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Rubber compounding ingredients — Precipitated silica — Determination of aggregate size distribution by disc centrifuge

Ingrédients de mélange du caoutchouc — Silice précipitée — Détermination de la distribution dimensionnelle par à disque centrifuge

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Contents

Page

Foreword

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This document 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*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The determination of the aggregate size distribution (ASD) of silica by disc centrifuge photosedimentometry can be used for characterizing and specifying these products. It is well accepted that the aggregate size distribution of silica could have an influence on the performance of these materials used in different applications. Therefore, a standardized procedure regarding the sampling preparation and the testing of the aggregate size distribution seems to be necessary in order to compare, discuss and interpret received results between the laboratories using this method.

See Annex A for physical principles of measurement.

Rubber compounding ingredients — Precipitated silica — Determination of aggregate size distribution by disc centrifuge

1 Scope

This document specifies a general method for determining the aggregate size distribution (ASD) of silica by using a disc centrifuge according to the principle of sedimentation. As pre-stage the silica is de-agglomerated in water using strong ultrasonic power treatment.

The method is used for precipitated silica.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
silica aggregate
discrete, rigid colloidal entity that is the smallest dispersible unit in a suspension

Note 1 to entry: In comparison to carbon black[3] the term silica aggregate is less defined and has to be seen always in context with the silica treatment (i.e. ultrasonic power in a silica suspension in water). The references apply to carbon black but are also broadly used by the rubber industry for precipitated silica.

4 Significance and use

A disc centrifuge is used for measuring the aggregate size distribution (ASD) of precipitated silica. As a function of test time and rotational speed, aggregate sizes in the range of approximately 5 nm to 100 µm can be analysed according to the principle of sedimentation. Firstly, the silica sample is dispersed in an aqueous medium by using ultrasonic power treatment. Afterwards, the suspension is transferred to the disc centrifuge and separated according to its aggregate size. The sedimentation is accelerated by centrifugal forces generated by the rotation of the centrifuge. By using a density gradient of sucrose solution the sedimentation can be stabilised. Over the course of the experiment, a separation in different silica aggregate sizes is possible and can be evaluated.

For investigations between different laboratories, it is recommended to use the IRM 100 silica standard[1)] according to ASTM D5900 (see Clause 7).

1) IRM 100 silica standard is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product. The IRM 100 silica standard can be provided from Balentine Enterprises, INC. (www.irmsilicastandard.com).

5 Apparatus

The usual laboratory apparatus and, in particular, the following.

5.1 Disc centrifuge allowing a rotational speed of 24 000 r/min.

5.2 Probe-type sonicator typically with a nominal power of 200 W or more.

5.3 Ultrasonic device with a recommended probe size of ½".

The chosen ultrasonic device shall guarantee that the values of the IRM 100 silica standard in dispersion are achieved (see Clause 7).

5.4 Cooling bath, e.g. cryostat.

5.5 Precision balance, to ±0,01 g.

5.6 Disposable syringe, 1,0 ml and 2,0 ml with adequate needle size.

5.7 Rolled rim bottles with a recommended size of 35 ml, d = 30 mm, h = 65 mm.

When using the IRM 100 standard, the fixing of the dimension of the vessel is not necessary any longer. However, an ejection of the suspension should be avoided.

6 Reagents and materials

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

6.1 Water, de-ionized.

6.2 Sucrose, powder, ≥99,7 %.

6.3 Dodecane, 99 %.

6.4 PVC calibration standard with a recommended size of approximately 220 nm ± 20 nm.

The determination of aggregate diameters from the Stokes equation relies on the measurement time and the knowledge of four other experimental parameters (see Annex B). Since the accuracy of those parameters strongly depends on other variables, such as the gradient preparation conditions, the operating temperature in the disc or the stability of rotational velocity, a relevant approach generally consists in setting the group of four parameters by prior calibration with a standard of known narrow size distribution. A suitable standard for the characterization of precipitated silica is PVC suspended in water, but any other standard is acceptable as long as its size distribution (peak and width) and density is known accurately. A size around 200 nm is a suitable size for rapid calibration.

The PVC standard can be provided by the instrument manufacturer. PVC latex with a narrow particle size distribution is used. However, slight variations from batch to batch are possible and have to be considered. The value of a new batch is disclosed by the supplier.

