
**Epoxidized natural rubber —
Determination of epoxidation and ring
opening level by NMR spectrometry**

*Caoutchouc naturel époxydé — Détermination de l'époxydation et du
niveau d'ouverture des anneaux par spectrométrie RMN*

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

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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

Epoxidized natural rubber (ENR) is one of the modified rubbers derived from natural rubber (NR). The modification process is done by introducing oxygen atom to the unsaturated molecule of NR. This chemical reaction produces an oxirane or epoxide compound that consists of a three-membered ether in a cyclic form. A few grades of ENR are currently available depending on the extent of modification such as ENR 25 (25 mole% epoxide) and ENR 50 (50 mole% epoxide).

ENR is used in many applications which include tyres, bearings and adhesives. Epoxidation and ring opening level are very important parameters to check ENR quality. Various techniques are available for quantification of the epoxidation level, such as elemental analysis (carbon, hydrogen and oxygen), infrared spectroscopy (IR), proton (^1H) and carbon (^{13}C) nuclear magnetic resonance spectroscopy (NMR), as well as the chemical titrimetric technique.

This document specifies a quantitative method, using proton (^1H) nuclear magnetic resonance spectrometry, for the determination of epoxidation and ring opening level of raw ENR. This test method is an important document to support ISO 24483, as these parameters are included as specifications for ENR. This work will benefit the market to specify a measurement method for the epoxidation and ring-opening level of ENR.

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Epoxidized natural rubber — Determination of epoxidation and ring opening level by NMR spectrometry

1 Scope

This document specifies a quantitative method, using proton (^1H) nuclear magnetic resonance (NMR) spectrometry, for the determination of epoxidation and ring opening level of raw epoxidized natural rubber (ENR). This method applies to ENR of all grades available commercially.

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 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/>

3.1

epoxidized natural rubber

ENR

natural rubber which has been chemically treated and modified through the addition of oxygen atom onto the double bond structure of the *cis*-1,4-polyisoprene to form three-membered ether (C-O-C) in a cyclic form by a process known as epoxidation reaction

[SOURCE: ISO 24483:2023, 3.1]

3.2

epoxidation level

level and/or degree of the epoxy groups (C-O-C) in the NR structure

[SOURCE: ISO 24483:2023, 3.4]

3.3

ring opening level

level and/or degree of ring opening due to the formation of secondary by product from uncontrolled condition of epoxidation reaction in the natural rubber structure

[SOURCE: ISO 24483:2023, 3.5]

3.4

ENR 25

epoxidized natural rubber with 25 mol % epoxidation

3.5

ENR 50

epoxidized natural rubber with 50 mol % epoxidation

4 Principle

^1H NMR technique is used to identify and quantify selectively the hydrogen atoms which are characteristic for both NR and ENR. The raw ENR is dissolved in appropriate solvent and the dissolved part is measured using NMR. Epoxidation and ring opening level are determined by taking the integration area of the proton from the epoxy group and the proton from the ring opening products, respectively, to the total integration areas of the proton from natural rubber, epoxy group and ring opening products.

5 Reagents

5.1 Deuterated chloroform, CDCl_3 , containing 0,03 % by mass fraction of tetramethylsilane (TMS) as internal standard. The purity of the CDCl_3 shall be $\geq 99,8$ %.

6 Apparatus

6.1 Analytical balance, accurate to 0,1 mg.

6.2 Sample vial.

6.3 NMR sample tube.

6.4 Pasteur pipette.

6.5 NMR spectrometer, Fourier transform nuclear magnetic resonance (FT-NMR) spectrometer with resonance frequency of more than 100 MHz, preferably with the following acquisition parameters:

- probe: ^1H ;
- degree pulse: 45° ;
- pulse delay: 5 s;
- number of scans: 256.

6.6 Data system, using an acquisition and a data processing software.

7 Procedure

7.1 Sample preparation

7.1.1 Weigh about 25 mg to 30 mg ENR sample and put into a sample vial (6.2).

7.1.2 Add about 2 ml of CDCl_3 into a specimen vial and shake for a few times.

7.1.3 Leave the sample to dissolve in the dark for 16 h to 24 h.

7.1.4 Transfer about 1 ml of the liquid sample into the NMR sample tube (6.3) using a Pasteur pipette (6.4). Cap the tube and shake for a few times.

