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Rubber and rubber products — Determination of biobased content —

Part 2: Biobased carbon content

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

Partie 2: Teneur en carbone biosourcé

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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 2:
Biobased carbon 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 biobased carbon contents in rubber and rubber products, including polyurethanes. The methods focus on carbon atoms in rubber or rubber products, and determine whether the carbon-containing component is biobased or not judging from the concentration of ^{14}C, radiocarbon isotope.

This document applies to rubber and rubber products such as raw materials, materials and final products.

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 123, *Rubber latex — Sampling*

ISO 124, *Latex, rubber — Determination of total solids content*

ISO 1382, *Rubber — Vocabulary*

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

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

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

ISO 19242, *Rubber — Determination of total sulfur content by ion chromatography*

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

3 Terms and definitions

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

3.1
percent modern carbon
pMC
normalized and standardized value for the amount of the ^{14}C isotope in a sample, calculated relative to the standardized and normalized ^{14}C isotope amount of oxalic acid standard reference material, SRM 4990c[1)]

Note 1 to entry: The reference value of 100 % biobased carbon is given in Table 2.

3.2
^{14}C activity
relative concentration of radiocarbon ^{14}C expressed as a counting of β-irradiation from the decayed radiocarbon atoms per minute

Note 1 to entry: The unit of ^{14}C activity is "dpm" (decay per minute).

Note 2 to entry: The ^{14}C activity is determined relatively using standard reference material (SRM 4990c) whose ^{14}C activity is set at 13,56 dpm.

4 Principle

This document specifies those methods to determine the biobased carbon contents derived from biomass resources.

When the formulation of the rubber product is available, the biobased carbon content can be calculated (see ISO 19984-1). The biobased carbon content is defined as the amount of biobased carbon to the total carbon in rubber or rubber products as Formula (1):

$$\chi_{\mathrm{B}}^{\mathrm{TC}} = \frac{C_{\mathrm{B}}}{C_{\mathrm{B}} + C_{\mathrm{F}} + C_{\mathrm{NB}}} \times 100 \quad (1)$$

where

$\chi_{\mathrm{B}}^{\mathrm{TC}}$ is the biobased carbon content (%);

C_{B}, C_{F} and C_{NB} are the mass of biobased, fossil-based and non-biobased carbon, respectively.

When there is no available information for the rubber or the rubber product, the biobased carbon content can be determined by the ^{14}C concentration. Due to its radioactive decay, ^{14}C hardly exists in fossil products older than 20 000 years to 30 000 years. Therefore, the ^{14}C present in products is estimated to have come from recent atmospheric carbon dioxide, and consequently, it can be considered as a tracer of recently produced bio-products.

The biobased carbon content values determined in accordance with this document can also be compared to the theoretical values calculated from the formulation, so that the reliability of the information about the rubber in the rubber product is confirmed.

In order to determine the biobased mass content for raw rubber, organic ingredient, rubber products or separated constituents, refer to ISO 19984-3.

1) SRM 4990c is an example of a suitable product supplied by the US National Institute of Standards and Technology. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

5 Sampling

5.1 In the case of latex, carry out sampling in accordance with ISO 123 and dry the sample in accordance with ISO 124.

5.2 In the case of raw material, carry out sampling in accordance with ISO 15528.

5.3 In the case of raw rubber, carry out sampling in accordance with ISO 1795.

5.4 In the case of vulcanized rubber, carry out sampling in accordance with ISO 4661-2.

NOTE The procedure of washing the surface of samples by acid and alkaline solution, which is a familiar preparation process for carbon dating, is not necessary.

6 Measuring method of biobased carbon content by determination of ^{14}C content for rubber products and raw materials

6.1 General

Sample preparation and two methods for the determination of the ^{14}C content are described in this document. With these modular approaches, it is possible for normally equipped laboratories to prepare samples and choose either to determine the ^{14}C content with their own equipment or to outsource the determination process to other laboratories who are specialized in this technique.

For the collection of the ^{14}C from the sample, commonly accepted methods for the conversion of the carbon present in the sample to carbon dioxide are adopted as indicated in Figure 1 (see also A.4.1 and B.4.1).

For the measurement of the ^{14}C content, two methods are adopted that have been generally accepted as age determination methods as indicated in Figure 1 (see also Annex A and Annex B).

