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Solution-polymerized SBR — Evaluation methods of viscoelastic properties

SBR polymérisé en solution — Méthodes d'évaluation des propriétés viscoélastiques

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Foreword

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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).

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For an explanation of the voluntary nature of standards, 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 www.iso.org/iso/foreword.html.

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

A variety of solution-polymerized styrene-butadiene rubber (S-SBR) have been developed and used for tires because they show excellent balance between rolling resistance and wet grip.

It is well known that functionalized S-SBR can strongly react with fillers, resulting in better dispersion and contributing to the low rolling resistance tire. These phenomena can be explained by the viscoelastic properties.

In other words, in order to describe the performance of S-SBR, it is necessary to evaluate viscoelastic properties. Therefore, a standard specifying the model compound formulation, mixing procedure, sample preparation, test conditions, etc. for evaluating the viscoelastic properties of the S-SBR compound is useful to the rubber industries.

Solution-polymerized SBR — Evaluation methods of viscoelastic properties

WARNING — Persons using this document should be familiar with normal laboratory practice. This document 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 determine the applicability of any other restrictions.

1 Scope

This document specifies the standard test formulation, mixing procedure and test methods for evaluation of viscoelastic properties in a compound based on solution-polymerized styrene-butadiene rubber (S-SBR), including functionalized S-SBR[7].

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 289-1, *Rubber, unvulcanized — Determinations using a shearing-disc viscometer — Part 1: Determination of Mooney viscosity*

ISO 2393, *Rubber test mixes — Preparation, mixing and vulcanization — Equipment and procedures*

ISO 4664-1, *Rubber, vulcanized or thermoplastic — Determination of dynamic properties — Part 1: General guidance*

ISO 6502-2, *Rubber — Measurement of vulcanization characteristics using curemeters — Part 2: Oscillating disc curemeter*

ISO 6502-3, *Rubber — Measurement of vulcanization characteristics using curemeters — Part 3: Rotorless curemeter*

ISO 23529, *Rubber — General procedures for preparing and conditioning test pieces for physical test methods*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4664-1 apply.

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

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

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

4 Test formulation

The standard test formulation given in Table 1 shall be used for the evaluation of any type of S-SBR.

Formulation A is an oil-extended S-SBR formulation. Formulation B is a non oil-extended S-SBR formulation.

International or national standard chemicals shall be used if available. Materials used shall be chemically equivalent to those indicated in Table 1.

Table 1 — Standard test formulation

Material	**pphr (parts per hundred rubber)**[a]	
	Formulation A	**Formulation B**
First stage		
S-SBR, extended with oil	70 + X[b]	—
S-SBR	—	70
BR[c]	30	30
Silica, precipitated[d]	70	70
Carbon black N234	10	10
Silane coupling agent TESPD[e]	5,6	5,6
ZnO[f]	3	3
Stearic acid[g]	2	2
Oil TDAE[h]	31,25 - X	31,25
Antioxidant (6PPD)[i]	1,5	1,5
Wax[j]	1,0	1,0
Second stage (no additional ingredient)		
Third stage		
DPG[k]	2	2
CBS[l]	1,5	1,5
Sulfur[m]	2,0	2,0
Total	229,85	229,85

[a] The abbreviation, pphr, is defined in ISO 1382:2020, 3.345.

[b] X = parts of oil, mass fraction, per 100 parts of base polymer in the oil-extended rubber.

[c] Butadiene rubber, manufactured with neodymium or cobalt catalyst, 96 % (mass fraction) *cis* 1,4 content.

[d] The CTAB surface area of 150 m^2/g to 180 m^2/g is used. The CTAB is measured according to ISO 5794-1.

[e] Bis(triethoxysilylpropyl)disulfide.

[f] Zinc oxide, indirect type, class B1a according to ISO 9298:2017, Table D.1.

[g] Stearic acid, stearic/palmitic 65/30, class B according to ISO 8312:2015, Table L.1.

[h] Treated distillate aromatic extract.

[i] *N*-(1,3-Dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine.

[j] Wax, mixture of refined hydrocarbons.

[k] *N,N'*-Diphenylguanidine.

[l] *N*-Cyclohexyl-2-benzothiazylsulfenamide.

[m] Sulfur, soluble (rhombic), grade W according to ISO 8332:2018, Table A.1.

