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Rubber and rubber products — Determination of biobased content —

Part 3:
Biobased mass content

Élastomères et produits à base d'élastomères — Détermination de la teneur en composés biosourcés —

Partie 3: Teneur en masse biosourcée

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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 on 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 the following URL: www.iso.org/iso/foreword.html.

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

A list of all parts in the ISO 19984 series can be found on the ISO website.

Introduction

The use of biomass materials in rubber compounds helps to decrease the rubber industry's dependence on fossil resources. It is also expected to lead to a reduction of carbon dioxide emission, reducing global warming and promoting a sustainable global environment.

In the ISO 19984 series, biomass is the term used for the biological material from living or recently living organisms such as wood and agricultural waste materials.

Industrial scale biomass is now readily being grown from numerous types of plants sources and a variety of tree species. Biomass nowadays also includes plant or animal matter used for the production of fibres or chemicals. It may also include biodegradable wastes. Biomass excludes organic materials which have been transformed by geological processes into substances, such as petroleum or coal. Although fossil fuels have their origin in ancient biomass, they are not considered biomass by the generally accepted definition because they contain carbon that has been "out" of the modern carbon cycle.

The composition of biomass is mainly carbon, hydrogen and oxygen. Nitrogen and small quantities of other elements can also be found.

The ISO 19984 series specifies methods for the determination of the biobased content of rubber and rubber products. The results will give manufacturers and users a quantitative indication of their contribution to the preservation of the environment.

ISO 19984-1 specifies how to categorize constituents of rubber and rubber products and also how to calculate the biobased content using the compound formulation and the chemical structure of each constituent.

ISO 19984-2 specifies how to determine the biobased carbon content by radio chemical analyses, i.e. determination of ^{14}C. It can be obtained from the fraction of carbon atoms derived from biomass against the whole amount of carbon atoms in the rubber or rubber products. The methods specified in ISO 19984-2 allow consumers to determine the biobased carbon content even when the formulation of the rubber is unavailable.

ISO 19984-3 specifies how to separate rubber compounds into constituents, how to obtain each constituent's composition ratio and how to determine the biobased carbon content of each constituent by chemical analyses. Thus, the biobased mass content for each constituent can be derived and the biobased mass content for the whole rubber can be obtained by summing up all the constituent values.

Rubber and rubber products — Determination of biobased content —

Part 3:
Biobased mass content

WARNING 1 — 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.

WARNING 2 — Certain procedures specified in this document might 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 document specifies measuring methods for the determination of the biobased mass contents in rubber and rubber products.

The biobased mass content of rubber materials or final products can be determined by separating the sample into the rubber, the inorganic ingredient (including carbon black) and the solvent extract, each of whose ^{14}C content is determined, and then converting the results to the biobased mass content using the procedure described in this document.

This document applies to NR, IR, BR, SBR, IIR, BIIR, CIIR and their modified rubbers, as well as to their mixtures.

This document uses only the accelerator mass spectrometry (AMS) method for the purpose of determination of biobased content.

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 1382, *Rubber — Vocabulary*

ISO 1407:2011, *Rubber — Determination of solvent extract*

ISO 4650, *Rubber — Identification — Infrared spectrometric methods*

ISO 4661-2, *Rubber, vulcanized — Preparation of samples and test pieces — Part 2: Chemical tests*

ISO 9924-3, *Rubber and rubber products — Determination of the composition of vulcanizates and uncured compounds by thermogravimetry — Part 3: Hydrocarbon rubbers, halogenated rubbers and polysiloxane rubbers after extraction*

ISO 17257, *Rubber — Identification of polymers — Pyrolytic gas-chromatographic method using mass-spectrometric detection*

ISO 19984-1:2017, *Rubber and rubber products — Determination of biobased content — Part 1: General principles and calculation methods using formulation of the rubber compound*

ISO 19984-2:2017, *Rubber and rubber products — Determination of biobased content — Part 2: Biobased carbon content*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 1382, ISO 19984-1 and ISO 19984-2 apply.

