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Styrene-butadiene rubber (SBR) — Determination of the microstructure of solution-polymerized SBR —

Part 2: **FTIR with ATR method**

Caoutchouc styrène-butadiène (SBR) — Détermination de la microstructure du SBR polymérisé en solution —

Partie 2: Méthode FTIR avec ATR

ICS: 83.060

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Foreword

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ISO 21561-2 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

ISO 21561 consists of the following parts, under the general title *Styrene-butadiene rubber (SBR) — Determination of the microstructure of solution-polymerized SBR*:

— *Part 1: ^{1}H-NMR and FTIR with cast-film method*

— *Part 2: FTIR with ATR method*

Styrene-butadiene rubber (SBR) — Determination of the microstructure of solution-polymerized SBR —

Part 2:
FTIR with ATR method

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all 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.

CAUTION — Certain procedures specified in this International Standard may involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This International Standard specifies procedures for the quantitative determination of the microstructure of the butadiene and the content of styrene in solution-polymerized SBR (S-SBR) by Fourier Transform Infrared Spectrometry (FTIR) with Attenuated Total Reflection (ATR) method. The styrene content is expressed in mass % relative to the whole polymer. The vinyl, trans and cis contents are expressed in mol % relative to the butadiene content. This method is only applicable to raw rubbers.

NOTE 1 Precision as shown in Annex A may not be obtained for S-SBRs containing polystyrene block or styrene content more than 45 mass %.

NOTE 2 Only “vinyl”, “trans” and “cis”, are used in this International Standard. However, the expression of vinyl, trans and cis mean as follows in general.

— vinyl: vinyl unit, vinyl bond, 1,2-unit, 1,2-bond, 1,2-vinyl-unit or 1,2-vinyl-bond;

— trans: 1,4-trans unit, 1,4-trans bond, trans-1,4 unit or trans1,4 bond;

— cis: 1,4-cis unit, 1,4-cis bond, cis-1,4 unit or cis-1,4 bond.

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 1795, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

3 Principle

The IR spectrum of the S-SBR sample is measured by FTIR with ATR. The absorbances that are characteristic of each microstructure component and styrene at the specified wavelengths are used to determine the content of each component by using the specific formulae presented in this standard.

4 Apparatus

4.1 FTIR, of the following specifications:

— Detector: Deuterium Tri-Glycine Sulfate (DTGS) or Tri-Glycine Sulfate (TGS);

— Number of scans: 32;

— Resolution: 2 cm^{-1};

— Range of wavelength: 600 cm^{-1} to 1 800 cm^{-1}.

4.2 ATR, of the following specifications:

— Type: Single bounce ATR;

— Crystal: Diamond;

— Angle of incidence: 45°;

— Sample pressure clamp: a concave or a flat shaped clamp which is capable of maintaining a constant pressure on the sample. The use of a torque wrench is preferable.

5 Calibration

5.1 FTIR

Adjust the optical bench alignment of FTIR spectrometer according to the manufacturer's instruction manual.

5.2 ATR

Set ATR in the sample chamber of FTIR and adjust the optical alignment of ATR according to the manufacturer's instruction manual.

6 Sampling

6.1 Prepare the test sample in accordance with ISO 1795.

NOTE The extraction of ordinary extender oils by solvent is not necessary.

6.2 Cut out a test piece from the test sample. The test piece shall have a flat surface to give good contact with the ATR crystal and be approximately the same size as the crystal, usually a few square millimetres.

7 Procedure for measuring ATR spectrum

7.1 Set up FTIR according to the manufacturer's instruction manual.

7.2 Set ATR in a sample chamber of FTIR.

7.3 Measure the background spectrum with the conditions shown in 4.1.

7.4 Put the test piece on the ATR crystal, and contact it as completely as possible to the crystal surface preferably using the clamp specified in 4.2. The contact between the test piece and the crystal affects the absorbance of ATR spectra.

7.5 Measure the sample spectrum with the conditions shown in 4.1.

7.6 The atmosphere of the sample chamber for FTIR shall be kept consistent during the background and test piece measurements in order to avoid the influences of absorbance at 668 cm^{-1} and 723 cm^{-1} by CO_2.