5 Procedure for sample preparation

5.1 General

Equipment and procedure for preparation, mixing and vulcanization shall be in accordance with ISO 2393. The following procedure is an example which has been found suitable for 600 cm^3 laboratory internal mixer.

At the beginning of each series of test mixes, a machine conditioning batch shall be mixed using the same formulation as the mixes under test.

5.2 First stage

- Filling factor: 0,70.
- Rotational speed: 50 r/min.
- Starting temperature: 90 °C ± 3 °C.
- Friction: 1:1,14.
- Ram pressure: 0,5 MPa.

The first stage procedure is given in 5.2 a) to 5.2 f).

The temperature of the batch discharged on completion of mixing shall be between 155 °C and 165 °C. If necessary, adjust starting temperature, rotation speed and/or filling factor to reach discharge temperature.

		Duration (min)	Cumulative time (min)
a)	Adjust the temperature of the laboratory internal mixer to a starting temperature of 90 °C ± 3 °C. Close the discharge door, set the rotor speed and raise the ram.	—	—
b)	Load the rubber, lower the ram and allow the rubber to be masticated.	0,5	0,5
c)	Raise the ram and load the half of the silica, silane coupling agent, oil. Lower the ram and allow the batch to mix.	1,5	2,0
d)	Raise the ram and load the half of the silica, antioxidant, wax, ZnO, stearic acid, carbon black. Lower the ram and allow the batch to mix.	1,5	3,5
e)	Raise the ram and clean the mixer throat and the top of the ram. Lower the ram and allow the batch to mix.	1,5	5,0
f)	Discharge the batch (batch temperature: 155 °C to 165 °C).		

After discharging the batch, immediately check the temperature of the batch with a suitable temperature measuring device. If the temperature as measured falls outside the range of 155 °C to 165 °C, discard the batch. Pass the batch three times through a mill with a mill opening of 2,5 mm and a roll temperature of 50 °C ± 5 °C.

Determine the mass of the batch. If the mass differs from the theoretical value by more than +0,5 % or −1,5 %, discard the batch and remix.

Leave the batch for at least 3 h and up to 24 h at room temperature, if possible, at standard temperature and humidity as defined in ISO 23529.

5.3 Second stage

- Filling factor: 0,69.
- Rotational speed: 50 r/min.
- Starting temperature: 90 °C (adjust so that the discharge temperature is 155 °C to 165 °C).
- Friction: 1:1,14.
- Ram pressure: 0,5 MPa.

The second stage procedure is given in 5.3 a) to 5.3 c).

		Duration (min)	Cumulative time (min)
a)	Plasticize the batch from the first stage.	2,0	2,0
b)	Maintain the batch temperature of 160 °C by adjusting the starting temperature.	3,0	5,0
c)	Discharge the batch (batch temperature: 155 °C to 165 °C).		

Pass the batch three times through a mill with a mill opening of 2,5 mm and a roll temperature of 50 °C ± 5 °C.

Leave the batch for at least 3 h and up to 24 h at room temperature before proceeding to the third stage, if possible, at standard temperature and humidity as defined in ISO 23529.

5.4 Third stage

- Filling factor: 0,70.
- Rotational speed: 30 r/min.
- Starting temperature: 50 °C ± 3 °C.
- Friction: 1:1,14.
- Ram pressure: 0,5 MPa.

The third stage procedure is given in 5.4 a) to 5.4 e).

		Duration (min)	Cumulative time (min)
a)	Adjust the temperature of the laboratory internal mixer to a starting temperature of 50 °C ± 3 °C. Close the discharge door, set the rotor speed and raise the ram.	—	—
b)	Load the batch of the second stage, lower the ram and allow the rubber to be masticated.	0,5	0,5
c)	Raise the ram and load DPG, CBS, and sulfur. Lower the ram and allow the batch to mix.	1,0	1,5
d)	Raise the ram and clean the mixer throat and the top of the ram. Lower the ram and allow the batch to mix.	0,5	2,0
e)	Discharge the batch (batch temperature: 90 °C to 110 °C).		

The batch is transferred to mill. Form a sheet for 20 s with a mill opening of 3 mm to 4 mm between the rolls. During the next 40 s, make 3/4 cuts three times from each side. Cut out the batch from the mill. Set the mill opening at 0,8 mm and pass the rolled batch endwise through the rolls six times, introducing it from each end alternately. Finally, form one sheet of the thickness 2,2 mm.