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

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle

As described in ISO 19984-2, measuring ^{14}C in a rubber sample only allows to determine its biobased carbon content. When the sample consists of a single component such as a raw rubber material or a certain chemical, the biobased carbon content equals to the biobased mass content theoretically. However, when the sample is a mixture of components each of which has different amount of carbon included, the two biobased content values will be different because of the varied carbon amount as well as the varied formulation ratio. Therefore, in order to determine the biobased mass content of the whole, the information of each component's biobased carbon content and the formulation ratio is required. For a vulcanized rubber, each content such as rubber, inorganic ingredients (including carbon black) and solvent extract, is to be analysed for calculations.

5 Separation of a vulcanized rubber sample and determination of the biobased mass content

5.1 General

To separate a vulcanized rubber sample, employ a series of thermal decomposition methods. Any organic ingredients that are free from cross-linking formations are extracted by the solvent. Inorganic filler ingredients, including carbon black, are to be separated by thermogravimetry. If it is known that there are carbonate included in the filler, apply hydrochloric acid treatment to remove them. As a result, the vulcanized rubber is to be separated into rubber, inorganic fillers (including carbon black and excluding carbonate) and solvent extract. When the rubber sample is unvulcanized, vulcanize it before the separation procedure.

The flow chart of the separation scheme of a vulcanized rubber is shown in Figure 1.