7 Calibration of the test equipment

7.1 Calibration of the ultrasonic device

Independent from the designated power of the ultrasonic generator under 5.2, the geometry of the ultrasonic probe and the pre-set amplitude, the energy input into the silica suspension can be supposed on a similar level when the documented parameters of the IRM 100 are in line with the detected results.

Additionally, the probe is underlying some significant ageing effects depending from the number of tests but also test conditions such as amplitude, time, pulsed/un-pulsed treatment of the suspension. These ageing effects can influence the ultrasonic power input into the sample and manipulate the results. The comparison of results with former data or between different laboratories is impeded or even impossible. By using the IRM 100 as calibration standard, the ageing effects can be detected very early and precautions up to a replacement of the ultrasonic probe can be undertaken timely.

7.2 Routine alignment check

Before starting a test run, screen the disc centrifuge by using a silica standard. It is recommended to revert to the international IRM 100 according to ASTM D5900.

Carry out the calibration procedure in accordance with Clauses 8 and 9.

By using the documented test parameters in Clause 9, the following results can be found.

— Mode, linear [nm]: most frequent aggregate size: 66,0 ± 2,8.

— Mean (dw) [nm]: average diameter by weight: 87,8 ± 3,9.

— D_{25} (25^{th} oversize weight percentile) [nm]: 97,2 ± 3,3.

— D_{50}, median (50^{th} weight percentile) [nm]: 76,4 ± 2,7.

— D_{75} (75^{th} oversize weight percentile) [nm]: 60,7 ± 2,5.

— FWHM, linear [nm]: 55,1 ± 2,5.

The given ranges are calculated on a 95 % confidence level based on the total variation determined by an analysis of variance.

This procedure makes sure that the production of the silica suspension has happened under the same ultrasonic energy input, independently from the used device and the adjusted conditions (i.e. power of the generator, ultrasonic time, suspension density, ageing status of the probe, etc). The ageing status of the probe can be eliminated up to a certain level.

Hereby, it is possible to compare test results received by different laboratories or within one laboratory (i.e. different operators).

8 Operating instructions

8.1 Preparation of the disc centrifuge

Turn on the disc centrifuge (5.1) and warm up the device as recommended by the supplier. Start program and set the rotational speed of the disc to 20 000 r/min. When the target speed is reached, fill the disc centrifuge with a density gradient of sucrose solutions.

The disc speed should be adjusted based on the size range of the sample to be measured. Typical values are 20 000 r/min to 24 000 r/min for fine silica.

The solutions of sucrose (6.2) in water consist of different concentrations. These solutions have to be prepared. The concentrations of sucrose solutions, $w_{sucrose}$, are between 8 % and 24 %. The density gradient is structured in 10 levels:

— 24,0 % - 22,2 % - 20,4 % - 18,7 % - 16,9 % - 15,1 % - 13,3 % - 11,6 % - 9,8 % - 8,0 %

Inject 1,8 ml of sucrose solution per density level into the disc centrifuge, starting with the highest concentration.

Alternatively, it is possible to prepare only two sucrose solutions with the highest and lowest concentration: respectively solution A = 24,0 % and solution B = 8,0 %. Mix them together in the injection syringe (5.6) according to Table 1.

It is also possible to use automatic gradient builder (for example offered by CPS Instruments) for preparing the solutions of sucrose.

Table 1

1	1,8 ml solution A + 0,0 ml solution B
2	1,6 ml solution A + 0,2 ml solution B
3	1,4 ml solution A + 0,4 ml solution B
4	1,2 ml solution A + 0,6 ml solution B
5	1,0 ml solution A + 0,8 ml solution B
6	0,8 ml solution A + 1,0 ml solution B
7	0,6 ml solution A + 1,2 ml solution B
8	0,4 ml solution A + 1,4 ml solution B
9	0,2 ml solution A + 1,6 ml solution B
10	0,0 ml solution A + 1,8 ml solution B

Before injection, shake the syringe after adding an air bubble in it in order to homogenize the sugar solutions. Finally, add a layer of 0,5 ml dodecane (6.3) as a cap fluid and allow stabilizing the gradient for at least 30 min.