Condition the batch at least 24 h at room temperature after mixing and prior to vulcanizing, if possible at standard temperature and humidity as defined in ISO 23529.

6 Testing of the uncured mix

Determine the viscosity at 100 °C using the shearing disc viscometer in accordance with ISO 289-1.

7 Evaluation of vulcanization characteristics

7.1 General

Evaluation of vulcanization characteristics is carried out according to either 7.2 or 7.3.

7.2 Evaluation according to oscillating disc curemeter test

Measure the following standard test parameters:

M_L, M_H, t_c' (10), t_c' (50) and t_c' (90)

in accordance with ISO 6502-2, using the following test conditions:

- oscillation frequency: 1,7 Hz (100 cycles per minute);
- amplitude of oscillation: ±1° arc;
- selectivity: to be chosen to give at least 75 % full scale deflection at M_H;
- die temperature: 160,0 °C ± 0,3 °C;
- pre-heat time: none.

7.3 Evaluation according to rotorless curemeter test

Measure the following standard test parameters:

M_L, M_H, t_c' (10), t_c' (50) and t_c' (90)

in accordance with ISO 6502-3, using the following test conditions:

- oscillation frequency: 1,7 Hz (100 cycles per minute);
- amplitude of oscillation: 0,5° arc;
- selectivity: to be chosen to give at least 75 % full scale deflection at M_H;
- die temperature: 160,0 °C ± 0,3 °C;
- pre-heat time: none.

8 Evaluation of dynamic viscoelastic properties

8.1 General

Regarding the dynamic viscoelastic properties, two kinds of evaluations, the strain dependency (see 8.4) and the temperature dependency (see 8.5), shall be carried out.

In the strain dependency, it is possible to evaluate the change in the filler network structure, that is, the dispersibility of the filler in a compound. In temperature dependency, temperature dependency of complex modulus, including glass transition temperature and mobility of molecular chain can be evaluated.

The strain dependency of the filling compound is known as the Payne effect[8][9] (see Annex D) and reflects the filler networks. The difference in absolute value of complex modulus between low strain and high strain is conventionally used as an indicator of the filler dispersibility. Especially, it is known that when the polymer type is changed to the functionalized polymer, the difference value greatly decreases. It is useful as an indicator of filler dispersibility by polymer types. See Figure C.1.

The temperature dependency is useful for expressing the properties of polymers at each service temperature of application products. Peak temperature of tan δ curve is useful for detecting the glass transition temperature. See Figure C.2.

The reliability of the obtained data may be confirmed by reference to Annex B.

Examples of viscoelastic measurement are given in Annex C.

8.2 Sample preparation

Test pieces may be moulded or cut from vulcanized sheet. Moulding is preferred for shear and compression test pieces. Metal plates for shear and compression test pieces may be bonded during moulding or bonded afterwards with a thin layer of suitable adhesive.

Vulcanization time is determined from the results of 7.2 or 7.3 to prepare a vulcanized sheet.

The test piece shall not be deformed before measurement. In addition, test pieces used once shall not be used again.

8.3 Test equipment and deformation mode

The dynamic viscoelastic properties shall be evaluated in accordance with ISO 4664-1.

Any forced vibration equipment in ISO 4664-1 may be used, but shear deformation mode is recommended. Shear deformation mode includes double, film and parallel plate type.

8.4 Evaluation of strain dependency

The strain dependency is preferably measured under the following conditions. The strain amplitude shall be changed from low strain side to high strain side.

— Mode of measurement: strain-dependency.

— Temperature: 60 °C, conditioning time: 10 min.

— Mode of deformation: double shear.