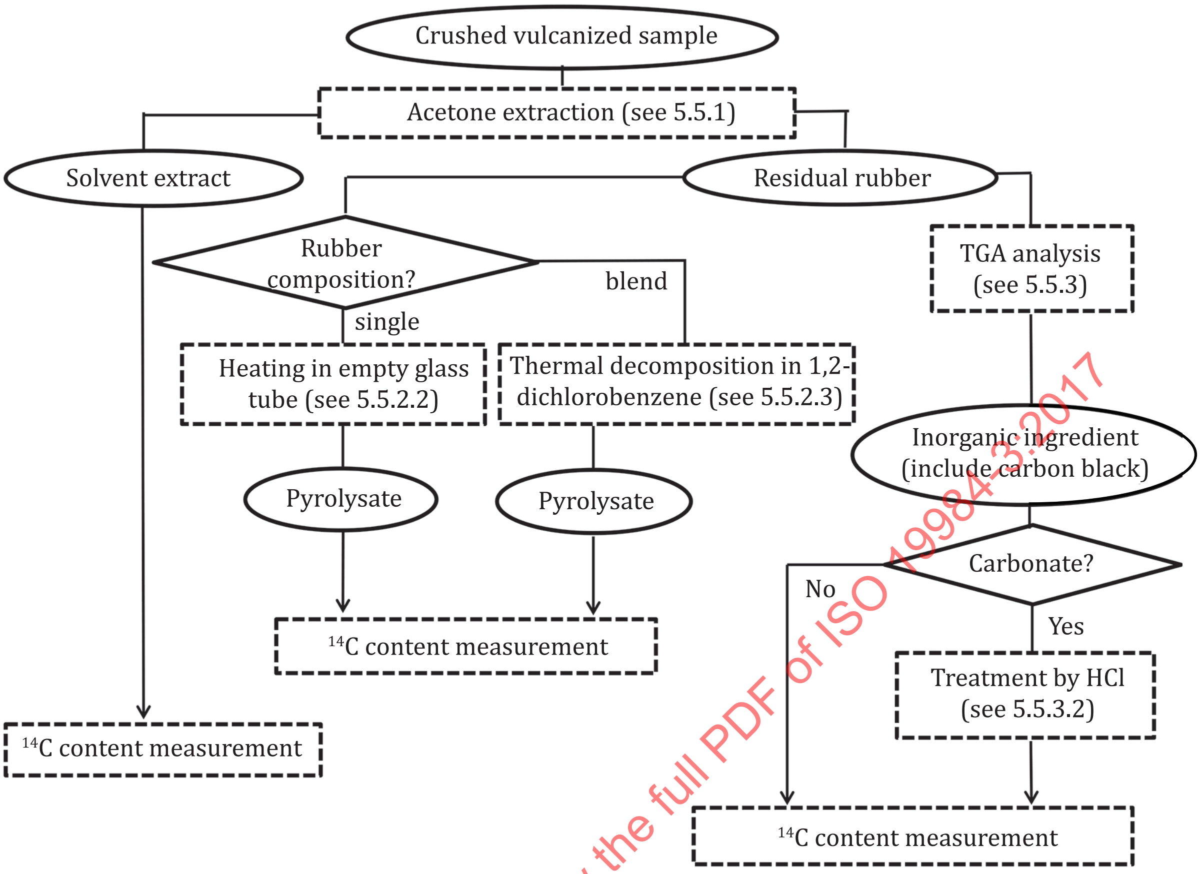


Figure 1 — Scheme of separating a vulcanized rubber to obtain a test sample for ^{14}C measurement

5.2 Reagents and materials

Use only reagents of recognized analytical grade.

5.2.1 Acetone.

5.2.2 1,2-Dichlorobenzene.

5.2.3 Chloroform.

5.2.4 Cyclohexane.

5.2.5 Toluene.

5.2.6 Diluted hydrochloric acid, dilute 1 volume of the concentrated hydrochloric acid with 5 volumes of water.

5.3 Apparatus

5.3.1 Freezer mill, capable to crush the rubber sample using liquid nitrogen into particles smaller than 0,15 mm.

5.3.2 Extraction apparatus, as specified in ISO 1407.

5.3.3 Heater, such as mantle heater or block heater, capable of being maintained at 180 °C ± 5 °C.

5.3.4 Centrifugal separator, capable of operation at the rotation speed of 15 000 rpm.

5.3.5 Thermogravimetric balance, as specified in ISO 9924-3.

5.3.6 Vacuum oven, capable to perform under 0,1 kPa condition.

5.3.7 Balance, accurate to the nearest 0,1 mg.

5.3.8 Rotary evaporator.

5.4 Sampling

Select a laboratory sample in accordance with ISO 4661-2.

5.5 Procedure

5.5.1 Solvent extraction

Crush the laboratory sample into particles around 0,1 mm size with the freeze crusher or freezer mill (5.3.1).

Perform extraction on 1 g of the crushed sample with acetone (5.2.1) for more than 8 h, in accordance with ISO 1407:2011, Method A.

Residual acetone will affect the result of following ^{14}C determination, so dry the extract completely with the vacuum oven (5.3.6) for 2 h at room temperature.

Weigh the extract after it is completely dried and calculate the content of the extract (m_e) in accordance with ISO 1407.

The extract obtained here will be applied for the determination of the biobased carbon content (see 5.5.4).

Set aside the residue from this solvent extraction for the separation procedure by thermal decomposition (see 5.5.2.2 or 5.5.2.3).

5.5.2 Separation of the rubber from a vulcanized rubber

5.5.2.1 Selection of method

When no information is available about the sample's rubber type(s), examine whether it is single or blended using procedures specified in ISO 4650 or ISO 17257 (if the type of rubber is already known, skip this process).

For a single rubber, apply the separation method in 5.5.2.2. For a blended rubber, select the separation method in 5.5.2.3 instead.

NOTE It is not necessary to degrade 100 % of the compound during this separation procedure.

5.5.2.2 Separation of rubber by heating an empty glass tube

5.5.2.2.1 Place the residue after solvent extraction (see 5.5.1) of test sample of 100 mg in a test tube capped with glass wool and heat it for about 10 min in a heater (5.3.3) regulated at 180 °C ± 5 °C.

5.5.2.2.2 Allow the heated residue to cool, transfer to a 100 ml flask fitted with a reflux condenser and add 50 ml of chloroform (5.2.3) to the flask. Cyclohexane (5.2.4) may be used instead of chloroform.