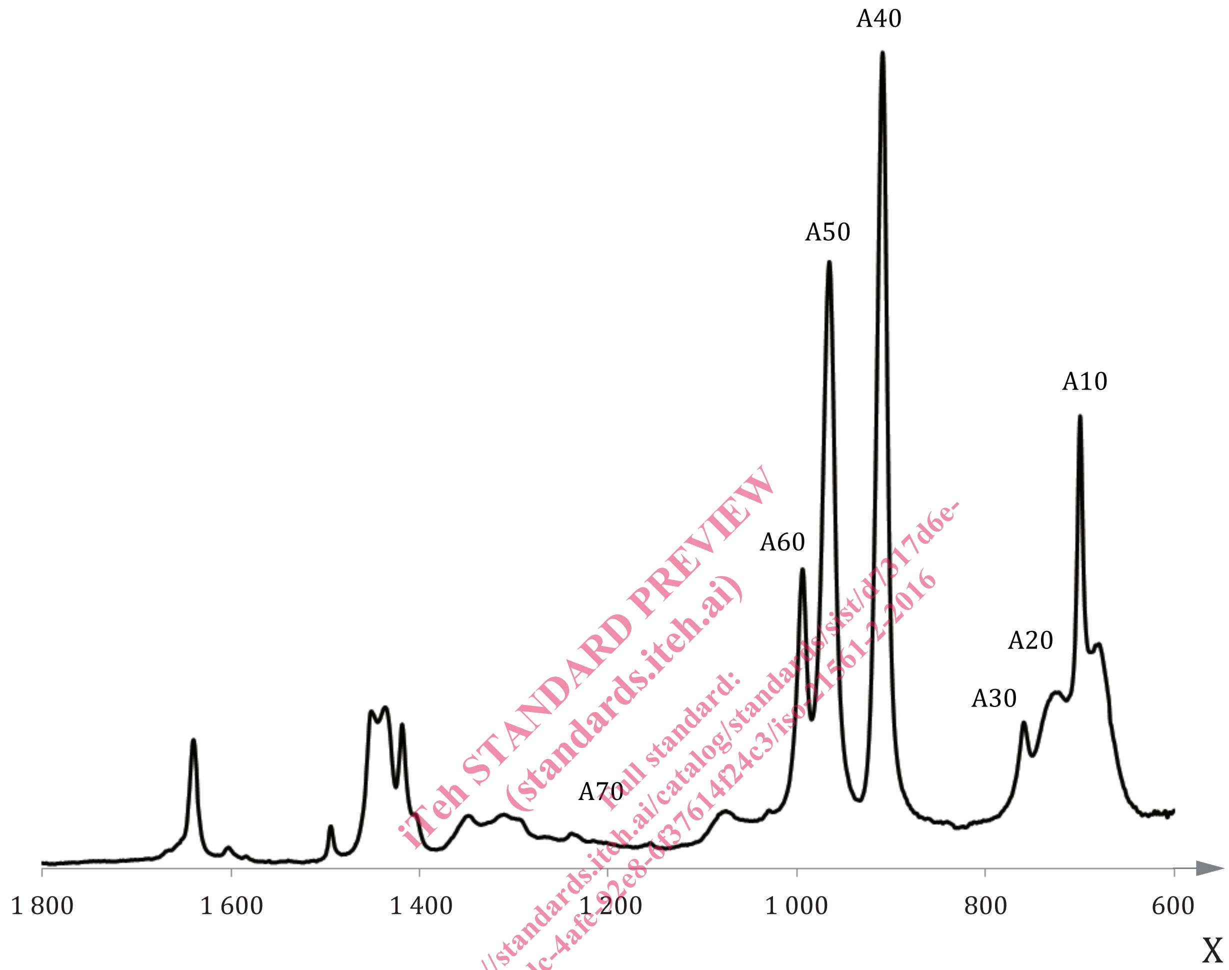
8 Determination of the microstructure of butadiene and the styrene content

8.1 Measurement of the absorbance for each microstructure component

Measure the absorbance values at the wave numbers corresponding to the microstructure components as specified in Table 1. For cis, the absorption peaks are weak and the wave number of the peaks is affected by the styrene content of the polymer.

Table 1 — Measurement of absorbances for each microstructure component of S-SBR

Notation for absorbance	Microstructure component	Remarks
A10	Styrene	Measure the absorbance at the peak maximum from 695 cm^{-1} to 700 cm^{-1}.
A20	cis	The wave number at this peak maximum is affected by the nature of the polymer, such as the styrene content. When the peak maximum is visible, read off the absorbance at the peak maximum from 720 cm^{-1} to 730 cm^{-1}. If the styrene content is over 30 %, the peak of the cis bond is hidden between the two large styrene absorptions at around 758 cm^{-1} and around 698 cm^{-1}. In this case, measure the absorbance value at 726 cm^{-1}.
A30	styrene	Measure the absorbance at the peak maximum from 755 cm^{-1} to 761 cm^{-1}
A40	Vinyl	Measure the absorbance at the peak maximum from 905 cm^{-1} to 912 cm^{-1}
A50	Trans	Measure the absorbance at the peak maximum from 962 cm^{-1} to 967 cm^{-1}
A60	Vinyl	Measure the absorbance at the peak maximum from 991 cm^{-1} to 996 cm^{-1}
A70	base line	Measure the absorbance at 1 200 cm^{-1} as zero point of each absorbance



Key

X wave number (cm^{-1})

Figure 1 — ATR spectrum of a typical S-SBR

8.2 Calculation of microstructures

8.2.1 General

The microstructure of S-SBR is calculated by using regression formulae and the measured absorbance values of the ATR spectra of each sample. The regression formulae were derived from a statistical study on the ATR spectra of various S-SBR samples with known microstructures. After adjusting the base line of the ATR spectra, the absorbance ratio values of respective absorptions are obtained as the parameter value for microstructure calculation. The microstructure results are calculated by substituting these parameter values in the regression formulae.