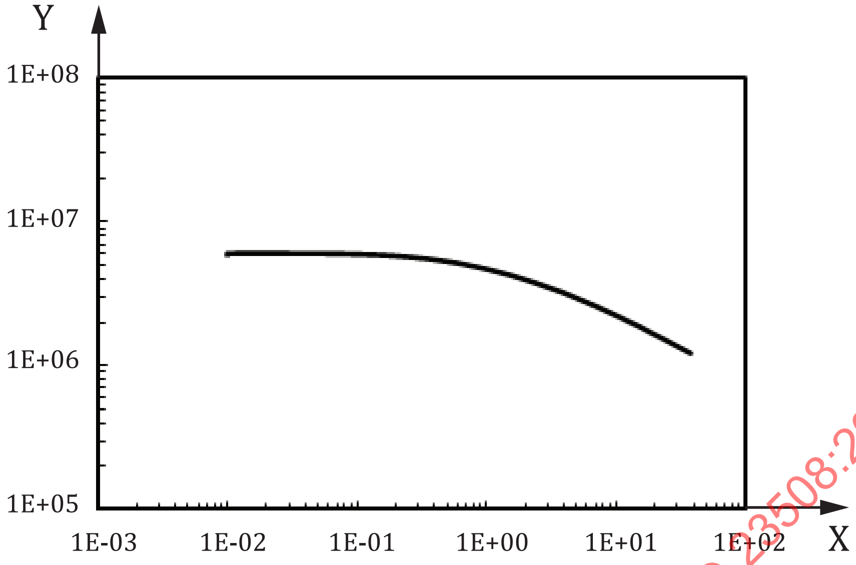
— Mean strain: 0 %.

— Strain amplitude: 0,01 % to 50 % (at least up to 10 %).

— Frequency: 10 Hz.

— Measurement parameter: G^*, G', G'', tan δ.

An example of measurement results is given in Figure 1.



Key

X strain amplitude (%)

Y absolute value of complex modulus (|*G**|) (Pa)

Figure 1 — Example of measurement results (strain dependency)

8.5 Evaluation of temperature dependency

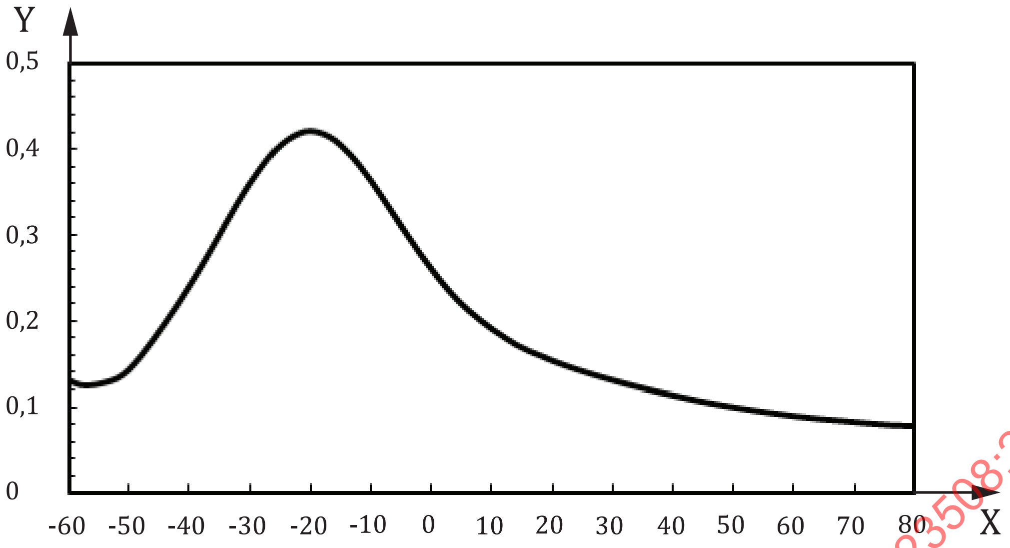
The temperature dependency is preferably measured under the following conditions. The temperature shall be raised from low temperature to high temperature.

- Mode of measurement: temperature-dependency.
- Temperature range: −60 °C to 80 °C.
- Temperature rising methods:
  a) method 1: step by step 2 °C at a time (hold for 2 min at each temperature, increase 2 °C /min between each temperature);
  b) method 2: continuously at a rate of 2 °C/min.

NOTE The temperature can be raised at 4 °C/min between 20 °C and 80 °C.

- Mode of deformation: double shear.
- Mean strain: 0 %.
- Strain amplitude: 0,1 %.
- Frequency: 10 Hz.
- Measurement parameter: G^*, G', G'', tan δ.

An example of measurement results is shown in Figure 2.



