorption apparatus, open the valve or stopcock, and evacuate the reservoir to below 2,7 Pa (20 µmHg). Continue evacuation for one more hour. Close off the path to the vacuum source and note whether any rise in pressure occurs. The pressure shall remain below 2,7 Pa (20 µmHg), with a rate of increase of less than 0,04 Pa (0,3 µmHg) per minute. When this has been achieved, close the valve or stopcock to maintain the vacuum within the calibration-volume reservoir.

6.10 Leave the closed-off, evacuated calibration-volume reservoir in place. Raise a Dewar flask (or other insulating container) around it, and pack wet, crushed ice firmly in the Dewar flask. Place an insulating cover on the ice. Start an analysis with target relative pressures of 0,025; 0,05; 0,10; 0,15; 0,20 and 0,25p/p_0. Use a 1 g mass and a p_0 of 101,325 kPa (760 mmHg) for the calculations.

On completion of the 0,25p/p_0 point, open the valve or stopcock of the reservoir (4.8) and complete the analysis.

6.11 Examine the "volumes adsorbed". Ideally, the first point at 0,025p/p_0 should show a zero amount. All other points should be within ± 1 % of the gas volume V computed using the following equation:

$$V = \left(\frac{p}{101{,}325}\right)V_R = \left(\frac{p}{p_0}\right)\left(\frac{p_0}{101{,}325}\right)V_R$$

where

p and p_0 are expressed in kPa;

p/p_0 is the relative pressure at which the point was actually equilibrated;

V_R is the internal volume of the reservoir (4.8) (as determined in 6.8).

6.12 Successful completion of this series of tests indicates that the gas apparatus meets the basic adsorption requirements of adequate vacuum level, compensation for free-space errors, linearity and accuracy of nitrogen gas metering.

7 Preparation of apparatus

7.1 Connect a clean adsorption cell (4.2) to the degassing station of the apparatus (4.1), and heat at 300 °C with the heating mantle (4.7) for 0,5 h at a pressure below 2,7 Pa (20 µmHg), or keep under nitrogen flow. (Insert a glass rod into the adsorption cell stem, thus improving test precision.)

7.2 Remove the heating mantle, allow the adsorption cell to cool to room temperature and backfill, preferably with helium (5.5) or nitrogen (5.4), to atmospheric pressure. Disconnect the adsorption cell from the degassing station, stopper it, weigh it to the nearest 0,1 mg and record the mass, m_1.

7.3 Weigh into the cell a test portion of the material to be tested, so that the cell contains an amount of material equivalent to 20 m^2 to 50 m^2 of surface area. Clean the sample cell stem with a pipe cleaner. A glass rod can be placed in the stem of the adsorption cell to adjust the void volume of the adsorption cell.

7.4 Connect the adsorption cell to the degassing station, and open the vacuum valve.

7.5 Place the heating mantle (4.7) around the adsorption cell, and degas the test portion as required by the table in Clause 3. To be sure that a pressure less than 1,35 Pa (10 μmHg) has been obtained and is being held, check the vacuum periodically with the McLeod gauge or similar instrument (4.3). Degassing of fillers under nitrogen flow is also possible.

NOTE The degassing time may vary significantly from sample to sample, and a reasonable margin of excess time is recommended.

7.6 Remove the heating mantle, and allow the adsorption cell to cool to room temperature. Backfill the adsorption cell with helium or nitrogen (the same gas as used in 7.2) to atmospheric pressure, disconnect the cell from the degassing station, stopper it, weigh it to the nearest 0,1 mg and record the mass, m_2.

NOTE It is important to use the same gas for weighing the empty and material-filled adsorption cell. Inconsistent use of helium may introduce a weighing error of about 1 mg per cm^3 of cell.

7.7 Calculate the mass of the test portion as follows:

$$m_0 = m_2 - m_1$$

where

m_0 is the test portion mass, in g;

m_2 is the mass of the adsorption cell, glass rod, stopper and test portion (see 7.6);

m_1 is the mass of the adsorption cell, glass rod and stopper (see 7.2).

8 Measurement procedure

8.1 Since most of the operations are conducted automatically, it is important to become thoroughly familiar with the procedures and to follow carefully the operating instructions.

8.2 Determine the saturation pressure of the liquid-nitrogen bath. This pressure (p_0) is affected by the purity of the liquid nitrogen and the ambient pressure. Simply assuming a p_0 of 2 kPa above the barometric pressure is not sufficient, as impurities dissolved in the liquid nitrogen usually cause the bath temperature to increase, with an associated increase in the saturation pressure of 1,4 kPa to 2,7 kPa (10 mmHg to 20 mmHg).

8.3 Connect the adsorption cell containing the degassed test portion to the surface area analyser.

8.4 Start the experiment. The instrument will complete the following steps:

— a leak test, to ensure that there is no leak in the connection between the adsorption cell and the instrument after application of the vacuum;

— calculation, and metering into the adsorption cell, of the successive volumes of pure nitrogen required to reach the selected relative pressures.

8.5 A minimum of five data points in the range 0,05 to 0,30p/p_0 shall be obtained. A data point consists of a relative equilibrium pressure and the total volume of nitrogen gas adsorbed by the test portion at that relative pressure. The data points should preferably be at as near equal spacing in terms of p/p_0 as possible.