5.5.2.2.3 Dissolve the degraded rubber in the chloroform for 15 min with the solvent refluxing.

5.5.2.2.4 Recover the chloroform from undegraded residue by decantation.

5.5.2.2.5 Using a rotary evaporator and/or other suitable equipment, remove the left chloroform completely and recover the remaining rubber.

5.5.2.2.6 Residual chloroform will affect the result of following ^{14}C determination, so dry the extract completely with the vacuum oven (5.3.6) for 2 h at room temperature.

The rubber obtained here will be applied for the determination of the biobased carbon content (see 5.5.4).

5.5.2.3 Separation of rubber by thermal decomposition in 1,2-dichlorobenzene

5.5.2.3.1 Place the residue, after solvent extraction of test sample (see 5.5.1), of 100 mg and 50 ml of 1,2-dichlorobenzene (5.2.2) in a 100 ml flask fitted with a reflux condenser.

5.5.2.3.2 Heat the contents with the heater (5.3.3) under a calmly boiling condition until the sample has dissolved. The time required for adequate dissolution is usually 4 h to 6 h. When the sample contains IIR, extend the dissolution time to 24 h.

5.5.2.3.3 Remove the 1,2-dichlorobenzene by using the rotary evaporator (5.3.8) and dry out the left degraded liquid by the vacuum oven (5.3.6).

5.5.2.3.4 Transfer the dried residue to a 50 ml flask and add 30 ml of toluene (5.2.5) to dissolve it.

5.5.2.3.5 Centrifuge the toluene solution with the centrifugal separator (5.3.4) at the rotation speed of 15 000 rpm for 60 min.

5.5.2.3.6 Separate the toluene solution from inorganic ingredients and undegraded rubber by decantation. Exercise great care during this process to leave the precipitated inorganic ingredients in the flask, for it will affect the test result.

5.5.2.3.7 Using a rotary evaporator and/or other suitable equipment, remove the toluene completely and recover all the remaining rubber.

5.5.2.3.8 Residual toluene will affect the result of following ^{14}C determination, so dry the extract completely with the vacuum oven (5.3.6) for 4 h at room temperature.

The rubber obtained here will be applied for the determination of the biobased carbon content (see 5.5.4).

NOTE Pyrolysis-gas chromatography described in Annex A is found useful to compare the blend ratios between the separated rubber and the original rubber.

5.5.3 Separation of inorganic ingredients (including carbon black) from a vulcanized rubber

5.5.3.1 Extraction of organic ingredients

Apply the heat treatment as described in Table 1 and Figure 2 with the thermogravimetric balance (5.3.5) to the 20 mg residue after solvent extraction from 5.5.1. Organic ingredients in the residue are to be separated and removed efficiently by this process, leaving carbon black and other inorganic ingredients from test sample.

Repeat this process until at least 10 mg is recovered. When it is known that there is no carbonate such as calcium carbonate containing carbon elements other than carbon black, the fragment obtained here can proceed to the biobased carbon content determination procedure (see 5.5.4).

5.5.3.2 Removal of carbonate

5.5.3.2.1 When carbonate can be contained, remove it with a hydrochloric acid treatment.

5.5.3.2.2 Add 30 ml of diluted hydrochloric acid (5.2.6) to the inorganic ingredients (including carbon black) obtained from 5.5.3.1, and calmly boil it for 15 min over a hot plate.

5.5.3.2.3 Remove the hydrochloric acid, add pure deionized water to flush the insoluble a few times, and dry it sufficiently.

The inorganic ingredients (including carbon black) obtained here from carbonate-containing sample will be applied for the determination of the biobased carbon content (see 5.5.4).