Try to eliminate the solid in 7.1.4 as it will cause the NMR peak to broaden and might affect the result.

7.2 NMR measurement

7.2.1 Place the NMR sample tube into the spinner and analyse the sample using the specified acquisition parameters.

7.2.2 Acquire the free induction decay (FID) signal and apply a Fourier transform to obtain the spectrum. See [Figure A.1](#) and [Figure A.2](#).

7.2.3 Adjust the resonance of the reference peak to 0,00 ppm for TMS.

7.2.4 Correct the baseline of the spectrum. Integrate the spectrum and record the following areas:

- I_1 the methine proton area of NR, from 5,3 ppm to 5,0 ppm;
- I_2 the methine proton area of epoxy group of ENR, from 2,9 ppm to 2,6 ppm;
- I_3 the furan proton area of ENR, from 3,8 ppm to 4,0 ppm;
- I_4 the hydroxyl proton area of ENR, from 3,3 ppm to 3,5 ppm.

8 Calculation

Calculate the percentage of epoxidation and ring opening levels, within one decimal, using [Formulae \(1\)](#) and [\(2\)](#).

$$E = \frac{I_2}{I_1 + I_2 + I_3 + I_4} \times 100 \quad (1)$$

$$O_r = \frac{I_3 + I_4}{I_1 + I_2 + I_3 + I_4} \times 100 \quad (2)$$

where

E is the epoxidation level, in %;

O_r is the ring opening level, in %;

I_1 is the methine proton area of NR;

I_2 is the methine proton area of epoxy group of ENR;

I_3 is the furan proton area of ENR;

I_4 is the hydroxyl proton area of ENR.

9 Precision

See [Annex B](#).

10 Test report

The test report shall include the following information:

- a) a reference to this document, i.e. ISO 5260:2023;
- b) all details necessary for the complete identification of the product tested;

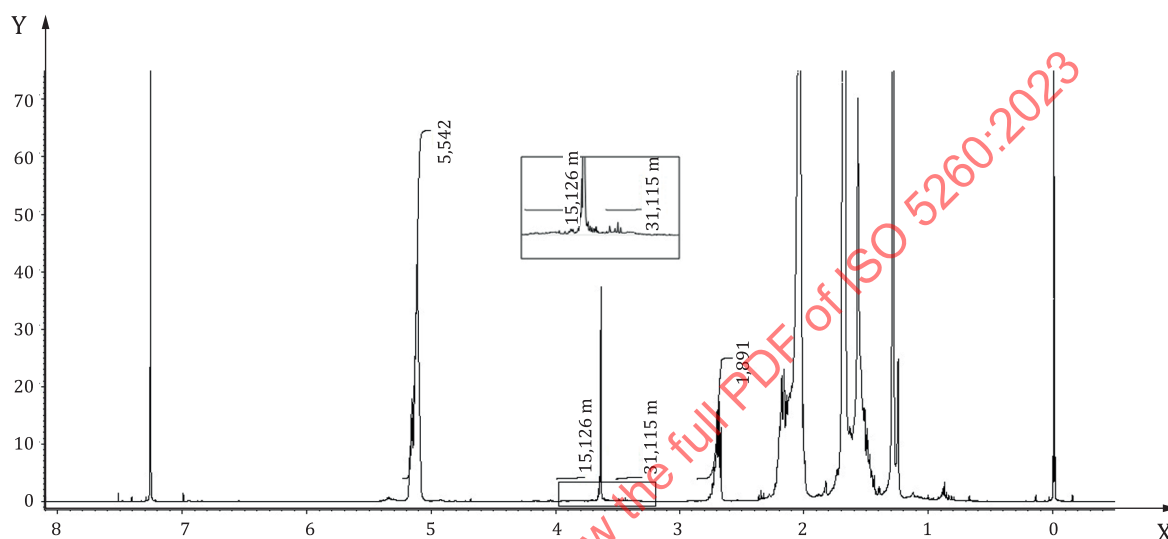
- c) the method of sampling used;
- d) the values of I_1 , I_2 , I_3 , I_4 , epoxidation level E and ring opening level O_r ;
- e) any unusual features noted during the determination;
- f) any operation not included in this document, or any operation regarded as optional such as the NMR parameters in (6.5) if different from the specified one;
- g) the date of the test.