Key

X temperature (°C)

Y tangent of loss angle

Figure 2 — Example of measurement results (temperature dependency)

8.6 Expression of test results

The result of the strain dependency is expressed by the absolute value of the difference between 0,1 % and 10 % of complex modulus (G^*), as given in Formula (1).

$$\Delta G^* = \left|G^*{}_{(0{,}1\,\%)}\right| - \left|G^*{}_{(10\,\%)}\right| \tag{1}$$

where

$|G^*{}_{(0{,}1\,\%)}|$ is absolute value of complex modulus at 0,1 %;

$|G^*{}_{(10\,\%)}|$ is absolute value of complex modulus at 10 %.

NOTE The strain dependency is known as the Payne effect and is used as an indicator of filler dispersion (see Annex A).

9 Precision

See Annex E.

10 Test report

The test report shall include the following information:

a) a reference to this document (i.e. ISO 23508);

b) sample details:

  1) all details necessary for the identification of the sample;

  2) the test formulation used (Clause 4);

  3) the viscosity of the uncured mix (see Clause 6);

    4) the cure characteristics (see 7.2 or 7.3);
    5) cure condition;

c) the test details:

    1) the laboratory temperature;
    2) the mode of deformation;
    3) the mechanical and thermal conditioning procedures used;
    4) the details of the test machine, including type, drive, capacity and measurement systems;
    5) the test conditions, including strain amplitude, frequency and temperature, as appropriate;
    6) the type of test piece used;
    7) the details of any procedures not specified in this document;

d) the test results (adding a chart if necessary):

    1) ΔG^*;
    2) peak temperature of tan δ;

e) any unusual features noted during the evaluations;

f) any operations not included in this document or in the International Standards to which reference is made, as well as any operation regarded as optional;

g) the date of the test.

Annex A
(informative)

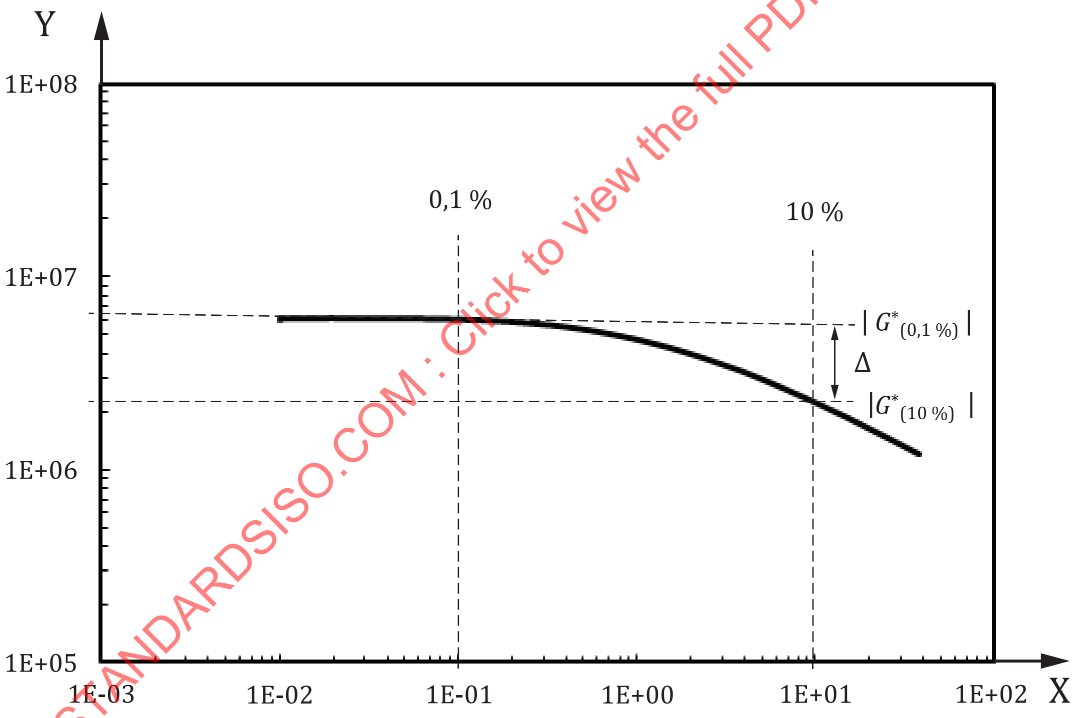
Evaluation of filler dispersibility

It is well known that Payne effect is an indicator of filler dispersibility in a compound.