Table 1 — Operating steps for separation of inorganic ingredients

Step	Units	Conditions
Initial temperature	°C	35 ± 10
Heating rate under nitrogen	°C/min	20
Target temperature under nitrogen	°C	600
Cooling under nitrogen	°C	600 to 50

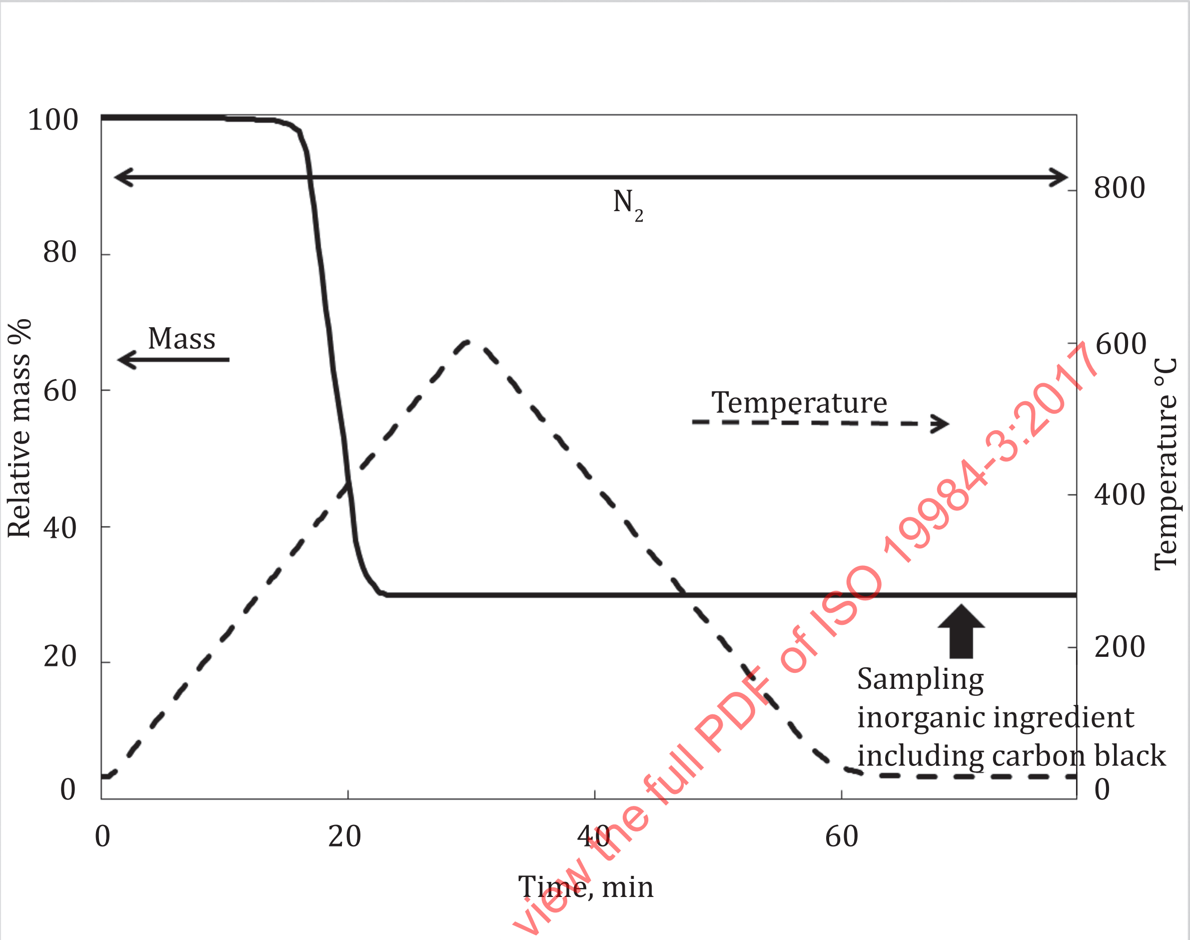


Figure 2 — Thermogram of thermogravimetric balance

5.5.4 Determination of the biobased carbon content

Determine the biobased carbon content, $\chi_{\mathrm{Br}}^{\mathrm{TC}}$, $\chi_{\mathrm{Bi}}^{\mathrm{TC}}$, $\chi_{\mathrm{Be}}^{\mathrm{TC}}$, of the separated rubber, the inorganic ingredients (including carbon black) and the solvent extract each in accordance with ISO 19984-2:2017, Annex A.