8.2.2 Base line correction of each absorbance peak

Obtain the absorbance of each of the peaks A11 to A61 with corrected base lines by using the following Formulae (1) to (6):

A11 = A10 – A70 (1)

$$A21 = A20 - A70 \qquad (2)$$

$$A31 = A30 - A70 \qquad (3)$$

$$A41 = A40 - A70 \qquad (4)$$

$$A51 = A50 - A70 \qquad (5)$$

$$A61 = A60 - A70 \qquad (6)$$

8.2.3 Ratio of absorbance

Obtain the ratios of the absorbances A12 to A62 by using the following Formulae (7) to (12):

$$A12 = (A11) / (A11 + A21 + A31 + A41 + A51 + A61) \qquad (7)$$

$$A22 = (A21) / (A11 + A21 + A31 + A41 + A51 + A61) \qquad (8)$$

$$A32 = (A31) / (A11 + A21 + A31 + A41 + A51 + A61) \qquad (9)$$

$$A42 = (A41) / (A11 + A21 + A31 + A41 + A51 + A61) \qquad (10)$$

$$A52 = (A51) / (A11 + A21 + A31 + A41 + A51 + A61) \qquad (11)$$

$$A62 = (A61) / (A11 + A21 + A31 + A41 + A51 + A61) \qquad (12)$$

8.2.4 Second order terms

Calculate the second order terms which are the squares of A12 to A62.

8.2.5 Styrene content and microstructures in mass % by regression equations

The content (mass %) of each microstructure component is expressed by the following regression Formulae (13) to (16):

$$S_m = 9{,}0 + 12{,}9 \times (A12) + 25{,}9 \times (A12)^2 - 111{,}2 \times (A22) + 412{,}5 \times (A22)^2 + 105{,}0 \times (A32) + 891{,}9 \times (A32)^2$$

$$- 0{,}5 \times (A42) - 21{,}5 \times (A42)^2 - 30{,}7 \times (A52) + 28{,}9 \times (A52)^2 + 24{,}5 \times (A62) - 47{,}2 \times (A62)^2 \qquad (13)$$

$$V_m = 32{,}9 + 5{,}3 \times (A12) - 12{,}9 \times (A12)^2 - 183{,}6 \times (A22) + 1\,168{,}4 \times (A22)^2 + 13{,}2 \times (A32) - 572{,}5 \times (A32)^2$$

$$+ 33{,}7 \times (A42) + 3{,}5 \times (A42)^2 - 90{,}5 \times (A52) + 33{,}5 \times (A52)^2 + 129{,}6 \times (A62) + 168{,}9 \times (A62)^2 \qquad (14)$$

$$T_m = 42{,}5 - 16{,}3 \times (A12) - 18{,}8 \times (A12)^2 + 61{,}4 \times (A22) - 1\,368{,}2 \times (A22)^2 - 65{,}1 \times (A32) - 127{,}7 \times (A32)^2$$

$$- 19{,}6 \times (A42) + 14{,}9 \times (A42)^2 + 93{,}3 \times (A52) - 13{,}9 \times (A52)^2 - 129{,}8 \times (A62) - 116{,}6 \times (A62)^2 \qquad (15)$$

$$C_m = 15{,}6 - 1{,}9 \times (A12) + 5{,}8 \times (A12)^2 + 233{,}5 \times (A22) - 212{,}6 \times (A22)^2 - 53{,}1 \times (A32) - 191{,}7 \times (A32)^2$$

$$- 13{,}6 \times (A42) + 3{,}1 \times (A42)^2 + 27{,}9 \times (A52) - 48{,}5 \times (A52)^2 - 24{,}3 \times (A62) - 5{,}1 \times (A62) \quad (16)$$

where

S_m is the styrene content of the S-SBR, in mass %;

V_m is the vinyl content of the S-SBR, in mass %;

T_m is the trans content of the S-SBR, in mass %;

C_m is the cis content of the S- SBR, in mass %.

8.2.6 Microstructures in mol %

The content (mol %) in butadiene is expressed by the following Formulae (17) to (19):

$$V = V_m / (V_m + T_m + C_m) \times 100 \quad (17)$$

$$T = T_m / (V_m + T_m + C_m) \times 100 \quad (18)$$

$$C = C_m / (V_m + T_m + C_m) \times 100 \quad (19)$$

where

V is the vinyl content of the butadiene portion of the S-SBR, in mol %;

T is the trans content of the butadiene portion of the S-SBR, in mol %;

C is the cis content of the butadiene portion of the S-SBR, in mol %.

9 Precision

See Annex A.

10 Test report

The test report shall include the following information:

a) sample details:

1) a full description of the sample and its origin;

2) if appropriate, method of preparation of test piece from the sample;

b) a reference to this International Standard;

c) test details including any details of any procedures not specified in this International Standard;

d) test results:

1) the number of test pieces used;

2) the results of the determination, expressed in % and rounded to one place of decimals;

e) date(s) of test.