Figure A.1 shows the relationship between the absolute value of complex modulus and the applied strain obtained by the strain dependency measurement in 8.4, plotting the absolute value of complex modulus on the y-axis with the strain on the x-axis.

When evaluating the dispersibility of polymers with different glass transition temperatures, measuring at a temperature away from the glass transition temperature, 60 °C is desirable to avoid the influence of the transition region.

If the strain is less than 0,1 %, the variation in the data tends to be large, and if the strain exceeds 10 %, the Lissajous tends to be distorted. Therefore, when the deformation mode is shear mode, 0,1 % as low strain and 10 % as high strain are used.



Key

X strain amplitude (%)

Y absolute value of complex modulus (Pa)

Figure A.1 — Measurement results (strain dependency)

The absolute value of the difference (Δ) between the complex modulus at low strain (0,1 %) and the complex modulus at high strain (10 %) in the strain dependency measurement of 8.4 shows the Payne effect (see Figure A.1).

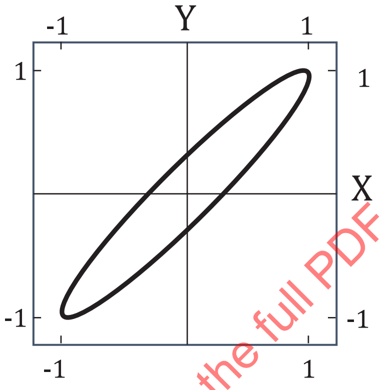
When this absolute value is small, the filler dispersibility in a compound is good, and when this absolute value is large, the filler dispersibility is poor.

Annex B
(informative)

Data reliability

In dynamic viscoelasticity measurement, vibration is applied to a sample with strain (deformation) as a sinusoidal waveform (sine curve) and measure the stress (force) response generated at that time.

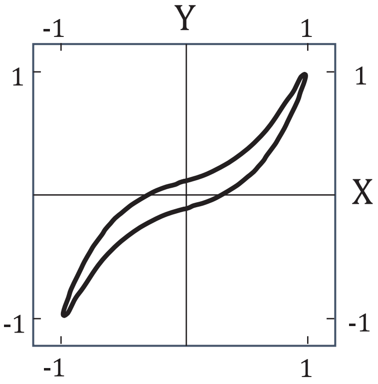
When a strain (deformation) is plotted on the x-axis and a stress (force) is plotted on the y-axis, if a viscoelastic material is used, a Lissajous figure as shown in Figure B.1 or Figure B.2 can be obtained.



X σ/σ peak

Y γ/γ peak

Figure B.1 — Example of an elliptical Lissajous figure



Key

X σ/σ peak

Y γ/γ peak

Figure B.2 — Example of a non-elliptical Lissajous figure

If the Lissajous figure is elliptical as shown in Figure B.1, the acquired data are considered to be reliable. However, when the Lissajous figure is deformed as shown in Figure B.2, the reliability of the acquired data in phase angle difference between stress and strain waves is considered as low, so careful handling of data is necessary.

Annex C
(informative)

Examples of viscoelastic measurement

C.1 General

Three different types of S-SBR were examined under the conditions described in C.2 and C.3. The results are shown in Figure C.1 and Figure C.2.

C.2 Strain dependency measurement

- Test equipment: Metravib DMA+1000[1].
- Mode of measurement: strain-dependency.
- Temperature: 60 °C.
- Temperature conditioning time: 10 min.
- Mode of deformation: double shear.
- Mean strain: 0 %.
- Strain amplitude: from 0,01 % to 50 %.
- Frequency: 10 Hz.
- Measurement parameter: complex modulus.
- The test piece was fixed to the measurement jig with a cyanoacrylate adhesive.