5.6 Determination of the content of rubber and carbon black

Determine the rubber and the carbon black content (m_{r} and m_{C}, respectively) in accordance with ISO 9924-3.

5.7 Calculation

5.7.1 Biobased mass content of each component

From the biobased carbon content values of degraded rubber, inorganic fillers and solvent extraction obtained in 5.5.4, calculate the biobased mass content of each component using Formulae (1) to (3).

$$m_{\mathrm{Br}} = \chi_{\mathrm{Br}}^{\mathrm{TC}} \times m_{\mathrm{r}} \div 100 \quad (1)$$

where

m_{Br} is the biobased mass content of the separated rubber, expressed as a mass percentage to the whole vulcanized rubber sample;

$\chi_{\mathrm{Br}}^{\mathrm{TC}}$ is the biobased carbon content, expressed as a percentage to the total carbon content, of the rubber separated (see 5.5.2.2 or 5.5.2.3) from vulcanized rubber sample;

m_{r} is the content of the rubber (see 5.6), expressed as a mass percentage to the whole vulcanized rubber sample.

$$m_{\mathrm{Bc}} = \chi_{\mathrm{Bi}}^{\mathrm{TC}} \times m_{\mathrm{c}} \div 100 \qquad (2)$$

where

m_{Bc} is the biobased mass content of the carbon black of the sample, expressed as a percentage to the mass of the whole vulcanized rubber sample;

$\chi_{\mathrm{Bi}}^{\mathrm{TC}}$ is the biobased carbon content, expressed as a percentage to the total carbon content, of the inorganic ingredients separated (see 5.5.3.1 or 5.5.3.2) from vulcanized rubber sample;

m_{c} is the content of the carbon black (see 5.6), expressed as a mass percentage to the whole vulcanized rubber sample.

NOTE In this document, $\chi_{\mathrm{Bi}}^{\mathrm{TC}}$ equals to the biobased carbon content of carbon black.

$$m_{\mathrm{Be}} = \chi_{\mathrm{Be}}^{\mathrm{TC}} \times m_{\mathrm{e}} \div 100 \qquad (3)$$

where

m_{Be} is the biobased mass content of the extract from vulcanized rubber sample, expressed as a percentage to the mass of the whole vulcanized rubber;

$\chi_{\mathrm{Be}}^{\mathrm{TC}}$ is the biobased carbon content, expressed as a percentage to the total carbon content, of the extract from vulcanized rubber sample (see 5.5.1);

m_{e} is the content of the extract (see 5.5.1), expressed as a mass percentage to the whole vulcanized rubber sample.

5.7.2 Calculation of the biobased mass content of a vulcanized rubber sample

The biobased mass content of the whole vulcanized rubber sample is calculated using Formula (4):

$$m_{\mathrm{Bs}} = m_{\mathrm{Br}} + m_{\mathrm{Bc}} + m_{\mathrm{Be}} \qquad (4)$$

where

m_{Bs} is the biobased mass content of a sample, expressed as a percentage to the total mass of the sample;

m_{Br} is the biobased mass content of the rubber, expressed as a percentage to the total mass of the sample;

m_{Bc} is the biobased mass content of the carbon black, expressed as a percentage to the total mass of the sample;

m_{Be} is the biobased mass content of the extract, expressed as a percentage to the total mass of the sample.

5.8 Examples of determinations

Annex C, Annex D and Annex E show the determination examples of biobased mass content of rubber composite, rubber/rubber products and a tyre, respectively.

6 Determination of the biobased mass content of raw materials or latices

6.1 Determination of the biobased carbon content

Determine the biobased carbon content of raw materials or latices in accordance with ISO 19984-2.

6.2 Calculation

6.2.1 When the sample consists of a single component, its biobased mass content equals to the biobased carbon content determined in 6.1.