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Annex A (informative)

^1H NMR spectra of ENR 25 and ENR 50

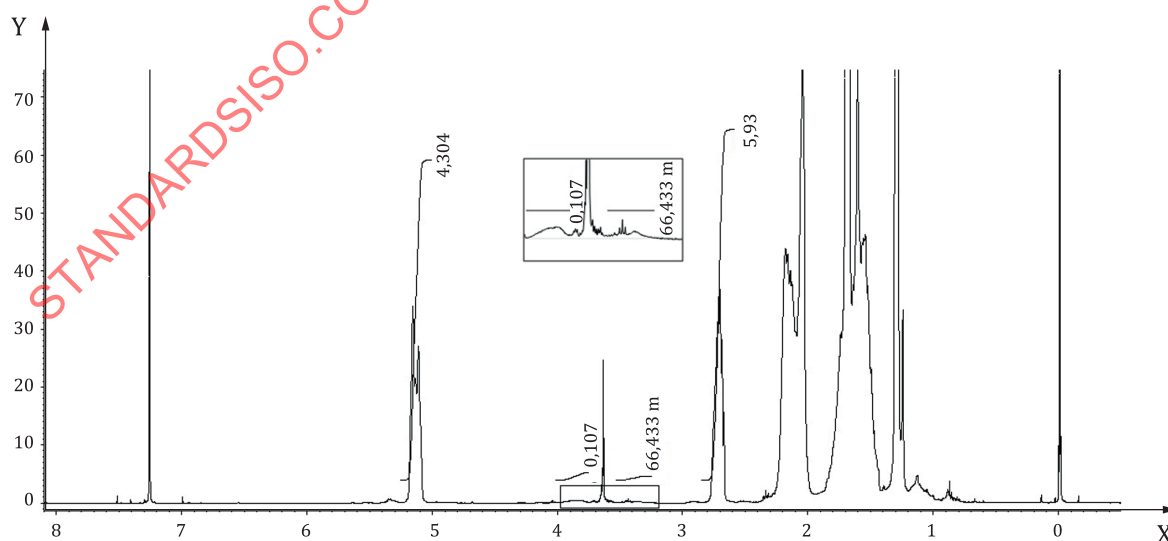
This annex provides examples of spectra obtained from an NMR spectrometer.



Key

X parts per million: proton
Y (thousandths)

Figure A.1 — ^1H NMR spectra of ENR 25



Key

X parts per million: proton
Y (thousandths)

Figure A.2 — ^1H NMR spectra of ENR 50

Annex B (informative)

Precision

The precision of the test method was determined in accordance with ISO 19983.

The precision data are given in [Table B.1](#) to [Table B.8](#). The precision parameters should not be used for acceptance or rejection of any group of materials without documentation that the parameters are applicable to those particular materials and specific test protocols of the test method. The precision is expressed on the basis of a 95 % confidence level for the values established for repeatability, r , and reproducibility, R .

The results contained in [Table B.1](#) to [Table B.8](#) are average values and give an estimate of the precision of this test method as determined in an interlaboratory test programme (ITP). The ITP was carried out in 2021, in which six laboratories took part, performing duplicate analyses on four different types of materials. Each participating laboratory was required to carry out the test method as provided on the scheduled dates given to them.

A type 1 precision was evaluated, based on the method of sampling used for the interlaboratory test programme.

Repeatability conditions: repeatability conditions are where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time.

Reproducibility conditions: reproducibility conditions are where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment.

Bias: in test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values do not exist for this test method since the value (of the test property) is exclusively defined by the test method. Bias cannot therefore be determined for this particular method.

Table B.1 — Precision data for the determination of epoxidation level for EKOPRENA 25

Average result %	Within-laboratory		Between laboratories	
	s_r	r	S_R	R
24,0	0,2	0,5	1,4	4,0
s_r is the within-laboratory standard deviation. r is the repeatability (in measurement units). S_R is the between-laboratory standard deviation. R is the reproducibility (in measurement units).				