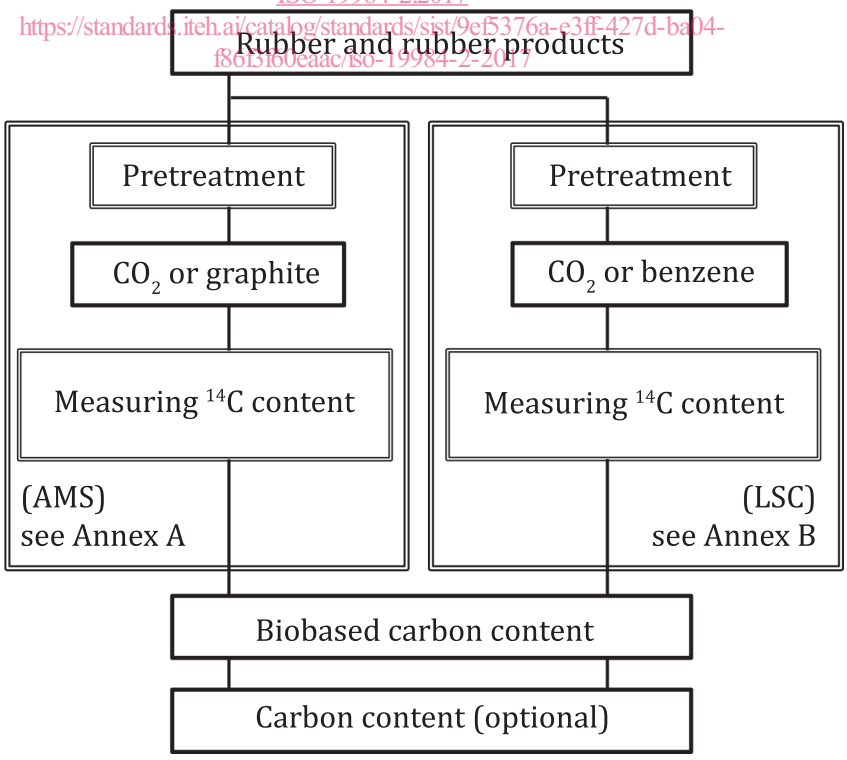

Figure 1 — Outline for the determination of biobased carbon content

6.2 Sample preparation and two methods to determine ^{14}C concentration

Carry out an oxidation of the sample as specified in A.4.1 and B.4.1. A complete oxidization of all the carbons present in the sample shall be performed to obtain exact results. The measurement shall be made according to one of the following two methods:

— Method A [Accelerator mass spectrometry (AMS)]: direct determination of the isotope abundance of ^{14}C, specified in Annex A;

— Method B [Liquid scintillation counter (LSC)]: indirect determination of the isotope abundance of ^{14}C through its emission of beta-particles (interaction with scintillation molecules), specified in Annex B.

The comparison between these test methods is given in Table 1.

Table 1 — Characteristics of the measurement methods of ^{14}C

Method	Determination	Sample amount	Measurement time	Relative standard deviation
Method A (AMS)	relative ratios between isotope ^{12}C, ^{13}C and ^{14}C	1 mg to 10 mg	10 min to 30 min	0,2 % to 2,0 %
Method B (LSC)	β counts of ^{14}C decay	0,5 mg to 2,0 g	4 h to 24 h	0,2 % to 10 %

6.3 Calculation of the biobased carbon content

6.3.1 General

The biobased carbon content as a fraction to the total carbon content, χ_B^{TC}, using the ^{14}C content value, is determined by calculation from one of the test methods specified in 6.3.3 or 6.3.4, and applying the correction factor in Table 2.

6.3.2 Correction factor

Before the above-ground hydrogen bomb testing (started around 1955 and terminated in 1962), the atmospheric ^{14}C level was constant with a few percent range of change for the past millennium. Hence, a sample grown before 1955 has a well-defined “modern” ^{14}C activity, and the fossil contribution could be determined in a straightforward way. After that, ^{14}C generated during the bomb-testing era increased the atmospheric ^{14}C level up to 200 % (pMC) and 27,12 dpm (^{14}C activity) in 1962. The values declined gradually, however, to 101 % (pMC) and 13,70 dpm (^{14}C activity), respectively by 2017, because the large emission of fossil C during the last decades have contributed to the decrease of the atmospheric $^{14}C/^{12}C$ ratio. The REF value of 100 % biobased carbon is indicated in Table 2 in accordance with ASTM D6866.

Table 2 — REF value of 100 % biobased carbon in determined year

Year	REF (pMC, %)
2015	102,0
2016	101,5
2017	101,0
2018	100,5
2019	100,0
2020	to be determined

For the calculation of the biobased carbon content, a ^{14}C content of 101 pMC [*REF* used in Formula (2) and Formula (3)] is considered as a 100 % biobased carbon content for biomass in 2017.

NOTE A hundred (100) % pMC obtained by AMS measurement (Method A) corresponds to 13,56 dpm obtained by LSC measurement (Method B). A hundred and one (101) % pMC for biomass carbon harvested in 2017 corresponds to 13,70 dpm.

6.3.3 Calculation of χ_B^{TC}, the biobased carbon content by Method A (AMS)

Calculate the biobased carbon content as a fraction of total carbon, χ_B^{TC}, expressed as a percentage, using Formula (2) (see Annex A):

$$\chi_B^{TC} = \frac{pMC_S}{REF} \times 100 \quad (2)$$

where

pMC_S is the measured value, expressed in pMC, of the sample;

REF is the reference value, expressed in pMC (see 6.3.2).

6.3.4 Calculation of χ_B^{TC}, the biobased carbon content by Method B (LSC)

Calculate the biobased carbon content as a fraction of total carbon, χ_B^{TC}, expressed as a percentage, using Formula (3) (see Annex B):

$$\chi_B^{TC} = \frac{^{14}C_{activity}}{13{,}56 \times \frac{REF}{100} \times m} \times 100 \quad (3)$$

where

$^{14}C_{activity}$ is the ^{14}C activity, expressed in dpm, of the sample obtained by calculation when using Method B (see Annex B);

REF is the reference value, expressed in pMC, of the sample (see 6.3.2);

m is the mass, expressed in grams, of the sample.

6.3.5 Examples

For examples of biobased carbon content determination, see Annexes C and D.