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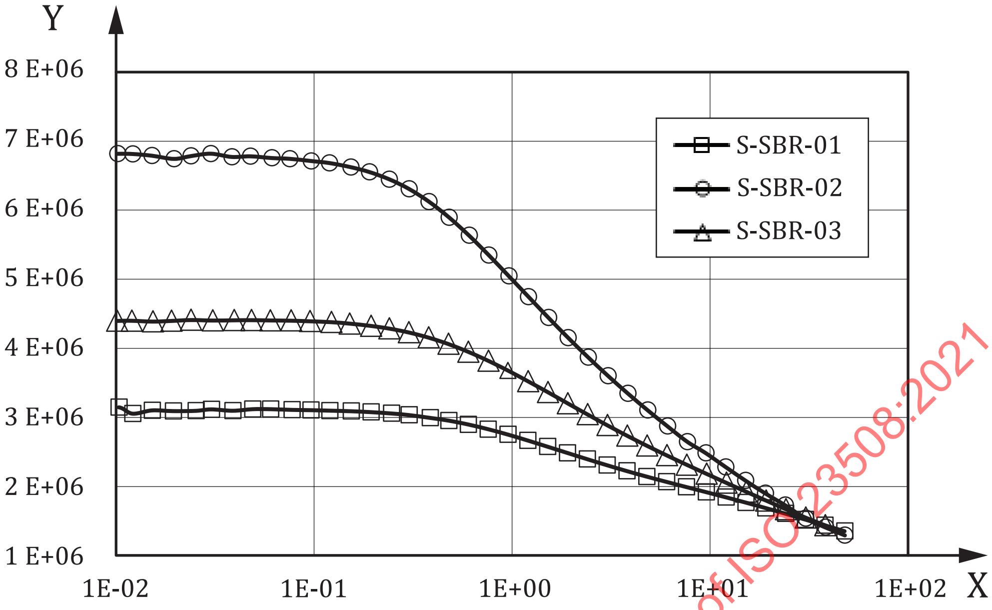
[1] Metravib DMA+1000 is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.



Key

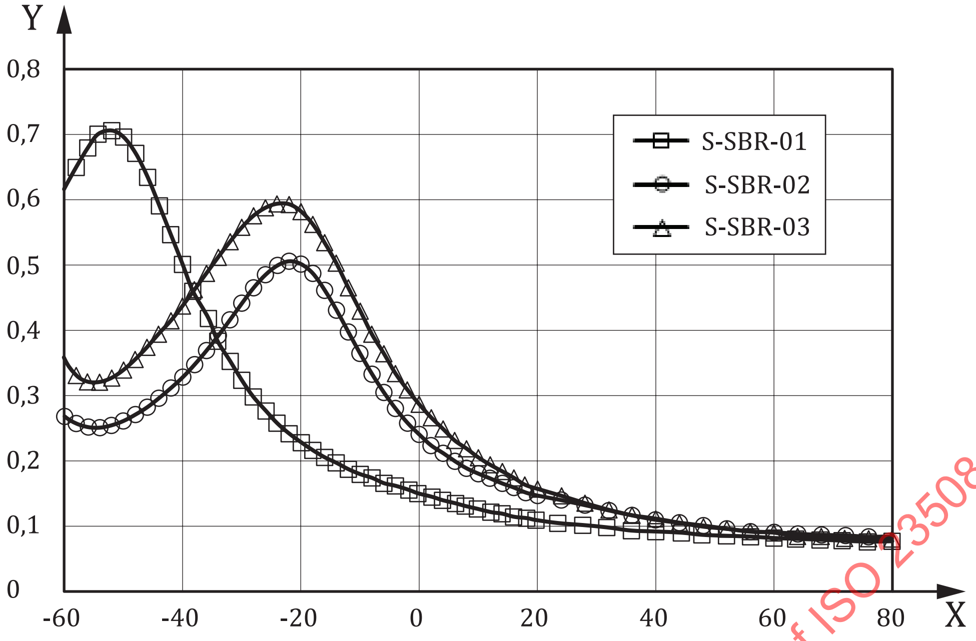
X strain amplitude (%)

Y absolute value of complex modulus (Pa)

Figure C.1 — Results of the strain dependency

C.3 Temperature dependency measurement

- Test equipment: Metravib DMA+1000[1].
- Mode of measurement: temperature-dependency.
- Temperature (range): from −60 °C to 80 °C.
- Temperature rising step: 2 °C between −60 °C and 20 °C; 4 °C between 20 °C and 80 °C.
- Temperature conditioning time: hold for 2 min at each temperature.
- Mode of deformation: double shear.
- Mean strain: 0 %.
- Strain amplitude: 0,1 %.
- Frequency: 10 Hz.
- Measurement parameter: tan δ.
- The test piece was fixed to the measurement jig with a cyanoacrylate adhesive.



Key

X temperature (°C)

Y tangent of loss angle

Figure C.2 — Test results of the temperature dependency