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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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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.