Longer waiting time for instance up to 60 min could have a slight influence on the results but also it should be considered that a longer testing time would influence the lab capacity. It is recommended to fix the time before testing, in case two or more laboratories intend to compare their test results (i.e. in cross checks).

Fresh sucrose solutions should be prepared daily to avoid microorganism growth.

In order to check the gradient stability, one should make sure that the base line signal does not evolve significantly over time (i.e. less than 3 % over the course of the experiment) Alternatively, the position of the peak of the PVC standard should not move significantly between two experiments indicating that the properties of the gradient are stable.

The stability of the sucrose gradient depends on the rotating speed, the number of injections and the concentration of the sample dispersion. A recommendation for the maximum number of injections and the maximum time under rotation should be defined by internal laboratory studies.

8.2 Sample preparation

Take 0,60 g ± 0,05 g of the silica sample and place it into a 35 ml rolled rim bottle (5.7). Then add 20 ml of de-ionized water (6.1). The concentration of the silica suspension is 30 g/l.

When testing granular silica, grind it with a mortar to reduce the size first, in order to avoid problems during the dispersion process, like the floating-up of granulates along the ultrasonic probe.

Use a clamp stand to fix the filled rolled rim bottle in place in a cooling bath (5.4). First, bring the cooling bath to a recommended temperature of 5 °C ± 1 °C. Position the ultrasonic probe (5.2) in a way that the probe is inserted deep enough to allow an homogenous distribution of the inserted energy into the liquid volume.

For the recommended rolled rim bottle (5.7) a submersion depth of 5,0 cm into the bottle - measured from the upper rim – should be suitable.

Apply ultrasound to the sample suspension for a time and a power level (amplitude) which meet the IRM 100 requirements (Clause 7). A recommended time is 15 min.

8.3 Cleaning the centrifuge

At the end of the test series, clean the disc centrifuge. Open the door and use a pipette to suck out the fluid through the injection hole. Then, clean the inner part of the disc by using a soft cloth. Fill the disc with demineralised water and some surfactant and rotate it by hand a few times. Remove the liquid, replace it by fresh water and rotate the disc by hand again. Repeat this procedure twice to three times. Subsequently, press a lint-free cloth to the outer edge and rotate by hand again. The cover can then be placed back, and the disc can be cleaned from the outside.

9 Procedure

In the equipment software, call up the measurement procedure to be used.

EXAMPLE For a DC24000 disc centrifuge of the producer CPS Instruments, Inc., adjust the software parameters according to the range of magnitude of the aggregate sizes of the silica, which have to be analysed.

Following settings can be suitable for an interval of aggregate sizes between 20 nm to 1,0 µm.

Procedure definitions:

— Sample parameters:

  — Maximum diameter: 1,0 µm for 20 000 r/min disc rotation; 0,79 µm for 24 000 r/min disc rotation;

  — Minimum diameter: 0,02 µm;

  — Particle density: 2,11 g/ml;

  — Particle refractive index: 1,46;

  — Particle absorption: 0,001 K;

  — Non-sphericity factor: 1,0.

  Depending on these values an estimated runtime is calculated by the software.

— Calibration standard parameters:

  — Peak diameter in µm: depending on the calibration standard used; following the manufacturer's information;

  — Half height peak width in µm: depending on the calibration standard used; following the manufacturer's information;

  - Particle density in g/ml: depending on the calibration standard used; following the manufacturer's information.

- Fluid parameters:
  - Fluid density: 1,051 g/ml (average density at the detector between 24 % to 8 % of sucrose solutions);
  - Fluid refractive index: 1,361 2. (average density at the detector between 24 % to 8 % of sucrose solutions);
  - Fluid viscosity: 1,28 $N \cdot s \cdot m^{-2}$ (average density at the detector between 24 % to 8 % of sucrose solutions).
- Presentation parameters:
  - Display Mode: weight;
  - X-axis scale: lin;
  - Y-Axis scaling/normalization: height.

By using these parameters, a particle size range between 20 nm to 1,0 µm can be analysed.

In order to measure sample distribution, change to the submenu "Operate Analyser". The steps required for the measurement are queried one after the other in the "Instructions" line.

Before each measurement, calibrate by using the PVC standard (6.4). The corresponding default setting is done under "Options" in the submenu "Operate Analyser".