6.2.2 When the sample is a mixture of components whose origins, chemical constitutions and composition ratio are identified, the sample's biobased mass content can be calculated using Formula (5):

$$m_{\mathrm{Bm}} = m_{\mathrm{Bs}} \times \frac{\chi_{\mathrm{Bm}}^{\mathrm{TC}}}{\chi_{\mathrm{Bc}}^{\mathrm{TC}}} \qquad (5)$$

where

m_{Bm} is the biobased mass content of the mixed raw material, expressed as a mass percentage;

m_{Bs} is the identified composition ratio of the biobased components, expressed as a mass percentage;

$\chi_{\mathrm{Bm}}^{\mathrm{TC}}$ is the biobased carbon content determined in 6.1, expressed as a percentage to the total carbon content, of the raw material;

$\chi_{\mathrm{Bc}}^{\mathrm{TC}}$ is the expected biobased carbon content, theoretically derived from the available information on the chemical composition as well as the mix ratio for each raw material, expressed as a percentage to the total carbon content.

6.2.3 When the chemical constitutes and the composition ratio of the sample components are not clarified, assume that the sample consists of a single component. The biobased mass content of the sample in this case also equals to the biobased carbon content determined in 6.1.

7 Precision

See Annex B.

8 Test report

The test report shall include at least the following information:

a) a reference to this document, i.e. ISO 19984-3;

b) all information necessary for complete identification of the rubber material or product tested, including the origin of the biomass from which the material or product is constituted;

c) test results: biobased mass content by total mass, expressed as mass %, of the sample;

d) any additional information, including details of any deviations from the test methods and any operations not specified in this document which could have had an influence on the results;

e) date of test.

Annex A
(informative)

Confirmation of the blend ratio of separated rubber

A.1 General

To confirm that the blend ratio of the rubber separated by thermal decomposition in 1,2-dichlorobenzene (see 5.5.2.3) corresponds to the blend ratio of the original rubber, use pyrolysis-gas chromatograph as described in the following procedure.

A.2 Procedure

A.2.1 Compare the chromatograms of the original rubber and the separated rubber obtained by pyrolysis-gas chromatography. See ISO 7270-1 for the apparatus and the test conditions.

NOTE A flame-ionization detector (FID) is known to have a high degree of accuracy.

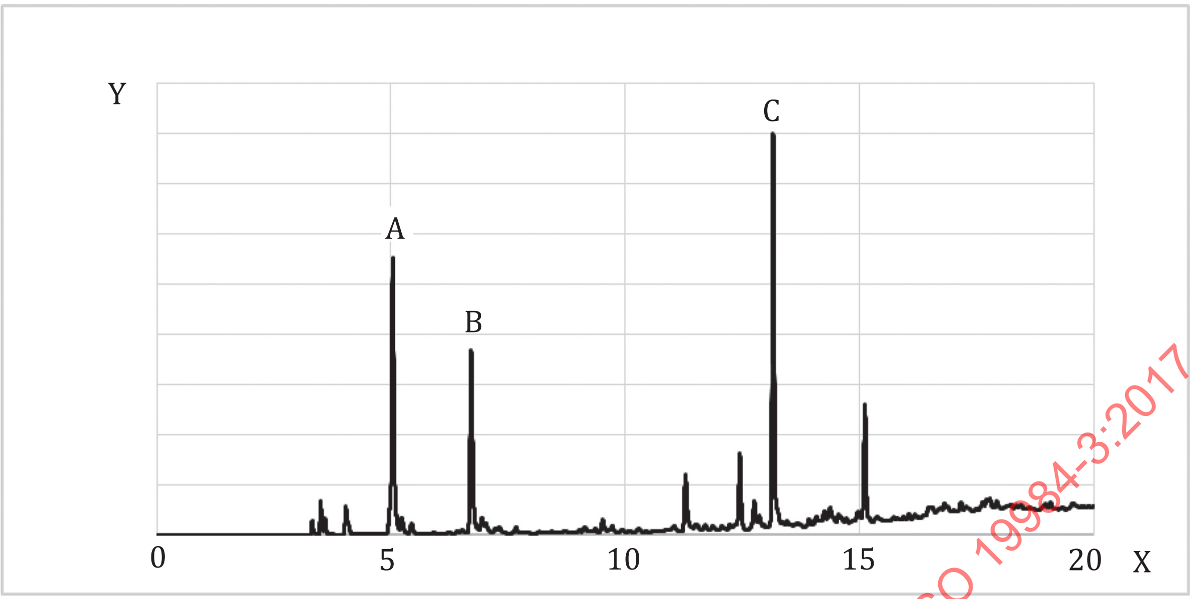
A.2.2 Calculate the peak-area ratio of pyrolyzed monomers (isoprene, butadiene, styrene and/or isobutene) of NR, IR, BR, SBR, IIR, BIIR and CIIR. Make sure the difference between the original rubber and the separated rubber is within ±1 %.