It is also recommended to carry out an inspection equipment monitoring with a silica standard before starting with the testing of silica samples. Preferably, the international silica standard IRM 100 according to ASTM D5900 should be used (see Clause 7).

If the results are in the specified range and the detector signal reach the baseline stable after the distribution (no baseline drift) the measuring of the samples can be started.

For measurement inject 0,1 ml of the PVC standard or silica dispersion each time. The measurement stops automatically when the "Minimum diameter" is reached. If the distribution finishes earlier and is stable at the baseline, the measurement can be stopped by the operator.

For each sample being analysed, a double determination is recommended.

10 Evaluation and documentation of the test results

Using the raw data curve (absorption measurement) the following weight-based aggregate size distribution parameters can be determined.

- Mode, linear [nm]: most frequent aggregate size, corresponding to the abscissa value of the maximum of the linear distribution function.
- Full width at half maximum [nm], lin. (FWHM) [nm]: corresponds to the width of distribution function at 50 % of its maximum value.
- Mean (dw) [nm]: average diameter by weight.
- D_{10} (10^{th} oversize weight percentile) [nm]: aggregate size above which 10 % of the distribution lies (from cumulative curve).
- D_{16} (16^{th} oversize weight percentile) [nm]: aggregate size above which 16 % of the distribution lies (from cumulative curve).

— D_{25} (25th oversize weight percentile) [nm]: aggregate size above which 25 % of the distribution lies (from cumulative curve).

— D_{50} Median (50th weight percentile) [nm]: aggregate size at 50 % of the cumulative curve.

— D_{75} (75th oversize weight percentile) [nm]: aggregate size above which 75 % of the distribution lies (from cumulative curve).

— D_{84} (84th oversize weight percentile) [nm]: aggregate size above which 84 % of the distribution lies (from cumulative curve).

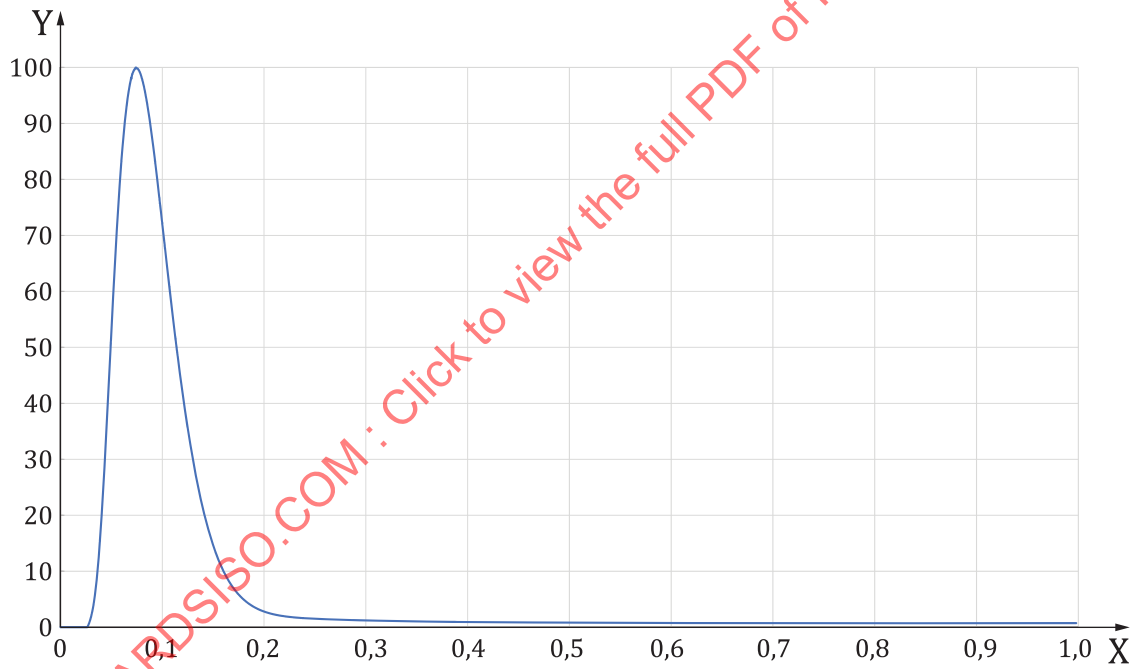
— D_{90} (90th oversize weight percentile) [nm]: aggregate size above which 90 % of the distribution lies (from cumulative curve).

— Quotient "FWHM / mode".

— Quotient "d75/d25".

Append the distribution curves to the findings.

See Figure 1.



Key

X aggregate size, in microns

Y relative weight

Figure 1 — Aggregate size distribution curve of IRM 100 when using the fixed test parameters

11 Precision data

See Annex B.

12 Safety precautions

Use the ultrasonic homogeniser only in the sound protection box.

The chemicals are used in compliance with the safety and health regulations. Further information can be found in the MSDS (Material safety data sheet) for each substance.

Annex A
(informative)

Physical principles of measurement

A.1 Disc centrifuge

The disc centrifuge is used for measuring the aggregate size distribution of precipitated silica. As a function of test time and rotational speed, aggregate sizes in the range of approximately 5 nm to 100 µm can be analysed according to the principle of sedimentation. The sample being investigated is dispersed in an aqueous medium and separated according to its aggregate size in a disc centrifuge. The sedimentation is accelerated by centrifugal forces generated by the rotation of the centrifuge. By using a density gradient of sucrose solution, the sedimentation can be stabilised.

At the outer edge of the disc centrifuge a light source is situated. The larger and heavier the particles are, the faster they move within the gravitation field inside the centrifuge. When the particles reach the outer rim of the disc, they pass the laser beam. Depending on the particle size, the light is scattered and absorbed differently. The light is reaching on a photoelectric detector, which is measuring the light extinction as a function against the time. From this data, the particle size distribution is calculated.

A.2 Stokes law

The Stokes equation can be used to determine the diameter of silica aggregates based on the knowledge of five parameters:

— viscosity of the suspension fluid;

— rotational velocity of the disc;

— density difference between the silica aggregates and the fluid;

— measurement time with $t = 0$ being the introduction of the silica suspension in the disc;

— ratio of the radial distance (detector to the center of the disc) to the radial distance (air-liquid interface to the center of the disc).

It is important to note that the Stokes law is valid only for the sedimentation of non-interacting rigid spherical particles in a laminar flow[4].

Particle interactions can generally be excluded by working in dilute conditions (i.e. <0,2 weight percent inside the disc) and laminar flow conditions are generally met for particles smaller than 50 µm in an aqueous medium under centrifugation up to 20 000 g (i.e. Reynolds number <1).

Silica aggregates are rigid objects, but their shape differs from that of a sphere. Therefore, the diameter obtained using Stokes equation should not be considered as the real hydrodynamic diameter of the aggregates, but more as the equivalent diameter of a sphere having the same drag coefficient.

A.3 Density gradient

When the average density of the sample suspension is higher than the fluid inside the rotating disc, an instability can arise after injection because the particles sediment in group rather than individually (condition for Stokes law validity). The consequence is an artificial broadening of the distribution.

This instability can easily be avoided by using a density gradient which ensures that, at any time during the sedimentation, a band of suspended particles will always have a net density lower than the fluid they go through.

For a silica suspension in water at around w_{silica} = 3 % (average density around 1,015 g/cm^3), such a gradient can be constructed by preparing and mixing sucrose solutions in water between $w_{sucrose}$ = 8 % (1,028 g/cm^3 at 25°C) and 24 % (1,088 g/cm^3 at 25 °C).

A.4 Production of a silica dispersion by ultrasonic treatment

Prior to the measurement of any size distribution, the silica needs to be de-agglomerated into aggregates by ultrasonic treatment.

To ensure a reproducible quality of fragmentation, one of the main parameters to put under control is the ultrasonic power delivered per unit volume of suspension, at constant silica concentration, and assuming that most of the volume is subjected to ultrasonic waves. This power should not be mistaken with the electric power mentioned on the device. However, because the ultrasonic power delivered per unit volume of suspension depends on many different parameters (sonication amplitude, volume, geometry of the vessel, geometry and size of the ultrasonic probe...), its quantification can be challenging. To get an estimate allowing a rough calibration, refer to the procedure described in Reference [4].

To circumvent this difficulty, a silica standard with a known ASD can be used. It is recommended to use the IRM100 silica standard according to ASTM D5900 (see Clause 7) and adjust the different operating conditions such that the resulting ASD matches the IRM100 reference ASD.