A.2.3 When the difference exceeds ±1 % in A.2.2, it is recommended to repeat the thermal decomposition (see 5.5.2.3).

A.3 Example

A gas chromatogram and the test results are provided in Figure A.1 and Table A.1.

It was confirmed that the blend ratio remained consistent after the decomposition procedure.



Key

A	peak of butadiene
B	peak of isoprene
C	peak of styrene
X	retention time (min)
Y	intensity

Figure A.1 — Example of pyrolysis-gas chromatogram of NR/SBR/BR blended rubber

Table A.1 — Peak-area ratio of pyrolysis-gas chromatography (%)

	Butadiene	Isoprene	Styrene
Original rubber	35,01	29,36	35,63
Separated rubber	35,41	29,72	34,86
Subtract	0,40	0,36	−0,77

Annex B
(informative)

Precision results from an interlaboratory test programme

B.1 General

The following interlaboratory test programme (ITP) was carried out in 2015.

All calculations to provide repeatability and reproducibility values were performed in accordance with ISO/TR 9272. Precision concepts and nomenclature are also given in ISO/TR 9272.

B.2 Precision results from the ITP

B.2.1 Programme details

The ITP was organized and conducted by Japan in 2015.

A single laboratory prepared a batch of vulcanized rubber (named JRMA-A) and separated it into three parts, i.e. solvent extract, residual rubber and separated carbon black. The NR/BR blend ratio of JRMA-A was 60/40, and the biobased mass content calculated from its formula was 38,6 %. The parts were sent to six laboratories for ^{14}C determination by accelerator mass spectrometry (AMS).

Each laboratory made two determinations a day without applying δ^{13}C correction.

The biobased mass percentage of JRMA-A was calculated from the determination results for each of the three parts in accordance with 5.7.1 and 5.7.2.

The number of laboratories on which precision data are based is given in Table B.1. The number of participating laboratories as noted in the table is the final number after identifying certain laboratory values as outliers.

B.2.2 Precision results

The precision results are listed in Table B.1.

Repeatability: The repeatability, *r*, of the test method has been established as the appropriate value tabulated in Table B.1. Two single test results that differ by more than the value should be considered suspect and suggest that some appropriate investigative action be taken.

Reproducibility: The reproducibility, *R*, of the test method has been established as the appropriate value tabulated in Table B.1. Two single test results that differ by more than the value should be considered suspect and suggest that some appropriate investigative action be taken.

The precision results as determined by this ITP should not be applied to acceptance or rejection testing for any group of materials or products without documentation that the results of this precision evaluation actually apply to the products or materials tested.

Table B.1 — Precision data for biobased mass % of JRMA-A

Compound	Mean level	Within-lab standard deviation (in measurement units) S_r	Repeatability (in measurement units) r	Repeatability (in percent of mean level) (r)	Between-lab standard deviation (in measurement units) S_R	Reproducibility (in measurement units) R	Reproducibility (in percent of mean level) (R)	Number of Laboratories[a]
JRMA-A	40,2	0,05	0,13	0,31	0,69	1,94	4,83	4

[a] Number of laboratories after outliers deleted (total number of laboratories in ITP: 6).

B.3 Guidance for using precision results

For the general procedure for using precision results, see ISO 19983.